SYNTHESIS AND CHARACTERIZATION OF SHELL/CORE NANOPARTICLES AND THE FABRICATION OF NANOPARTICLE THIN FILMS

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Presented to

the Faculty of the Department of Chemistry

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In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Sang Ho Lee

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SYNTHESIS AND CHARACTERIZATION OF SHELL/CORE NANOPARTICLES AND THE FABRICATION OF NANOPARTICLE

THIN FILMS

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Dedication

I would like to dedicate this dissertation to my family; parents, spouse, sister, son, and daughter.

Acknowledgments

I clearly remember that Dr. T. Randall Lee and Dr. Allan J. Jacobson, my two advisors, gave me a joyous welcome when I first joined to the groups five years ago. They were the most influential persons in my whole life. I feel truly grateful for their leadership, counsel, and research assistance that they gave me. I respect them as my professors from the bottom of my heart. Their names will never fade out from my memory. Sincere appreciation is extended to my graduate committee members, Dr. David M. Hoffman, Dr. Arnold M. Guloy, and Dr. Jeffrey M. Rimer, for their assistance, encouragement, helpful suggestions, and discussions. I must say that I couldn't complete my research without Dr. David M. Hoffman's assistance. All professors in the Department of Chemistry are also thanked for their insights and guiding during my studies. In addition, special thanks to Dr. Jim Meen, Dr. Irene Rusakova, and Mrs. Ellen Lee for their valuable help. Appreciation is also expressed to all group members of Jacobson group and Lee group. Finally, I feel thanks to the administrative and technical staff of the UH chemistry department and NSM for their help.

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ABSTRACT

Due to their unique optical and electronic properties, metal nanoparticles have been used as nanoscale materials for various applications in the fields of opto-electronics, solar cells, lithium ion batteries, gas sensors, and catalysis. Our research focuses on the synthesis of shell/core nanoparticles and the design of thin films that incorporate these nanoparticles.

We have examined the stability of colloidal gold nanoparticles coated with tin oxide (SnO₂) and silicon dioxide (SiO₂), where the shell/core nanoparticles were dispersed in solution over wide range of pHs. The stabilities of the particles were monitored visually and by UV-vis spectroscopy, since these particles could potentially be used in harsh environments in applications such as chemical sensing and solar cells. The systematically designed experiments showed that the tin oxide-coated Au nanoparticles were more stable in basic solutions than the corresponding silica-coated Au nanoparticles.

We also developed a sol-gel-based approach to fabricate tin oxide semiconductor thin films with tin oxide-coated Au nanoparticles dispersed within the layer. These composite nanoparticles were dispersed homogeneously in a SnO_2 sol-gel precursor because the SnO_2 coating prevented aggregation of the metal core particles and enhanced their miscibility with the 2-propanol-based SnO_2 sol-gel precursor. The morphologies, sizes, and/or dimensions of the composite nanoparticles and thin films were characterized by SEM, TEM, XRD, and UV-vis spectroscopy.

We also synthesized Zn(II)- and Sb(V)-doped SnO₂-coated Au nanoparticles using a hydrothermal method. Antimony-doped tin oxide (ATO) and zinc-doped tin oxide (ZTO) are promising transparent conducting oxide materials due to their high mobility and optical transmittance. The sizes and morphologies of these unique particles were characterized by SEM and TEM, and the growth and nature of the metal oxide shell was evaluated by XRD, XPS, and UV-vis spectroscopy.

Finally, we demonstrated that gold nanoshell-dispersed polymeric thin films could be fabricated via electrostatic layer-by-layer assembly. In this process, negatively charged gold nanoshells were adsorbed electrostatically on positively charged organic polymers that were deposited on transparent glass substrates. The SEM images verified that the gold nanoshells were homogeneously dispersed in the polymeric thin film. The optical properties of the nanoshell thin films were evaluated by UV-vis spectroscopy.

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CHAPTER 1. General Introduction to Shell/Core Nanoparticles

1.1 Nanoparticles

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Nanotechnology has the capacity to create new materials and devices for various applications in the fields of medicine, electronics, energy, and environmental remediation.^{1,2} Research and development in these fields is growing rapidly around the world. A major outgrowth of nanotechnology is the development of practical materials on the nanometer scale, including nanoparticles, nanowires, nanotubes, quantum dots, thin films, and surface coatings.¹ Among them, nanoparticles have been of significant interest to scientists worldwide for the past few decades due to their interesting and useful physical and chemical properties. Two principal factors are responsible for the fact that the properties of nanoparticles differ significantly from other bulk-materials: quantum effects and their relatively large surface area. These factors can change or enhance specific properties, including reactivity, strength, electrical properties, and optical characteristics. The potential applications of nanoparticles are increasing every day.

1.2 Gold Nanoparticles

Colloidal gold nanoparticles exhibit unique optical and electronic properties that are tunable by judiciously adjusting the size, shape, composition, and/or degree of aggregation. Nowadays, gold nanoparticles have emerged as a surprising catalyst for a series of reactions.³ Gold-based catalysts have shown excellent activity in the selective oxidation of organic compounds, including alkenes, alkanes, alcohols, and others.³ Besides catalyzing reactions, another promising application of gold nanoparticles lies in the field of vapor sensing.⁴ Gold is also highly active in catalyzing low temperature CO oxidation and hydrochlorination of ethyne to vinyl chloride.⁴ These unique properties have been studied and utilized in a variety of technological applications, such as organic photovoltaics, catalysis, sensory probes, therapeutic agents, drug delivery, and related biomedical applications.

1.3 Shell/Core Nanoparticles

Shell/core nanoparticles constitute a special class of nanocomposite materials. They consist of concentric particles in which the particles of one material are coated with a thin layer of another material, as shown in figure 1.1. Shell/core nanoparticles are diverse and continue to develop with various advanced synthetic techniques. It is possible to synthesize them not only in uniform sizes, but also in the desired forms of shell/core spheres, cubes, nanorods, and hollow particles.⁵ Shell/core nanoparticles can be synthesized using practically any material, including metals, semiconductors, and Further, shell/core nanoparticles can be synthesized in a variety of insulators. combinations. such as (shell/core) metal/dielectric, semiconductor/dielectric, dielectric/dielectric, metal/semiconductor, metal/metal, semiconductor/semiconductor,

dielectric/semiconductor, and dielectric/metal. Some of these structures show tunable optical properties from the visible to the infrared region of the electromagnetic spectrum by choosing different combinations of the core and shell. Moreover, the shell/core structures show enhanced thermal stability, colloidal stability, and/or surface chemical and catalytic properties when compared simple nanoparticles. In this chapter, we broadly classify these particles based on the material with which the core and shell are composed.



Figure 1.1. Structure of shell/core nanoparticles.

1.4 Metal Shell/Dielectric Core Nanoparticles: Nanoshells

For the last couple of decades, a new type of metal shell/dielectric core nanoparticle, called a "nanoshell", has drawn much interest because of its unique physical properties. A nanoshell is a type of spherical nanoparticle consisting of a dielectric core (usually silica), which is covered by a thin metallic shell (usually gold). Many studies have been conducted by various research groups for the purpose of synthesizing and characterizing nanoshells.⁶⁻¹¹ The synthesis of nanoshells involves a multistep route and also requires highly controlled and sensitive synthesis protocols to generate a perfect shell. Although several methods have been developed, it is still difficult to obtain specific shell thicknesses with smooth and homogeneous morphologies.

1.4.1 Synthesis of Gold Nanoshells

One of the successful approaches to synthesize gold nanoshells has been the "seeded growth" method for which our research group has been instrumental in developing.^{6,7} Scheme 1.1 illustrates the overall synthetic procedure used to obtain gold nanoshells. The first step in the synthesis of gold nanoshells involves the preparation of a uniformly spherical dielectric core, such as silica, and the preparation of precursor small gold seed particles, formed during a separate process, to be anchored on the dielectric core by specialized procedures, and then the subsequent growth of the polycrystalline gold shell.

1.4.2 Dielectric Core: Silica Nanoparticle Synthesis

Silica (SiO₂) is a popular material used in shell/core particles because of its ease of synthesis in monodisperse form, stability against coagulation, and versatile surface functionalization.¹² It is also chemically inert, optically transparent, and does not affect redox reactions at core surfaces.¹³ We use a modified Stöber method for the synthesis

silica nanoparticles, which involves the hydrolysis and condensation of TEOS (tetraethlyorthosilicate, $Si(C_2H_5O)_4$).¹⁴ In the first step (hydrolysis; eq 1), ethoxy groups are replaced by OH groups in alcoholic medium in the presence of ammonium hydroxide (NH₄OH) as catalyst. In the second step (polycondensation; eq 2), SiO₂ particles are formed by the condensation silicon hydroxides. Particles can be formed in various sizes ranging from ~50 nm to 1 µm by controlling the relative ratio of TEOS, solvent, and catalyst.¹²

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$
(1)

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$
 (2)

Scheme 1.1. Synthesis of Gold Nanoshells Using the "Seeded Growth" Method.⁶



1.4.3 Surface Functionalization of Silica Nanoparticles with APTMS

The surface of silica core particles can be modified using bifunctional organic molecules such 3-aminopropyltrimethoxysilane (APTMS) 3as and aminopropyltriethoxysilane (APTES) the organosulfur analogs 3or mercaptopropyltrimethoxysilane (MPTMS) and 3-mercaptopropyltriethoxysilane (MPTES). These molecules possess a methoxy or ethoxy group at one end and an amine or thiol group at the other end. These molecules form a covalent bond with the silica particles through the OH group and the surface becomes either NH-terminated or SHterminated, respectively.

1.4.4 Gold Seed Preparation and Attachment to Amino-terminated Silica Nanoparticles

Colloidal gold seeds can be synthesized by the reduction of gold salts in the presence of surfactants or stabilizers. Two preferred reductants/stabilizers are sodium citrate and tetrakis(hydroxymethyl)phosphonium chloride (THPC). The reduction of hydrogen tetrachloroauric acid (HAuCl₄) with THPC affords relatively small gold particles (e.g., ~2 nm in diameter) with a net negative interfacial charge and also might require several days of aging for their size to stabilize before they are seeded onto the surface of the functionalized silica core. Importantly, gold seed attachment on the silica can be enhanced by electrostatic effects, where the negatively charged THPC gold

nanoparticles are attracted to the NH-terminated silica particles, which are positively charged at the pH that is used for the attachment process.

1.4.5 Growth of Gold Nanoshells

The THPC-gold nanoparticles attached on the surface of the silica can act as nucleation sites to grow additional gold metal by further addition of gold reduced from HAuCl₄ to form a continuous complete layer of gold shells around the silica core. Reducible gold salt solutions can be prepared from a mixture of HAuCl₄ and K₂CO₃ in water, where the solution is allowed to stir overnight in the dark at room temperature for the HAuCl₄ hydrolyze and give a colorless gold hydroxide solution. This solution is often referred to as "K-Gold" solution. Gold shells can then be grown by adding the gold-seeded silica nanoparticles to the K-Gold solution. This reaction leads to an almost immediate color change: red, purple, blue, or green depending on the thickness and completeness of the shell.

1.4.6 Tunable Optical Properties of Gold Nanoshells

One of the most interesting optical attributes of metal nanoparticles arises from their unique interaction with light. In the presence of the oscillating electromagnetic field of light, the conduction of electrons of the metal nanoparticles are driven by the electric field to oscillate collectively in response to optical excitation.¹⁵ This process is

resonant at a particular frequency of light and is termed the localized surface plasmon resonance (LSPR) oscillation.¹⁵ The LSPR oscillation decays by radiating its energy and leads to light scattering, or decays non-radioactively and leads to a conversion of absorbed light to heat.¹⁵

Mie theory predicted the optical extinction of homogeneous metallic sphere for small particles as in the following the equation (3),¹⁶ where $E(\lambda)$ is the extinction, which is

$$E(\lambda) = \frac{24\pi^2 N_A a^3 \varepsilon_m^{3/2}}{\lambda \cdot \ln(10)} \left[\frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2} \right]$$
(3)

equal to the sum of absorption and Rayleigh scattering, N_A is the areal density of nanoparticles, "*a*" is the radius of the metallic nanosphere, ε_m is the dielectric constant of the medium surrounding the metallic nanosphere (assumed to be a positive, real number and wavelength independent), λ is the wavelength of the absorbing radiation, ε_i are ε_r the imaginary and the real portion of the metallic nanoparticle's dielectric function, respectively. The LSPR spectrum of an isolated metallic nanoparticle sembedded in an external dielectric medium will depend on the nanoparticle radius "*a*", the nanoparticle material (ε_i and ε_r), and the dielectric constant of the surrounding environment (ε_m).¹⁶

The LSPR peak position is sensitive to the dielectric constant (refractive index) of the surrounding environment. Materials with high dielectric constants are effectively more polarizable and thus couple with the surface plasmon electrons more readily, and the energy required to induce the collective oscillation of the electrons is diminished.

That is, the LSPR peak maximum shifts to lower energy (longer wavelength). According to the Mie theory, the cross section of extinction of a metallic nanoparticle in an isotropic medium is also expressed with involving the dielectric function of both the sphere material (ε) and the medium (ε_m) as following the equation (4),¹⁷

$$C_{ext} = \frac{4\pi}{k^2} Re\left(i\left(\frac{\varepsilon - \varepsilon_{\rm m}}{\varepsilon + 2\varepsilon_{\rm m}}\right)\right) \tag{4}$$

where $k=2\pi n_{\rm m}/\lambda$ and a_v and b_v are the so-called Mie coefficients expressed in terms of Ricatti-Bessel functions. The refractive index of the external medium, $n_{\rm m}$, is related to the dielectric constant by $\varepsilon_{\rm m} = n_{\rm m}^{2.17}$ Solving the equation (4), a plot of peak resonance wavelength versus the refractive index of the surrounding medium should be linear (5).¹⁷

$$\lambda = \lambda_p \sqrt{2\varepsilon_m + 1} \cong \sqrt{2\lambda_p} \ n_m \tag{5}$$

Such plots are called response functions. They have been characterized in terms of a responsiveness equation (6).

•
$$\lambda_{\text{peak}} = \lambda_{\text{response}} n_{\text{m}}$$
 (6)

where • λ_{peak} is the shift in the LSPR peak position and $\lambda_{\text{response}}$ is the responsiveness of the nanoparticles. Therefore, high responsiveness indicates a relatively large shift in wavelength upon change in medium refractive index. A red-shift in the LSPR peak position was observed as the refractive index of the surrounding medium increases.^{17,18} Refractive index for some common materials is listed on Table 1.1.

Material	Refractive Index	Material	Refractive Index
Vacuum	1.00 (Default)	SiO ₂	1.46
Air	1.00	SnO ₂	2.0
Ice	1.31	ZnO	2.4
Water	1.33	Cu ₂ O	2.56
Ethanol	1.36	PbS	3.91
Acetone	1.36	Si	4.01
Diamond	2.42	TiO ₂	2.496

Table 1.1. Refractive Index for Some Common Materials.

Simple gold nanoparticles show intense absorptions in the visible range of the electromagnetic spectrum, as shown in Figure 1.2. Gold nanoparticles in the 10 nm size range have a strong absorption maximum of around 520 nm in water, due to their LSPR.^{10,19} With an increase in the nanoparticle size, there is some LSPR red-shifting due to electromagnetic retardation in larger particles.^{10,19} The position of the extinction band of simple gold nanoparticles shows small variations from 517 nm to 575 nm as a function of particle size.¹⁹ That is, the tunability of the LSPR of simple gold nanoparticles is quite limited.



Light is adsorbed & converted to heat!

Figure 1.2. Comparison of optical resonances of simple gold nanoparticles and gold nanoshells.²⁰

For many biological applications, it is desirable to work in the near-infrared (NIR) region of the spectrum, especially at 650 nm-900 nm, due to the high transmission of tissue, blood, and water in this window.²¹ Alternatively, the growth of gold shells on dielectric nanoparticles shows a wide range of the tunable extinction bands from the visible to the near-infrared regions of the electromagnetic spectrum. The relative thickness of the gold shell layer is sensitive toward the position of the LSPR band. Thus, by changing the shell thickness, the LSPR band position can be tuned to a desired wavelength, as shown in Figure 1.3. Gold nanoshells having LSPR in the infrared region are well suited for biological applications, as this range of the electromagnetic spectrum is transparent for biological tissues.



Figure 1.3. Size tunability of the plasmon resonance of gold nanoshells.²⁰

1.4.7 Gold Nanoshells in Biomedical Applications

Due to their unique physical characteristics and non-toxic nature, gold nanoshells have been at the forefront of a growing number of biomedical applications.²²⁻²⁴ By carefully choosing the core-to-shell ratio, it is possible to design nanoshell structures that either absorb light or scatter it effectively.²⁵ Strong absorbers can be used in photothermal therapy, while efficient scatters are promising for use in optical imaging and labeling of biological systems.²⁵ Gold nanoshells can be conjugated with specific antibodies that target diseased tissues or tumors.²⁶ When nanoshells are inserted in the body, they can attach selectively to targeted (diseased) cells without significant binding to healthy cells and can be selectively labeled by the nanoparticles. Further, in cases where a tumor has been labeled, subsequent irradiation at the LSPR absorption maximum of the nanoshells can lead to the selective heating and destruction of cancer cells at much lower laser powers than those required to destroy healthy cells.²⁶ As such, gold nanoshells offer effective and relatively safe strategies for biomedical therapies.

1.5 Dielectric Shell/Metallic Core Nanoparticles

The core-shell structure of metal oxide-coated metal nanoparticles has become increasingly important because of their numerous potential applications, including catalysis, optical coatings, gas sensing, solar cells, and biomedical applications. The development of shell/core nanoparticles has allowed for enhancements in chemical and colloidal stability, the preparation of bioconjugates, the charging of metal cores, and the luminescence of semiconductor nanoparticles. The most widely used dielectric shell/metal core nanoparticles are gold or silver cores with a silica shell. Silica is highly stable, chemically inert, and biocompatible, so that gold-silica shell/cores have proven to be useful in biological applications. Over the past few years, there have been a significant number of new methods developed for the fabrication of dielectric shell/ gold core nanostructures. We have tried to classify them here based on the type of metal oxide shell of which the nanocomposite is composed.

1.5.1 Silica-coated Gold Nanoparticles

Silica-coated gold nanoparticles are one of the most known shell/core structures due to their rich surface chemistry, high biocompatibility, controllable porosity, and good transparency. Silica (SiO₂) has been widely used to coat colloidal gold nanoparticles to prevent particle coalescence. A number of methods have been used to synthesize the silica-coated nanoparticles, since the pioneering work by Mulvaney and co-workers in 1996.²⁷ To prepare the SiO₂-coated gold nanoparticles, first of all, gold nanoparticles were synthesized by the sodium citrate reduction method.²⁸ The silica-coating of citrate-stabilized gold nanoparticles involves functionalization of the silica surface with APTMS in aqueous solution. The NH₂ groups bind to the gold surface, and the Si(OEt)₃ groups extend outward for hydrolysis and condensation with sodium silicate (Na₂SiO₃) to deposit a thin silica layer. Thick silica shells can be grown on surface-stabilized gold nanoparticles by further hydrolysis/condensation of tetraethyl orthosilicate (TEOS), a typical precursor of silicon alkoxides.²⁷ Scheme 1.2 illustrates the synthetic procedure used to synthesize Au@SiO₂ shell/core nanoparticles.

Since amorphous silica is much more soluble than crystalline silica, amorphous silica will dissolve in hot concentrated alkali or fused hydroxide (SiO₂ + 2NaOH \rightarrow Na₂SiO₃ + H₂O).²⁹ The solubility of silica in aqueous solution has been shown to increase above pH 9 because of the formation of silicate ions in addition to Si(OH)₄ in solution (Si(OH)₄ + (OH⁻) \rightarrow (HO)₃SiO⁻ + H₂O).^{30,31} Therefore, silica-coated metal nanoparticles are unstable in aqueous hydroxide solution because the silica shells will

dissolve, leaving the bare metal nanoparticles to aggregate. Using the dissolution of silica, Zhang et al.³² reported the conversion of dense silica coatings into porous silica shells through surface-protected etching. The presence of PVP on the particle surface considerably increases the stability of silica spheres against etching by NaOH solution.

Scheme 1.2. Synthesis of Silica-coated Gold Nanoparticles.²⁷



Etching initially forms porous structures, and eventually can remove the core materials to leave behind hollow spheres with highly porous shells. Ge et al.³³ further reported the ability to fabricate more complex nanostructures of porous silica protected by $Fe_3O_4@SiO_2@Au@pore-SiO_2$ through a series of simple sol-gel and surface-protected etching processes. The NaOH-etching process was well controlled by monitoring the transmittance of the colloidal solution. At extended etching times, more silica materials dissolve in the form of soluble silicate oligomers. Over-etching can occur as the silica shells become thinner, incomplete, and incapable of fully retaining the enclosed Au nanoparticles.

Multi-functional silica-coated optical, electronic, and magnetic nanostructures are creating new opportunities for novel applications.^{34,35} With these many possible applications, other metal oxide-coated metal nanoparticles are also expected to receive a more intensified research interest as alternatives to silica-coated nanostructures.

1.5.2 Tin Oxide-coated Gold Nanoparticles

An alternative approach to shell/core nanoparticles involves tin oxide-coated metal nanoparticles, for which there are, to the best of our knowledge, six prior reports in the literature.³⁶⁻⁴¹ Tin oxide (SnO₂), as with silica (SiO₂), is a suitable material for optical coatings because of its transparency in the visible range. Tin oxide is a candidate for use in many optoelectronic devices, gas sensors, transparent conducting electrodes, and catalyst supports. The preparation of SnO₂-coated Au nanoparticles involves gold nanoparticle synthesis using the sodium citrate reduction method followed by encapsulation within the tin oxide shell via a hydrothermal reaction with sodium stannate (see Scheme 1.3). In this process, sodium stannate reacts with atmospheric CO₂ and water to form tin(IV) hydroxide (Na₂SnO₃ + H₂O + CO₂ \rightarrow Sn(OH)₄ + Na₂CO₃).⁴² Annealing at 60 °C promotes dehydration of the initial hydrated gel to form crystalline tin dioxide (Sn(OH)₄ \rightarrow SnO₂ + 2H₂O).

Tin oxide is an n-type semiconductor with a wide band gap ($E_g = 3.62 \text{ eV}$). As such, it is perhaps the most important material for use in gas sensing applications.⁴³ Nanostructured SnO₂ is the dominant choice for the solid-state detection of gases in

commercial and industrial settings because of its high sensitivity and low manufacturing cost.^{43,44} Millions of commercial carbon monoxide (CO) alarms using SnO₂ have been produced and have demonstrated the long-term dependable performance of tin dioxide sensors. Typically, SnO₂-based sensors are operated at high temperatures (e.g., > 400 °C) in order for catalytic oxidation of the gas and for high sensitivity.⁴³

Scheme 1.3. Synthesis of SnO₂-coated Gold Nanoparticles.³⁶⁻⁴¹



Current research involving SnO₂ gas sensors have focused on miniaturization, low temperature operation, and low power consumption, as well as improving the response and selectivity. In addition, it is known that Au is highly active for catalyzing low temperature CO oxidation and the hydrochlorization of ethyne to vinyl chloride.⁴ In recent years, therefore, there has been increasing interest in Au-decorated or doped SnO₂ sensor materials because gold can significantly enhance the gas sensor performances due to its exceptional catalytic activity.^{45,46} For example, Yu et al.⁴⁰ reported a CO sensor using Au@SnO₂ shell/core nanoparticles as sensing materials. The Au@SnO₂ shell/core particles showed higher sensor response to CO gas than corresponding SnO₂
nanoparticles over a broad temperature range (i.e., from room temperature to 350 °C). The role of the Au core as a catalyst in enhancing the adsorption and oxidation of CO gas is important for effective low temperature responses. Nevertheless, many challenges still remain that prevent full realization of the diagnostic potential of SnO_2 sensors beyond carbon monoxide detectors, including the need to improve selectivity, sensitivity, stability, and the time response of the sensors.

1.5.3 Zinc Oxide-coated Gold Nanoparticles

As one of the important wide-band gap semiconductors, zinc oxide (ZnO), has also been studied both experimentally and theoretically. A search of the literature reveals three prior reports of ZnO-coated gold nanoparticles.⁴⁷⁻⁴⁹ Two possible methods for the fabrication of the Au@ZnO shell/core composites have been reported, as shown in Scheme 1.4.⁴⁷⁻⁴⁹ To synthesize water-soluble ZnO-coated Au nanoparticles, zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was dissolved in water, and a white precipitate of zinc hydroxide (Zn(OH)₂) was formed upon the addition of sodium hydroxide solution (eq 1). Then, an excess amount of sodium hydroxide solution was added to form sodium zincate (Na₂ZnO₂) (eq 2). The zinc oxide-coated gold nanoparticles were then prepared by the addition of the sodium zincate to citrate-stabilized gold-nanoparticle solutions (eq 3). In this process, sodium zincate reacts with atmospheric CO₂ hydrothermally to form a Au@ZnO shell/core nanocomposite particle.

Scheme 1.4. Synthesis of ZnO-coated Gold Nanoparticles.⁴⁷⁻⁴⁹



Another possible mechanism for the formation of Au@ZnO shell/core nanoparticles is also presented in Scheme 1.4 (4). To synthesize the shell/core particles, gold nanoparticles were synthesized first using either the sodium citrate or the NaBH₄ reduction method,²⁸ and then a solution containing CTAB and Zn(NO₃)₂ was added to the gold nanoparticle solution. Gold nanoparticles have the ability to store electrons.³ Such electron storage within the gold nanoparticles leads to a substantial absorption of Zn²⁺ and NaOH, which can react with Zn²⁺ to produce Au@ZnO shell/core nanoparticles with concomitant protection by CTAB.





1.5.4 Titanium Oxide-coated Gold Nanoparticles

Over the past few years, a reliable method has been developed for the fabrication of TiO_2 -coated Au nanoparticles.^{50,51} A typical procedure for synthesizing the Au@TiO₂ shell/core nanoparticles involves a hydrothermal route using TiF₄ as the precursor, as shown in Scheme 1.5. In this process, gold nanoparticles are synthesized from the reduction of HAuCl₄ by sodium citrate. An aqueous solution of TiF₄ is added to the Au nanoparticle solution, and then the mixture is transferred to a Teflon-lined stainless steel autoclave. The hydrothermal reaction is then conducted at 180 °C for 48 h. During this process, anatase TiO₂ crystallites aggregate on the surface of Au cores to give the desired TiO₂-coated Au nanoparticles.

1.5.5 Copper Oxide-coated Gold Nanoparticles

Copper oxide (Cu_2O) is an important *p*-type semiconductor that possesses unique optical and electronic properties useful in various photovoltaic and photocatalytic

applications.⁵² Cu₂O nanostructures such as nanoparticles, nanowires, nanocubes, and nanoshells exhibit geometrically tunable properties. In particular, Au@Cu₂O shell/core nanoparticles can be synthesized simply by preparing a mixture of Cu(NO₃)₂, polyvinylpyrrolidone (PVP), and N₂H₄·H₂O in the presence of Au nanoparticles.⁵³ The synthesis procedure is illustrated in Scheme 1.6. In this process, Au nanoparticles serve as seeds to mediate the hierarchical assembly of Cu₂O nanocrystallites, which gives rise to the formation of a polycrystalline Au@Cu₂O shell/core nanoparticles with PVP as a structural directing agent.⁵³





1.5.6 Other Metal Oxide-coated Gold Nanoparticles

The coating of a thin layer of dielectric or semiconductor onto gold nanoparticles makes possible the control of interparticle and particle-matrix interactions, thereby further improving functional properties of devices on their basis and expanding the range of potential applications. Other metal oxides, such as MnO_2^{54} and $Al_2O_3^{55}$ have also been used to coat Au nanoparticles for selected applications. Studies suggest that the

shells completely protect the particles, and the shell thickness can be varied by simple procedures. Tian and colleagues^{54,55} used these particles in studies of surface-enhanced Raman scattering (SERS), which they called shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). In these studies, Raman signal amplification was provided by gold nanoparticles with an ultrathin SiO₂, Al₂O₃, or MnO₂ shell. There is still great demand to fabricate high quality dense and porous metal oxide shell-coated nanostructures for their important properties and diverse applications.

1.6 Metal Nanoparticles Embedded in Metal Oxide Thin Films

Noble metal nanoparticles embedded in dielectric or semiconductor thin films present a special class of materials due to their unique and tunable physical properties. The unique optical properties derived from the ability of nanoparticles by localized surface plasmon resonance (LSPR) characteristics and the tunability features arise due to the possibility of shifting the LSPR peak position from visible to the near IR region of the electromagnetic spectrum by either varying the dielectric function of the surrounding medium or by engineering the shape, size, and distribution of nanoparticles. Consequently, metal nanoparticles dispersed in metal oxide matrices are regarded as functional materials and exhibit characteristics that are not observed in the corresponding bulk metal oxides.

One of the important applications of metal nanoparticles embedded in oxide thin films is their potential use in plasmonic solar cells,⁵⁶ for which photovoltaic devices

represent one example.⁵⁷ These architectures have great potential in reducing the cost of solar cells. Currently, most common solar cells use silicon wafers that constitute about 40% of the cost.⁵⁸ However, plasmonic solar cells use substrates that are cheaper than silicon, such as glass, plastic, or steel.⁵⁸ One method that has been explored for the purpose of increasing the absorption of light in thin-film solar cells is the use of scattered light from metallic nanoparticles excited at their surface plasmon resonance.

A common design for plasmonic solar cells is to deposit metal nanoparticles on the top surface or to disperse metal nanoparticles in thin-film solar cells.⁵⁹ When light hits the metal nanoparticles, the light is scattered in many different directions (Figure 1.4), allowing the light to travel along the solar cells and bounce between the substrate and the nanoparticles and thus enabling the solar cells to absorb more light.⁵⁹ Novel metals are ideal for this purpose, and significant enhancements in photocurrent measurements have been found using silver and gold nanoparticle dopants.⁵⁷



Figure 1.4. Plasmonic solar cell using metal nanoparticle dopants.

Using gold nanoparticle dopants, Schaadt et al.⁶⁰ obtained enhancements of up to 80% at wavelengths of around 500 nm. Subsequently, Hagglund et al.⁶¹ reported the enhanced carrier generation by plasmonic nanoparticles in dye-sensitized TiO₂ films. In addition, Standridge et al.⁵⁶ used atomic layer deposition of TiO₂ onto transparent-conductive-oxide-supported silver nanoparticles as a means of protecting the particles. The resulting assemblies were exposed to a corrosive Γ/I_3^- environment (i.e., a dye-sensitized solar cell-like environment), and the oxides were able to protect the nanoparticles from any corrosion or photocorrosion. Further, structuring the solar cells so that light is trapped inside leads to increases the absorbance of light.^{57,58}

1.7 Research Objectives and Outline of Dissertation

The research goals of this dissertation are the development of reliable routes to metal oxide/metal shell/core nanoparticles and the generation of metal nanoparticleembedded metal oxide thin films with no particle aggregation or phase separation. In particular, there have been no reports describing the effective dielectric function of Au nanoparticles embedded in SnO_2 films, to the best of my knowledge. I have organized my efforts with these goals in mind.

As described above, colloidal gold nanoparticles possess unique opto-electronic properties and are widely used for catalysis, sensing, and energy conversion. Tin oxide semiconductors have also been used in many applications, including solar cells, lithium ion batteries, gas sensing, and catalysis. Due to their unique properties, Au and SnO₂

have long been studied as multifunctional materials for various applications. In my research, I have focused on the development of shell/core nanoparticles and nanoparticle-embedded thin films, especially those comprised of tin oxide matrices with embedded gold nanoparticles.

Chapter 1 provides a general introduction to the field of shell/core nanoparticles and a summary of my research objectives. Each following chapter describes an individual introduction, providing research background and objectives, experimental details, results and discussion, and literature references. Chapter 2 describes the synthesis of both colloidal Au@SiO₂ and Au@SnO₂ shell/core nanoparticles and investigates the effect of pH on their solubility and stability in aqueous solution. Dispersion and aggregation of both shell/cores were monitored and examined at various pHs to facilitate the prediction of their behavior during ambient use. Chapter 3 describes a new strategy for the fabrication of gold-nanoparticle-embedded tin oxide thin films for use in various nanoparticle thin-film applications. To incorporate Au nanoparticles homogeneously in the SnO_2 thin films, Au@SnO₂ shell/cores were employed to enhance their miscibility with the SnO_2 matrix and to prevent their aggregation. Chapter 4 describes the fabrication and characterization of the new composite nanoparticles that consist of Zn-doped Au@SnO₂ and Sb-doped Au@SnO₂ shell/core nanoparticles. Chapter 5 describes the synthesis and characterization of gold nanoshells and a process for the fabrication of the nanoshell-dispersed polymeric thin films using electrostatic layer-by-layer assembly. Finally, Chapter 6 provides general conclusions and suggests future research objectives related to the work described in this dissertation.

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CHAPTER 2. Stability of Colloidal SiO₂-coated and SnO₂-coated Gold Nanoparticle Solutions as a Function of pH

2.1 Abstract

Aqueous acidic and basic colloidal SiO₂-coated and SnO₂-coated Au nanoparticle solutions were prepared, and their stability was monitored visually and by UV-vis spectroscopy. Notably, the SnO₂-coated Au nanoparticle solutions were stable up to pH 12.5. At pH 13 and 14, the SnO₂-coated Au nanoparticles underwent aggregation, which could be fully reversed upon neutralization of the solutions. In contrast, the SiO₂-coated Au nanoparticle solutions were unstable at pH > 10.5, irreversibly producing a precipitate composed of bare Au nanoparticle aggregates. Under acidic conditions, precipitation was observed from both the colloidal SiO₂-coated and SnO₂-coated Au nanoparticle solutions, but the colloidal SiO₂-coated and SnO₂-coated Au nanoparticle solutions. The precipitation at low pH coincided with the reported isoelectric pH values of SiO₂ and SnO₂, respectively.

2.2 Introduction

Core-shell structure of metal oxide or semiconductor coated metal nanoparticles have become increasingly important in the last decade because of many potential applications such as catalytic¹, optical coating², gas sensing^{3,4}, solar cell⁵, and biomedical applications⁶. These core-shells have allowed for the enhancement of luminescence of semiconductor nanoparticles, preparation of bioconjugates, chemical

and colloidal stability, charging of metal cores, and so on. Various metal oxides such as $SiO_2^{1,6-8}$, $TiO_2^{5,9-11}$, ZnO_2^{12-14} , MnO_2^{15} , $Al_2O_3^{16}$, and $SnO_2^{2-4,17,18}$ have been used as the shell materials since they offer a range of refractive indices and electronic conductivities. Among these core-shell nanoparticles, silica-coated metal nanoparticles are one of the most well known core-shell structures. Silica-coated metal nanoparticles generally involve rich surfaces chemistry, high biocompatibility, controllable porosity, and good transparency. The excellent silica property has been widely used to coat on colloidal metal nanoparticles to prevent particle coalescence. Number of methods has been used to synthesize the silica-coated nanoparticles since the pioneering work by Mulvaney and co-workers in 1996.⁷ A further approach to core-shell nanoparticles is SnO₂-coated metal nanoparticles. A search of the literature reveals five prior reports of SnO₂-coated gold nanoparticles.^{2-4,17,18} Tin oxide (SnO_2) as with silica (SiO_2) is also a suitable material for optical coatings because of transparency in the visible range. Tin oxide is electroconductive and has consequently been used in the fabrication of transparent electrodes and infrared reflectors.

We are interested in finding durable coatings for core-shell nanoparticles that can tolerate the potentially harsh environments encountered in many solar energy conversion applications, including photovoltaic devices and solar-to-hydrogen fuel cells.¹⁹⁻²² A material commonly used in conventional solar conversion applications is tin oxide (SnO₂), which can be doped to form a transparent conductor.²³ Little is known about SnO₂-coated nanoparticles, however, and no studies of their stability or of the stability of their colloidal solutions under acidic or basic conditions have been published.^{2-4,17,18} In

this paper, we report on the stability of colloidal SnO_2 -coated Au nanoparticle solutions compared to SiO₂-coated Au nanoparticle solutions over a wide pH range. We compared SnO₂-coated Au nanoparticles with SiO₂-coated Au nanoparticles specifically because of the widespread use of silica as a coating in core-shell nanoparticles.^{1,6-8}

2.3 Experimental Section

2.3.1 General Considerations

Commercial samples of chloroauric acid (Strem), 3-aminopropyltrimethoxysilane (Aldrich), sodium citrate (Aldrich), sodium silicate solution (Aldrich, reagent grade; ~10.6% Na₂O, ~26.5% SiO₂), and Na₂SnO₃·3H₂O (Aldrich) were used as received. All manipulations were performed in air. De-ionized water was used in the synthetic preparations and stability studies. The syntheses of citrate-stabilized, SiO₂-coated, and SnO₂-coated Au nanoparticles were based on published procedures.^{1-4,6-8,17,18}

2.3.2 Synthesis of Citrate-stabilized Au Nanoparticles

In a beaker, an aqueous solution of chloroauric acid (0.50 mL, 1.0 wt %,) was diluted with water (150 mL), and the resulting solution was heated to boiling with stirring. An aliquot of a sodium citrate solution (10. mL, 1.0 wt %) was added quickly to the hot chloroauric acid solution with stirring. The color of the solution changed from light yellow to dark red within an hour. This red solution, presumed to contain citrate-stabilized gold nanoparticles, was allowed to cool to room temperature. The as-prepared solution was used subsequently in the syntheses of SiO₂- and SnO₂-coated Au

nanoparticle solutions as described below.

2.3.3 Synthesis of SiO₂-coated Au Nanoparticles

A freshly prepared aqueous solution of 3-aminopropyltrimethoxysilane (1.0 mL, 1.0 mM) was added with vigorous stirring to an aliquot of the aqueous citrate-stabilized gold nanoparticle solution (100 mL) described above. After the addition was complete, the mixture was stirred at room temperature for 30 min. The mixture was then heated (80 °C) with vigorous stirring, and an aqueous solution of sodium silicate (1.0 mL) was added rapidly. A dark purple colloidal solution was obtained immediately. The solution was cooled to room temperature and centrifuged (6000 rpm/30 min). The supernatant liquid was removed with a pipette and discarded. Water was added to the resultant sticky solid, giving a dark purple colloidal solution.

2.3.4 Synthesis of SnO₂-coated Au Nanoparticles

An aqueous solution of $Na_2SnO_3 \cdot 3H_2O$ (5.0 mL, 40 mM) was added rapidly with stirring to a hot (80 °C) aliquot of the aqueous citrate-stabilized gold nanoparticle solution (150 mL) described above. A purple colloidal solution was obtained immediately. The solution was cooled to room temperature and centrifuged (6000 rpm/30 min). The supernatant liquid was removed with a pipette and discarded. Water was added to the resultant sticky solid, giving a dark purple colloidal solution.

2.3.5 Nanoparticle Characterization

The size and morphology of uncoated and coated Au nanoparticles were determined using a JEOL JEM-2000 FX transmission electron microscope (TEM) operating at a bias voltage of 200 kV. The samples for TEM analyses were prepared by placing a drop of the colloidal solution from a pipette onto a TEM copper grid and then drying in air. This process was repeated (10 times or more) to obtain a quantity of sample suitable for analysis.

UV-vis spectra were obtained in the range 400–1000 nm using a Cary 50 Scan UV-vis spectrometer. The samples for analyses were prepared by placing the asprepared aqueous solutions in a quartz cuvette.

X-ray photoelectron spectroscopy (XPS) data were collected on a Physical Electronics Model 5700 instrument. Photoemissions were produced using a monochromatic Al K α X-ray source (1486.6 eV) operated at 350 W. The XPS samples for analysis were prepared by placing a drop of the colloidal solution from a pipette onto a silicon wafer (NESTEC, <100>) and then drying in air. This process was repeated (10 times or more) to obtain a quantity of a sample suitable for analysis. XPS scans were conducted at high resolution with pass energy 23.5 eV, a photoelectron takeoff angle of 45°, and an analyzer spot diameter of 2 nm. The Sn 3*d*, O 1*s*, and C 1*s* binding energies were referenced to the Au $4f_{7/2}$ peak (84 eV).

2.3.6 Stability Studies

The pH of colloidal solutions was adjusted using 0.1 M solutions of HCl, NaOH,

and CsOH, as appropriate, and was measured by using pH test paper (EMD Chemicals ColorpHast[®]). The solutions were monitored visually for the appearance of a precipitate and/or a color change, and a UV-vis spectrum was collected for each solution to compare with the spectrum of the parent solution. In selected cases, precipitates were collected with a pipette and placed on a silicon wafer for analysis by XPS as described above.

2.4 Results and Discussion

Citrate-stabilized, SiO₂-coated, and SnO₂-coated Au nanoparticles were synthesized via procedures based on published methods.^{1-4,6-8,17,18} Figure 2.1 illustrates the synthetic procedure used to obtain Au@SnO₂ core-shells and Au@SiO₂ core-shells. To prepare the SiO₂- and SnO₂-coated Au nanoparticles, first of all, gold nanoparticles were synthesized by the sodium citrate reduction method. Silica-coating procedure to the citrate-stabilized gold nanoparticles involves the surface attachment with 3aminopropyl trimethoxysilane (APTMS) in aqueous solution. The NH₂ groups are bound to the gold surface and Si(OEt)₃ groups are extended outward for hydrolysis and condensation with sodium silicate (Na₂SiO₃) to deposit a thin silica layer. The preparation of the SnO₂-coated Au nanoparticles also starts with the synthesis of gold nanoparticles followed by their encapsulation within the tin oxide shell by an addition of sodium stannate trihydrate (Na₂SnO₃·3H₂O) via a simple hydrothermal process.



Figure 2.1. Synthesis of SnO_2 -coated Au nanoparticles and SiO_2 -coated Au nanoparticles.



Figure 2.2. TEM images of (left) citrate-stabilized Au nanoparticles, (center) SiO_2 coated gold nanoparticles, and (right) SnO_2 -coated gold nanoparticles. The scale bars are 100 nm.



Figure 2.3. Extinction spectra of citrate-stabilized Au nanoparticles (Au NPs), SiO_2 coated Au nanoparticles (Au@SiO₂ NPs), and SnO₂-coated Au nanoparticles (Au@SnO₂ NPs).

Figure 2.2 shows TEM images of the nanoparticles. For all samples, the Au nanoparticle diameter is about 15 nm. The thicknesses of the SiO₂ and SnO₂ coatings are approximately 7 and 20 nm, respectively, giving rise to composite particle diameters of ~30 and ~55 nm, respectively. In the sample of the nanoparticles collected from the SnO₂-coated Au nanoparticle solutions, gold-free SnO₂ nanoparticles were also observed, representing approximately ~10 % of the samples. The TEM images show that all of the nanoparticles have excellent uniformity; notably, the SnO₂-coated Au nanoparticles show greater uniformity than those reported previously.^{2-4,17,18}

Figure 2.3 shows the extinction spectra of the colloidal uncoated and coated Au nanoparticle solutions. The surface plasmon resonance (SPR) observed for the citrate-stabilized, SiO₂-coated, and SnO₂-coated Au nanoparticle solutions had maxima at 522,

529, and 533 nm, respectively, consistent with previously reported values.^{17,24} The red shifts of the SPR bands for the coated particles are due to the high refractive indexes of $SiO_2 (1.46)^{25}$ and $SnO_2 (2.2)^{26}$ coatings.



Figure 2.4. Photographs of colloidal (a) SiO₂-coated Au nanoparticle and (b) SnO₂coated Au nanoparticle solutions at various pH values. The photographs were taken approximately 1 h after the solution pH values were adjusted using 0.1 M NaOH. The loss of dispersion for the SiO₂-coated Au nanoparticles at high pH, however, occurred immediately upon adjustment of the pH.

To determine the stability of the coated nanoparticles and their colloidal solutions under acidic and basic conditions, colloidal nanoparticle solutions with various pH values were prepared and monitored over time by visual inspection and collection of extinction spectra. Figure 2.4 shows photographs of colloidal SiO₂-coated and SnO₂coated Au nanoparticle solutions under neutral and basic conditions. The color changes observed for the SiO₂-coated Au nanoparticle solutions (Figure 2.4 (a)), which occurred within a few minutes of adjusting the pH, indicate that the solutions were unstable under basic conditions. Extinction spectra (Figure 2.5 (a)) were consistent with the visual observations. The blue shift of the SPR band maxima to 522 nm for the solution at pH 10.5 (Figure 2.5 (a)) is consistent with the formation of a bare Au nanoparticles, and spectra for the solutions with pH > 10.5 are consistent with agglomeration and precipitation of the Au nanoparticles.^{27,28} The agglomeration observed for the SiO₂coated nanoparticle solutions at high pH is attributed to the solubility of SiO₂ in basic solution: at high pH, the SiO₂ coating dissolves,²⁹ leaving the bare Au nanoparticles to coagulate.^{27,28}

In contrast to the behavior exhibited by the SiO₂-coated Au nanoparticle solutions at high pH, the SnO₂-coated Au nanoparticle solutions appeared to be stable at high pH after 1 h by visual inspection (Figure 2.4 (b)). We note, however, that at pH 13 and 14, the SnO₂-coated nanoparticle solutions displayed evidence of agglomeration and precipitation after 24. The stability of the SnO₂-coated Au nanoparticle solutions under basic conditions is corroborated by extinction spectra (Figure 2.5 (b)). The SPR band maxima of the SnO₂-coated Au nanoparticles were centered at 533 nm for solution pH 7–12, consistent with a stable colloidal solution. At pH 13 and 14, however, the SPR maxima were red shifted (545 nm), suggesting nanoparticle agglomeration.³⁰



Figure 2.5. Extinction spectra of colloidal (a) SiO_2 -coated Au nanoparticles and (b) SnO_2 -coated Au nanoparticle solutions at various pH values. The spectra were recorded approximately 1 h after the solution pH values were adjusted using 0.1 M NaOH.

Interestingly, the effect was fully reversible: when the pH 13 and 14 solutions were adjusted to pH 12.5 with 0.1 M HCl and the extinction spectra re-measured, the SPR maxima shifted to 533 nm, consistent with re-constitution of the stable colloidal SnO₂-coated Au nanoparticle solution. These results suggest that at pH 13 and 14 the

 SnO_2 coatings remain intact despite the agglomeration. A possible explanation for these observations is that at high pH, highly charged (deprotonated) SnO_2 -coated Au nanoparticles are formed, and these charged species interact with Na⁺ to form clusters.³¹ In contrast, the nanoparticles at lower pH are not as highly charged and consequently do not extensively form clusters with Na⁺.³¹

To test the notion of whether the agglomeration of SnO_2 -coated Au nanoparticles at high pH depended specifically on the intermediacy of Na⁺, the experiments for SnO_2 coated Au nanoparticle solutions were repeated using CsOH to adjust the pH. As shown in the spectra presented in Figure 2.6, the SPR peak maxima for the pH 13 and 14 solutions are not red shifted, in contrast to when Na⁺ was present. We attribute this phenomenon to the lower charge density of Cs⁺ compared to Na⁺, which in turn leads to diminished cluster formation at high pH.



Figure 2.6. Extinction spectra of colloidal SnO_2 -coated Au nanoparticle solutions at various pH values. The spectra were recorded approximately one hour after the pH values were adjusted with 0.1 M CsOH.



Figure 2.7. Photographs of colloidal (a) SiO_2 -coated Au nanoparticles and (b) SnO_2 coated Au nanoparticle solutions at various pH values. The photographs were taken approximately one hour after the pH values were adjusted with 0.1 M HCl.

The stabilities of the colloidal nanoparticle solutions were also compared under acidic conditions. In Figure 2.7, photographs are presented showing the SiO₂-coated and SnO₂-coated Au nanoparticle solutions at low pH. Over the pH range 2–7, the SiO₂-coated Au nanoparticles displayed excellent dispersion (Figure 2.7 (a)), and the SPR peak maxima at 529 nm in the corresponding extinction spectra were invariant (Figure 2.8 (a)). In contrast, at pH 2–4 the nanoparticles precipitated from the SnO₂-coated Au nanoparticle solutions (Figure 2.7 (a)), with the precipitation rate increasing with increasing pH. The agglomeration was reflected in the extinction spectra, which showed a red shift for the SPR maxima to 542–545 nm for the pH 2.0, 2.5, 3.0, and 4.2 solutions

from the maxima at 533 nm for pH 7. The contrasting behavior between the SiO₂-coated vs. SnO₂-coated nanoparticle solutions at pH 2–4 corresponds with the different isoelectric points of SiO₂ and SnO₂, which are reported to be pH \approx 2 and 4–4.5, respectively.^{32,33} Correspondingly, the SiO₂-coated nanoparticles precipitated slowly (\approx 7 d) at pH 2, but there was no precipitation from solutions with pH > 2. Colloidal solutions of the SiO₂ and SnO₂-coated nanoparticles reformed upon neutralization of the solutions from which precipitation had occurred. The reversibility suggests that the coatings remained intact.

X-Ray photoelectron spectroscopy (XPS) studies were performed to determine the species present in the SnO₂-coated Au nanoparticles that precipitated from solutions at pH 4.2 and 13. For comparison, XPS data were also collected for particles collected from a colloidal solution at pH 7. The spectra for the three samples shown in Figure 2.9 are similar, with each revealing peaks at 84.0 and 87.7 eV assigned to Au⁰ 4f_{7/2} and 4f_{5/2}, respectively,^{34,35} and peaks at 487.4 and 495.8 eV assigned to Sn⁴⁺ 3d_{5/2} and 3d_{3/2}, respectively.³⁶ These data are consistent with the presence of intact SnO₂-coated Au nanoparticles, suggesting that precipitation of the particles is not accompanied by removal of the SnO₂ coating. This stability is corroborated by the observation of reversible colloid formation upon neutralization of the solutions from which precipitation had occurred.



Figure 2.8. Extinction spectra of colloidal (a) SiO₂-coated gold nanoparticle and (b) SnO₂-coated Au nanoparticle solutions at various pH values. The spectra were recorded approximately one hour after the pH values were adjusted using 0.1 M HCl.



Figure 2.9. High-resolution XPS spectra of SnO_2 -coated Au nanoparticles that precipitated from solution at pH 4.2 and 13; (a) Au_{4f} and (b) Sn_{3d}. Data were also collected from a colloidal solution at pH 7 for comparison. The peak at 498 eV at pH 13 can be assigned to a sodium Auger signal (Na_{KLL}).

2.5 Conclusions

Our results show that colloidal solutions composed of SnO_2 -coated Au nanoparticles are more stable under basic conditions (up to pH 14) than those composed

of SiO₂-coated Au nanoparticles. Furthermore, the results suggest that the instability of the SiO₂-coated Au nanoparticle solutions at high pH is due to the dissolution of the SiO₂ coatings. Additionally, we observed agglomeration at low pH for both SiO₂ and SnO₂-coated Au nanoparticles, and the pH at which agglomeration was observed coincided approximately with the isoelectric pH values of the oxides. The agglomeration at low pH was reversible by neutralizing the solution.

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CHAPTER 3. Homogeneous Tin Oxide (SnO₂) Thin Films Containing SnO₂-coated Gold Nanoparticles

3.1 Abstract

A sol-gel-based approach to the fabrication of tin oxide (SnO_2) semiconductor thin films containing SnO₂-coated gold nanoparticles is described. In this approach, gold nanoparticles with a mean diameter of ~15 nm were coated with thin layers of SnO₂. The composite particles were ~55 nm in diameter with SnO₂ shells that were ~20 nm thick. These nanoparticles were doped homogeneously into a SnO₂ sol-gel precursor, and the mixture was deposited as a thin film via spin-coating methods. The SnO₂-coated nanoparticles and the SnO₂ films doped with the nanoparticles were characterized by transmission and scanning electron microscopy (TEM and SEM) and X-ray diffraction (XRD). The optical properties of the nanoparticles and the composite films were evaluated by UV-vis spectroscopy.

3.2 Introduction

Because of potential applications in nonlinear optics,^{1,2} plasmonic solar cells,³ photocatalytic degradation of pollutant,⁴ and gas sensing,^{5,6} simple and efficient strategies for incorporating metal nanoparticles into dielectric metal oxide films have been investigated. In the last decade synthetic processes for embedding metal nanoparticles within various metal oxide (e.g., SiO₂, TiO₂, SnO₂, ZnO, and ZrO₂) thin films have been developed.⁶⁻¹³ In most cases, metal salts or preformed metal

nanoparticles are mixed with a dielectric material or a sol-gel precursor material and deposited as a film via dip-coating or spin-coating.^{7,8,14} These efforts have been largely motivated by the desire to make use of the surface plasmon resonance (SPR) properties of the metal nanoparticles in optoelectronic nanocomposite thin films.^{2,7}

Tin oxide (SnO₂) is an attractive material for optical coatings because it is transparent in the visible range. Tin oxide is also electroconductive and has consequently been used in the fabrication of transparent electrodes and infrared reflectors. Tin oxide is also an attractive semiconductor material for many other optoelectronic devices because it possesses high photostability and good carrier mobility. SnO₂ is a large band gap semiconductor like TiO₂ and ZnO; therefore, much of the reported work utilizes these films for solar energy conversion and for optoelectronic devices.¹⁵

Tin oxide films can be fabricated by many techniques, including chemical vapor deposition,¹⁶ sputtering,¹⁷ spray pyrolysis,¹⁸ reactive evaporation,¹⁹ and sol-gel methods.^{11,20} In general, sol-gel methods are more flexible than conventional technologies, offering many advantages, such as excellent homogeneity, facile control of film thickness, simple and low-cost processing, low-temperature processing, and most significantly the ability to produce fine films.^{20,21}

The incorporation of metal nanoparticles into dielectric metal oxide films is most commonly accomplished using sol-gel methods, where the metal is introduced in the form of a soluble salt, and then reduced to form metal nanoparticles in situ through reductive annealing processes.^{11,14,22} Epifani et al.¹¹ reported SnO₂ thin films prepared

by sol-gel processing doped with various metals (nickel, palladium, platinum, and osmium). A chloride-based inorganic sol-gel route was used for preparing the metaldoped SnO₂ sol. SnCl₄ used as the tin precursor was first reacted with propanol to synthesize tin alkoxide and then resulting compound was hydrolyzed and subsequently mixed with solutions of the metal dopants to prepare the composite sol solution. After film deposition and heat treatment, Pd and Pt nanoparticles were formed in the SnO₂ matrix. This in-situ method, however, offer limited control of the nucleation process and the particle size, shape, and polydispersity. In contrast, ex-situ synthesis, offers greater flexibility in the design and fabrication of the nanoparticles embedded within the sol-gel matrix. The features of the nanoparticles are optimized, the particles are mixed with the sol-gel precursor, and then the mixture is deposited as a film. Buso et. al⁷ reported goldnanoparticle-doped TiO₂ thin films using ex-situ sol-gel processing. In order to phase transfer the particles into ethanol, gold nanoparticles were first functionalized with mercaptoundecanoic acid, the optimized particles were mixed with sol-gel Ti butoxide solution (TiO_2 precursor), and then the mixture was deposited by spin coating and followed by annealing process as a film.

In the present study, we report a new strategy for the fabrication of goldnanoparticle-doped SnO_2 thin films. To incorporate Au nanoparticles homogeneously in the SnO_2 sol and ultimately the thin films, the Au nanoparticles were pre-coated with SnO_2 to enhance their miscibility and to prevent their aggregation. SnO_2 -coated Au nanoparticles were mixed with a tin oxide sol. Spin-coating methods were used to obtain SnO_2 thin films doped with SnO_2 -coated Au nanoparticles. We also report the optical properties of the SnO_2 -coated gold nanoparticles prior to and after incorporation into the thin film. Importantly, this ex-situ synthesis method can be readily extended to other nanoparticles and dielectric metal-oxide thin films, which have the potential to serve as optical materials in plasmonic devices and solar energy conversion systems.

3. 3 Experimental Section

3.3.1 Synthesis of Au Nanoparticles

A solution containing 0.5 mL of 1% $HAuCl_4$ was diluted to 150 mL of H_2O and then heated to boiling while being stirred in 250 mL beaker. A 10 mL aliquot of a 1.0 wt% sodium citrate solution was quickly added to the hot $HAuCl_4$ solution. The solution changed color within an hour from light yellow to dark red.

3.3.2 Synthesis of SnO₂-coated Au Nanoparticles

A 150 mL aliquot of the citrate-stabilized gold nanoparticles was placed in a water bath at 60 °C and stirred vigorously followed by the rapid addition of 5.0 mL of sodium stannate trihydrate (Na₂SnO₃·3H₂O 95 %, 40 mM, Aldrich). A purple colloidal solution was obtained, consistent with the formation of SnO₂-coated gold nanoparticles. The colloidal particles were collected by centrifugation (7000 rpm/20 min) and washed with deionized water to remove any unreacted species and impurities (e.g., sodium chloride).
3.3.3 Preparation of SnO₂ Sol Solution Containing the SnO₂-coated Au Nanoparticles

Tin oxide containing the core-shell nanoparticles was developed using a sol-gel technique. A 1.0 mL aliquot of tin isopropoxide $(Sn(i-OPr)_4, 10\%)$ in isopropanol, Alfa Aesar) was dissolved in 2.0 mL of isopropanol and stirred for 30 min. A 2.0 mL aliquot of complexing agent 2,4-pentadione (acetylacetone; AcAc) was then added to stabilize the hydrolysis of the $Sn(i-OPr)_4$. To facilitate the dispersion of the SnO_2 -coated Au nanoparticles in the sol-gel solution, the aqueous nanoparticle solution was centrifuged and re-dispersed into a minimum volume of isopropanol and then added to the AcAc-stabilized SnO_2 sol. After 24 h of stirring in room temperature, a dark-purple transparent sol solution containing SnO_2 -coated Au nanoparticles was obtained.

3.3.4 Fabrication of SnO₂ Thin Films Containing the SnO₂-coated Au Nanoparticles

Nanocrystalline SnO_2 thin films containing the SnO_2 -coated Au nanoparticles were fabricated by spin coating, the sol on silica substrate; where the rotation speed was gradually increased to 1500 rpm for 20 seconds. The process was repeated for up to 5 times until the desired thickness was achieved. After spin coating, the gel film was dried in air for an hour and in an oven at 200 °C for 1 hour.

3.3.5 Characterization

The SnO₂-coated Au nanoparticles were imaged using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Specifically, to

characterize the size and morphology of the nanoparticles, we used a JEOL JEM-2000 FX TEM operating at a voltage of 200 kV and a JEOL JSM 6330F field-emission scanning electron microscope (FE-SEM) operating at 1.0, 5.0, and 15.0 kV. A variety of magnifications were employed to evaluate the size and morphology of the nanoparticles. FE-SEM analysis of the composite films by energy-dispersive X-ray spectroscopy (EDX) allowed us to determine the approximate content of Sn, Si, O, and Au in the samples. UV-vis spectra were obtained using a Cary 50 Scan UV-vis spectrometer over the wavelength range of 400-1000 nm. We also used a Siemens D-5000 powder X-ray diffraction (XRD) equipped with a monochromatic Cu K_{α} (λ =1.540562Å) radiation to analyze the samples. The data were collected between scattering angles (2 θ) of 20° and 90° in steps of 0.02°.

3.4 Results and Discussion

The synthetic goal of this work was the design of a process for dispersing gold nanoparticles in tin oxide thin films without particle aggregation or phase separation. A tin oxide sol-gel solution was prepared by mixing $Sn(i-OPr)_4$, AcAc, and isopropanol. Attempts to disperse the Au nanoparticles in SnO_2 films by direct mixing of the citratestabilized aqueous gold nanoparticles with the isopropanol-based SnO_2 sol-gel solution were unsuccessful due to rapid hydrolysis and condensation reactions of the tin isopropoxide, which led to the rapid aggregation of the gold nanoparticles. A key step in solving this problem was the encapsulation of the gold nanoparticles within a tin oxide shell so that they can be the phase-transferred into 2-propanol without aggregation,

which enables the preparation and ready manipulation of highly concentrated Au nanoparticle solutions.



Figure 3.1. Strategy used to prepare tin oxide thin films containing SnO₂-coated Au nanoparticles.

A search of the literature reveals six prior reports of SnO_2 -coated gold nanoparticles.²³⁻²⁸ The preparation of these core-shell nanoparticles starts with the synthesis of gold nanoparticles followed by their encapsulation within the tin oxide shell by an addition of sodium stannate trihydrate (Na₂SnO₃·3H₂O) via a simple hydrothermal process. Importantly, solid oxides in aqueous suspension are generally electrically charged so that gold nanoparticles coated with tin oxide layers are generally resistant to coagulation due to the negative charges at the surface of the particles.²⁹

To facilitate the phase transfer of the particles into isopropanol, the synthesized SnO₂-coated Au nanoparticles were centrifuged and washed with deionized water to remove any unreacted species and impurities and then re-dispersed into a minimum volume of isopropanol, where the SnO₂-coated Au nanoparticles showed no obvious signs of aggregation. The composite nanoparticles were then added to the AcAc-stabilized SnO₂ precursor solution. The resulting composite solution was well mixed without precipitations. Importantly, this strategy circumvented the need to add compatibilizing agents, such as poly(vinyl alcohol) (PVA) or polyvinylpyrrolidone (PVP). Nanocrystalline SnO₂ thin films containing the SnO₂-coated Au nanoparticles were fabricated on substrate surfaces (e.g., silicon wafers and glass slides) by spin coating (1500 rpm, 20 sec) and allowing the deposited film to dry undisturbed under ambient conditions. Figure 3.1 illustrates the overall synthetic procedure used to obtain nanocrystalline SnO₂ thin films with homogeneously embedded SnO₂-coated Au nanoparticles.

Figure 3.2 shows SEM and TEM images of the SnO_2 -coated gold nanoparticles. The diameters of the Au core nanoparticles are ~15 nm. The thickness of the SnO_2 coating is ~20 nm, giving an overall diameter of ~55 nm in diameter for the composite particles. A few free SnO_2 nanoparticles with no Au cores are also present in the sample, representing approximately ~10 % of the samples. The images show that all of the nanoparticles have excellent uniformity.



Figure 3.2. (a) TEM and (b) SEM images of SnO_2 -coated Au nanoparticles.



Figure 3.3. Powder X-ray diffraction (XRD) patterns of the SnO_2 -coated Au nanoparticles. Calculated patterns for Au (FCC structure) and SnO_2 (rutile structure) are presented for reference.

Figure 3.3 shows the room-temperature powder X-ray diffraction (XRD) pattern of the SnO₂-coated nanoparticles. All of the peaks correspond either to tin oxide or gold. The peaks at $2\theta = 38.08^{\circ}$, 44.26°, 64.38°, 77.31°, and 81.45° corresponds to the (111), (200), (220), (311), and (222) lattice planes of gold nanoparticles with a face-centered cubic structure (JCPDS Card No. 04-0784). Separately, the peaks at $2\theta = 26.56^{\circ}$, 33.87°, and 51.77° corresponding to the (110), (101), and (211) lattice planes of tin dioxide with a rutile structure (JCPDS Card No. 77-0451). The crystalline particle size *D* can be estimated from the X-ray Au (111) and SnO₂ (101) diffraction peaks using the Scherrer equation,³⁰ $D = 0.94 \cdot \lambda/\beta \cdot \cos\theta$, where λ is the wavelength of the X-ray source, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle in the diffraction pattern. From this analysis, we estimate that the diameter of the Au nanoparticle is ~10 nm and the mean grain SnO₂ size of the shell is ~4 nm from the values of $\lambda = 0.15406$ nm, $2\theta = 38.41^{\circ}$ (Au), $2\theta = 34.08^{\circ}$ (SnO₂), $\beta = 0.84^{\circ}$ (Au), and $\beta = 2.01^{\circ}$ (SnO₂), respectively; indicating that the spherical SnO₂ shells may consist of smaller particles, as confirmed by TEM.

Figure 3.4 shows the optical absorption spectra of the gold nanoparticles, SnO₂coated gold nanoparticles, and the latter particles embedded in the SnO₂ film. The surface plasmon resonance (SPR) of the gold nanoparticles in aqueous solution was centered at 522 nm. Coating the particles with SnO₂ shifted the peak to longer wavelength (545 nm). The red shift of the extinction band is consistent with coating the nanoparticles with a high refractive index material; the refractive index of SnO₂ is 2.006, which is higher than that of water (1.333).²³ That is, the red shift is due to the increase in the local refractive index around the particles.³¹ The SPR band of the core-shell nanoparticles embedded in the SnO₂ film is further red-shifted to 554 nm. This further red shift might arise due to the decrease of the interparticle distance within the nanoparticle film. With the decrease of the interparticle distance, the absorption peak begins to red-shift due to the interparticle plasmon coupling.³² Therefore, the Au@SnO₂ nanoparticles in SnO₂ thin films are expected to have less interparticle distance than that in solution phases and can be served further red-shifted. Notably, the initial SnO₂ coating prevents the gold cores from aggregating in the film environment (vide infra).



Figure 3.4. Extinction spectra of (a) Au nanoparticles, (b) SnO₂-coated Au nanoparticles, and (c) core-shell nanoparticles embedded in a thin film of SnO₂.

Uncoated gold nanoparticles are prone to aggregation in high ionic strength solutions due to their strong van der Waals attraction³³; this type of aggregation typically broadens and further red-shifts the SPR band. Figure 3.5 (a) shows, however, that in our system, the position of the SPR band does not vary with the number of the layers. That is, the position of the extinction maximum is unaffected by the doping concentration. In contrast, the intensity of the band increases with the increasing number of coating layers.

The images in Figure 3.5 (b) shows four samples: a tin oxide film with no Au nanoparticles and a series of films with embedded SnO_2 -coated Au nanoparticles, where the number of spin-coated layers is increased from 1 to 5. The sample dimensions can be deduced from the scale bar. The spin-coated films are optically transparent. While the undoped SnO_2 film is colorless, the Au-doped SnO_2 films exhibit a pink color that becomes more intense with the increase in the number of spin-coated layers.



Figure 3.5. (a) Extinction spectra of spin-coated SnO_2 thin films with and without embedded SnO_2 -coated Au nanoparticles; (b) photograph of the composite films deposited on glass substrates. The scale bar is in centimeters.



Figure 3.6. (a) EDX analysis of SnO_2 thin films containing SnO_2 -coated Au nanoparticles. (b and c) SEM images showing cross-sectional views of the 1 layer of films spin coated on silicon wafers. (d and e) SEM images showing top views of spin-coated monolayer and five-layer films, respectively.

The Au-doped SnO₂ films were examined by scanning electron microscope. The films were fabricated on both silicon wafers and glass slides by spin-coating (1500 rpm for 20 sec). Analysis of the films by EDX confirmed the presence of Sn, O, and Au. Cross-sectional views of the films (Figures 3.6 (b) and (c)) indicate a uniform SnO₂ film thickness of ~200 nm. The gold nanoparticles appear as white spots randomly distributed within the ~200 nm thick SnO₂ films. The SEM images in Figures 3.6 (d) and (e) confirm the existence of well-dispersed core-shell nanoparticles in the SnO₂ thin film. In a few cases, some small aggregates can be discerned. Notably, the overwhelming majority of particles remain statistically well dispersed, which is consistent with the extinction spectra in Figure 3.5.

3.5 Conclusions

We have demonstrated the fabrication of nanocrystalline tin oxide (SnO_2) semiconductor thin films in which SnO_2 -coated Au nanoparticles are embedded and uniformly dispersed. The gold nanoparticles were encapsulated within SnO_2 shells to prevent their direct interaction and to facilitate phase transfer into an isopropanol-based SnO_2 sol solution. The nanocrystalline composite films were fabricated by spin coating methods, and the surface morphology of the films was investigated by scanning electron microscopy. The images confirmed that the core-shell nanoparticles are well dispersed in the SnO_2 thin films because the individual Au particles were pre-coated to prevent

their direct interaction. The extinction maximum of the Au-doped SnO_2 films was redshifted compared to that of Au nanoparticles in aqueous solution due to the high refractive index of the sol-gel matrix. This ex-situ synthesis and doping strategy allows the fabrication of SnO_2 thin films with homogeneous distributions of embedded metal nanoparticles.

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CHAPTER 4. Synthesis and Characterization of Zinc- and Antimony-doped Au@SnO₂ Core-Shell Nanoparticles

4.1 Abstract

Due to their unique properties, nanocomposites of gold (Au) and tin oxide (SnO₂) have been studied as multifunctional materials for various applications. A hydrothermal method was used to synthesize Au@SnO₂ core-shell nanoparticles doped with antimony (Sb) and zinc (Zn) oxides. The morphologies of the composite nanoparticles were characterized by using scanning and transmission electron microscopy (SEM and TEM). The composite particles were ~45-55 nm in diameter with shells that were ~15-20 nm thick. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were used to show that the dopants were incorporated into the particles. The optical properties of the composite nanoparticles were analyzed by UV-vis spectroscopy. A red shift in the plasmon resonance absorption was observed on doping with both zinc and antimony oxides.

4.2 Introduction

Tin dioxide (stannic oxide or tin oxide, SnO_2) is one of the most important transparent conductive oxide (TCO) materials and has many applications in, for example, solar cells,¹ light emitting diodes,² and gas sensors.³ SnO_2 has been reported to be an *n*-type semiconductor with wide band gap ($E_g \sim 3.6 \text{ eV}$), high electrical conductivity, high transmittance in the ultraviolet-visible (UV-vis) region, and high infrared (IR)

reflectivity.⁴ The chemical and physical properties of SnO_2 -based materials can be improved by the introduction of a wide range of dopants, for example, fluorine (FTO)⁵-, tungsten (WTO)⁶-, antimony (ATO)⁷-, indium (ITO)⁸-, and zinc (ZTO)⁹-doped tin oxide. Indium tin oxide (tin-doped indium oxide, ITO) is still the most commonly used TCO materials due to its low resistivity and high optical transmittance. A demand exists, however, to develop new TCO materials that can replace ITO in commercial optoelectronic devices in order to reduce their cost and overcome a possible supply shortage of indium oxide. For example, antimony-doped tin oxide (ATO) and zincdoped tin oxide (ZTO) have high carrier mobilities and good optical transmittance and are promising *n*-type conductivity materials and they are also thermally and chemically more stable than undoped SnO_2 .^{7,9-11}

Core-shell structures of Au and Ag cores and tin oxide shells have been reported recently.¹²⁻¹⁹ The intrinsic optical and crystal structure characteristics of core-shell nanoparticles can be maintained at high temperatures because coalescence of the cores is greatly restricted by the inorganic oxide shell materials.^{14,15,20} Joo et. al.²⁰ reported the design of a high-temperature thermally stable model catalytic system that consists of a Pt metal core coated with a mesoporous silica shell (Pt@mSiO₂). Core-shell nanoparticles which are prepared with organic capping agents such as polymers or surfactants does not prevent aggregation at high temperature (> 300 °C) because the organic layers decompose and the metal core nanoparticles can deform and aggregate.²⁰ Consequently, after the high temperature reactions, the nanoparticles change their size or shape compared with those of pristine nanoparticles. Recently, Au@SnO₂ core-shell

nanoparticles have been used in tin oxide (SnO₂) gas sensors for carbon monoxide (CO) detection because the nanoparticles with a core-shell structure can be maintained at high temperatures and also because Au nanoparticles are highly active for catalyzing low temperature CO oxidation.^{14,16} The Au core improves the adsorption of CO and acts as an efficient catalyst for oxidation of CO gas for a higher sensor response.

In this chapter, we describe the hydrothermal synthesis and characterization of novel Au@SnO₂ core-shell nanoparticles doped with Zn (II) and antimony (V) oxides. Doped Au@SnO₂ core-shell nanoparticles have not previously been reported. SEM and TEM were used to verify the morphologies of the core-shell nanoparticles. The presence of antimony and zinc oxides in the nanoparticles was confirmed by powder X-ray diffraction and XPS measurements. The introduction of Sb and Zn into the Au@SnO₂ core-shell nanoparticles resulted in a red shift of the plasmon absorption band as determined by UV-vis spectroscopy.

4.3 Experimental Section

4.3.1 General Considerations

Chloroauric acid (HAuCl₄, Strem), sodium citrate (Aldrich), sodium stannate trihydrate (Na₂SnO₃·3H₂O, Aldrich), sodium antimonate trihydrate (NaSbO₃·3H₂O, Alfa Aesar), zinc nitrate hydrate (Zn(NO₃)₂·xH₂O, Aldrich), and sodium hydroxide (NaOH, Aldrich) were used as received. All manipulations were performed in air. De-ionized water used in all experiments was obtained from Milli-Q Reagent Water System.

4.3.2 Synthesis of Citrate-stabilized Au Nanoparticles

A solution containing 2.00 mL of 1% HAuCl₄ was diluted to 400 mL of H_2O and then heated to boiling with stirring. An aliquot of a sodium citrate solution (10 mL, 1.0 wt %) was quickly added to the diluted HAuCl₄ solution. The solution changed color within an hour from light yellow to dark red. This red solution of citrate-stabilized gold nanoparticles was allowed to cool to room temperature.

4.3.3 Synthesis of Undoped-Au@SnO₂ Core-Shell Nanoparticles

An aliquot of citrate-stabilized gold nanoparticles (10 mL) was placed in a water bath at 60 °C and stirred vigorously then 1.00 mL of sodium stannate trihydrate (Na₂SnO₃·3H₂O 95 %, 40 mM, Aldrich) was added rapidly. A purple colloidal solution was obtained, consistent with the formation of SnO₂-coated gold nanoparticles. The colloidal particles were collected by centrifugation (7000 rpm/20 min) and washed with de-ionized water twice to remove any unreacted species and impurities (e.g., sodium chloride).

4.3.4 Synthesis of Zn-doped Au@SnO₂ Nanoparticles (Au@ZTO)

To prepare water soluble and stable Au@ZTO core-shell nanocomposites, a novel colloidal approach was used. A total of 0.189 g of zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$ was dissolved into 10 mL of deionized water. A white precipitate of zinc hydroxide $(Zn(OH)_2)$ formed after adding 1.0 mL (1M) of sodium hydroxide solution. Then, an excess amount (8.0 mL) of sodium hydroxide solution was added to dissolve the white precipitate to form sodium zincate (Na₂ZnO₂). An aqueous solution of Na₂SnO₃·3H₂O (1.0 mL, 40 mM) was added rapidly with stirring to a hot (60 °C) aliquot of the aqueous citrate-stabilized gold nanoparticle solution (10.0 mL) described above. A purple colloidal solution was obtained immediately. The sodium zincate (Na₂ZnO₂, 0.2 mL) was then added to the hot mixture of sodium stannate trihydrate and citrate-stabilized gold nanoparticle solution. The solution was transferred to a Teflonlined stainless steel autoclave of 50 mL capacity and heated at 150 °C for 5 h, then aircooled to room temperature. The resulting colloidal solution was centrifuged (7000 rpm/20 min) and washed with water twice.

4.3.5 Synthesis of Sb-doped Au@SnO₂ Nanoparticles (Au@ATO)

In order to synthesize Au@ ATO core-shell nanoparticles, a similar approach to that describe above for Au@ZTO particles was used. Sodium antimonate trihydrate (NaSbO₃·3H₂O, Alfa Aesar) is very slightly soluble in water. 10 mM of sodium antimonate trihydrate aqueous solution was prepared by heating in a hot water bath. An aqueous solution of Na₂SnO₃·3H₂O (1.0 mL, 40. mM) was added rapidly with stirring to a hot (60 °C) aliquot of the aqueous citrate-stabilized gold nanoparticle solution (10.0 mL) as described above. A purple colloidal solution was obtained immediately. The sodium antimonate trihydrate (NaSbO₃·3H₂O, 10 mM, 1.0 mL) solution was then added to the hot sodium stannate trihydrate citrate-stabilized gold nanoparticle solution. The solution was then transferred to a Teflon-lined stainless steel autoclave of 50 mL capacity and heated at 150 °C for 5 h, then air-cooled to room temperature. The 72

resulting colloidal solution was cooled to room temperature and centrifuged (7000 rpm/20 min). The supernatant liquid was removed with a pipette and discarded. Deionized water was added to the resultant solid, giving a pink transparent solution.

4.3.6 Nanoparticle Characterization

The size and morphology of Sb- and Zn-doped Au@SnO₂ core-shell nanoparticles were determined using a JEOL JEM-2000 FX transmission electron microscope (TEM) operating at a voltage of 200 kV. The samples for TEM analyses were prepared by placing a drop of the colloidal solution from a pipette onto a TEM copper grid and then drying in air. This process was repeated to obtain a suitable quantity of sample for analysis. Analysis by SEM was performed using a JSM 6330F JEOL field emission scanning electron microscope with an accelerating voltage of 15kV. Different magnifications (× 33,000-100,000) were used to examine the product morphology.

UV-vis spectra were obtained in the range 400-1000 nm using a Cary 50 Scan UVvis spectrometer. The samples for analyses were prepared by placing the as-prepared aqueous solutions in a quartz cuvette. Powder X-ray diffraction was performed with nickel-filtered Cu K_{α} radiation using the PANalytical X'Pert PRO diffractometer. The data were collected between scattering angles (2 θ) of 20° and 90° in steps of 0.008°.

X-ray photoelectron spectroscopy (XPS) data were collected on a Physical Electronics Model 5700 instrument. Photoemission spectra were produced using a monochromatic Al K α X-ray source (1486.6 eV) operated at 350 W. The XPS samples

for analysis were prepared by placing a drop of the colloidal solution from a pipette onto a silicon wafer (NESTEC, <100>) and then drying in air. This process was repeated several times to obtain a suitable quantity of a sample for analysis. XPS scans were conducted at high resolution with pass energy 23.5 eV, a photoelectron takeoff angle of 45° , and an analyzer spot diameter of 2 nm.

4.4 Results and Discussion

The experimental work was intended to synthesize the composite core-shell nanoparticles of $Au@SnO_2$ doped with zinc (II) and antimony (V) oxides. Figure 4.1 illustrates the synthetic procedure used to prepare both Zn-doped Au@SnO₂ (Au@ZTO) and Sb-doped Au@SnO₂ (Au@ATO) core-shell nanoparticles. To prepare the composite core-shells, first of all, gold nanoparticles were synthesized by the sodium citrate reduction method.²¹ The SnO₂-coated Au nanoparticles were then synthesized by the addition of an aqueous sodium stannate solution (Na₂SnO₃·3H₂O) in a simple hydrothermal process. When the sodium stannate solution was added with stirring to a hot gold nanoparticle solution, a purple colloidal solution was obtained immediately. In order to prepare the Zn- and Sb-doped Au@SnO₂ composite nanoparticles, sodium zincate (Na₂ZnO₂) solution and sodium antimonate (NaSbO₃) solution were added after the addition of sodium stannate solution. The combined solutions in autoclaves wear heated in an oven at 150 °C for 5 h. The final product solutions, presumed to contain the composites of Zn- and Sb-doped Au@SnO2 nanoparticles, remained transparent and purple in after the hydrothermal treatment.



Figure 4.1. Synthesis of Zn-doped Au@SnO₂ (Au@ZTO) and Sb-doped Au@SnO₂ (Au@ATO) core-shell nanoparticles.

Figures 4.2 – 4.4 show TEM and SEM images of the Zn-doped Au@SnO₂ and Sb-doped Au@SnO₂ nanoparticles, respectively. The core-shell structure of the nanoparticles is clearly observed in the both nanoparticles. The diameters of the Au core nanoparticles were approximately ~15 nm; free oxide nanoparticles without Au cores are also present in the samples, representing approximately ~40-50 % of the samples. The sizes of the nanoparticles without Au cores and nanoparticles with cores are different. The free oxide nanoparticles without Au cores are spheres ~22 ± 2 nm in diameter while the core-shell shaped nanoparticles have a diameters of ~39 ± 4 nm (Zn-doped Au@SnO₂) and ~51 ± 4 nm (Sb-doped Au@SnO₂). The thickness of Zn-doped SnO₂ shells are ~12 ± 2 nm, giving an overall diameter of ~39 ± 4 nm and the thickness of Sbdoped SnO₂ shells are about ~18 ± 2 nm, giving an overall diameter of ~51 ± 4 nm for the composite particles. The Sb-doped SnO₂ coatings are slightly thicker than the Zndoped SnO₂ coatings in the images obtained.



Figure 4.2. TEM images of Zn-doped Au@SnO₂ core-shell nanoparticles.



P157_001 P157-1 Cal: 0.133369 nm/pix 3:09:32 PM 5/9/2012 TEM Mode: Imaging





P157_002 P157-2 Cal: 0.080019 nm/pix 3:12:47 PM 5/9/2012 TEM Mode: Imaging

20 nm HV=200.0kV Direct Mag: 250000x



Figure 4.3. TEM images of Sb-doped Au@SnO₂ core-shell nanoparticles.



Figure 4.4. SEM images of (a, b) Zn-doped Au@SnO₂ core-shell nanoparticles and (c, d) Sb-doped Au@SnO₂ core-shell nanoparticles with different magnification scales.

Figure 4.5 shows the UV-vis absorption spectra of Zn-doped Au@SnO₂ and Sbdoped Au@SnO₂ nanoparticles. Spectra of citrate-stabilized gold nanoparticles and undoped Au@SnO₂ nanoparticles are also shown for comparison. Au core nanoparticles show a very intense surface plasmon absorption band in the visible resign. Gold core nanoparticles showed a maximum absorption peak at 521 nm, and their optical response was markedly affected by the composite coatings. Upon deposition of a SnO₂ shell, the plasmon resonance of the particles was red-shifted to 542 nm. The shift in the plasmon resonance on encapsulation may be principally due to the change in the refractive index of the medium. After the coating, the tin oxide shell has a much higher refractive index $(n_{se02}=2.006)$ than water $(n_{teo}=1.333)$.¹² In addition, when zinc and antimony oxides are doped into the tin oxide shell, the plasmon resonance of the particles was observed to further red-shift to 557 nm and 556 nm, respectively. The plasmonic red shifts observed in the Zn- and Sb-doped Au@SnO₂ core-shell particles are related to the unique dielectric properties (refractive indexes) of the materials. A red shift in the SPR peak position was observed as the refractive index of the surrounding SnO₂ medium increases on Sb and Zn ion doping.²²⁻²⁴

Figure 4.6 shows the XRD patterns of Zn- and Sb-doped Au@SnO₂ and undoped Au@SnO₂ nanoparticles for comparison. Calculated patterns for ZnSnO₃ (LiNbO₃ structure), Au (fcc structure), and SnO₂ (rutile structure) are also presented for reference. For the undoped SnO₂-coated Au nanoparticles, all of the peaks correspond either to tin oxide or gold. The peaks at 2θ = 38.1°, 44.2°, 64.4°, 77.4°, and 81.5° corresponds to the (111), (200), (220), (311), and (222) lattice planes of gold nanoparticles with a face-centered cubic structure using the Joint Committee on Powder Diffraction Standards (JCPDS Card No. 04-0784). Separately, the peaks at 2θ = 26.6°, 33.8°, 51.7°, 54.8°, 57.8°, 61.9°, 66.0°, and 71.3° corresponding to the (110), (101), (211), (220), (002), (310), (301), and (202) lattice planes of tin dioxide with a tetragonal rutile structure (JCPDS Card No. 77-0451). Figure 4.6 (b) shows the XRD patterns of the Sb-doped Au@SnO₂ nanoparticles. It reveals that all patterns were corresponding to the

polycrystalline SnO₂ with tetragonal rutile structure. No other phase can be further detected in the XRD patterns. This was due to the antimony ions entering the crystal lattice of tin dioxide, creating the SnO₂ tetragonal rutile structure. For the Zn-doped Au@SnO₂ nanoparticles (Figure 4.6 (a)), most of the peaks are similar in position intensity to those from undoped Au@SnO₂ and Sb-doped Au@SnO₂. This was also due to the zinc ions entering the crystal lattice of tin dioxide. However, the intense peaks were found at $2\theta = 23.2^{\circ}$, 32.1, 33.8° , 46.5° , and 52.5° , which can be indexed to the (012), (-114), (-120), (024), and (-126) lattice planes of the structure of zinc stannate (ZnSnO₃) (JCPDS Card No. 11-0274). In our experimental condition, the stannic (Na₂SnO₃·3H₂O) and zincate (Na₂ZnO₂·3H₂O) precursors were reacted with a molar ratio of Zn²⁺/Sn⁴⁺/Na⁺ of 1:1:10 and ZnSnO₃ was then formed.²⁵ The formation of ZnSnO₃ can be explained as follows in equations:²⁵

$$Zn^{2+} + Sn^{4+} + 6OH^{-} \rightarrow ZnSn(OH)_{6}$$
(1)

$$ZnSn(OH)_6 \rightarrow ZnSnO_3 + 3H_2O$$
 (2)

The combination of Zn^{2+} , Sn^{4+} , and OH^- in the precursor solution led to the formation of the unstable intermediate $ZnSn(OH)_6$ in the solution. Under hydrothermal conditions, the $ZnSn(OH)_6$ unstable intermediate is transformed into $ZnSnO_3$.²⁵ Zinc stannate has two compositions in two with a different Zn/Sn/O ratio: $ZnSnO_3$ (LiNbO₃ structure) and Zn_2SnO_4 (spinel structure).²⁵ In the Zn-doped Au@SnO₂ nanoparticle samples, no peaks from Zn_2SnO_4 phases were detected.



Figure 4.5. Extinction spectra of (a) Zn-doped Au@SnO₂ nanoparticles and (b) Sbdoped Au@SnO₂ nanoparticles. Spectrum of citrate-stabilized gold nanoparticles and undoped Au@SnO₂ nanoparticles are also shown for comparison as denoted.



Figure 4.6. Powder X-ray diffraction (XRD) patterns of (a) Zn-doped Au@SnO₂ nanoparticles, (b) Sb-doped Au@SnO₂ nanoparticles, and (c) undoped Au@SnO₂ nanoparticles with calculated patterns for (d) ZnSnO₃ (LiNbO₃ structure), (e) SnO₂ (rutile structure), and (f) Au (fcc structure) for references.

XPS is a valuable technique to characterize the composition of the surface of the nanoparticles. The elemental compositions and chemical status of both Zn- and Sb-doped Au@SnO₂ were further analyzed by XPS and showed strong peaks of Zn_{2p}, O_{1s}, Sn_{3d}, and Sb_{3d} as shown in Figure 4.7-4.8. In both core shell nanoparticles, the metallic

core Au_{4f} peaks, which are normally observed at 84 eV (Au $4f_{7/2}$) and 87 eV (Au $4f_{5/2}$), were not observed because Au was encapsulated perfectly by the oxide shell. XPS is surface sensitive with a detection depth ~ 10 nm. However, the small peaks at 91.7 eV and 89.1 eV in Figure 4.7 (a) and at 99.0 eV in Figure 4.8 (a) are observed. They were assigned to Zn 3p_{1/2}, Zn 3p_{3/2}, and the signal for the Si substrate species, respectively. The observed doublet peaks of Sn $3d_{5/2}$ and Sn $3d_{3/2}$ at 487.0 eV and 495.5 eV in both samples of Figure 4.7 (b) and Figure 4.8 (b) indicates the presence of SnO₂, respectively. The peak of O 1s at about 531 eV was assigned to the lattice oxygen in the SnO₂, while that at 533 eV is due to the chemisorbed oxygen caused by the absorption of H_2O molecule to the surface. Figure 4.7 (d) shows a strong peak from Zn $2p_{3/2}$ at about 1022.5 eV, which is characteristic of Zn^{2+} in the Zn-doped Au@SnO₂ sample. The Sb 3d region of the spectrum of the Sb-doped Au@SnO₂ nanoparticles is shown in Figure 4.8 (d); the peak position is characteristic of Sb^{5+} . The determination of the antimony was not straight forward, as its signal appears at similar binding energy to the oxygen 1s peak. The peak at 531.1 eV had to be separated into an oxygen (O 1s) peak and antimony (Sb $3d_{5/2}$) peak. Therefore, we chose to constrain the peak position only, based on the energy difference 9.34 eV of the Sb $3d_{3/2}$ doublet.²⁶ This was done by making use of the relation between the Sb $3d_{5/2}$ peak at 531.1 eV and the Sb $3d_{3/2}$ peak at 540.4 eV which was fixed to be 1.45.²⁶ The real areas of the peaks were calibrated towards the particular elements. The dopant concentration in Zn- and Sb-doped Au@SnO₂ nanoparticles was confirmed by quantitative determination from the XPS measurements in Table 4.1. The quantitative analysis using Sn 3d_{5/2}, Sb 3d_{5/2}, and Zn 2p_{3/2}, peaks revealed a Sn/Sb and

Sn/Zn atomic ratio of 16:1 and 2.5:1 with the initial Sb doping concentration of 25 and 50 mol%, respectively. A small amount of Zn or Sb dopant have been distributed through the tin oxide shells as confirmed in XPS measurement, however, it is difficult to analyze the dopant distributions because they are not visible in a conventional electron micrograph. Moreover, it is complicated to quantify distribution of dopant zinc ions from the strong peak from Zn $2p_{3/2}$, which is characteristic of Zn²⁺, because there is a second phase present in Zn-doped Au@SnO₂ particles as confirmed in a XRD measurement.



Figure 4.7 XPS spectra of Zn-doped Au@SnO₂ nanoparticles; (a) Au_{4f}, (b) Sn_{3d}, (c) O_{1s}, (d)Zn_{3d}



Figure 4.8 XPS spectra of Sb-doped Au@SnO₂ nanoparticles; (a) Au_{4f}, (b) Sn_{3d}, (c) O_{1s}, (d)Sb_{3d}

Table 4.1 Composition Derived from XPS Measurements of Zn- and Sb-dopedAu@SnO2 Nanoparticles.

	Zn-doped Au@SnO ₂	Sb-doped Au@SnO ₂
C 1s	24.32	4.98
O 1s	51.25	63.95
Sn 3d _{5/2}	17.39	29.24
Zn 2p _{3/2}	7.03	
Sb 3d _{5/2}		1.83
Au 4f	0.00	0.00

4.5 Conclusions

In this work, we have described the synthesis and characterization of zinc- and antimony-doped Au@SnO₂ core-shell nanoparticles via a hydrothermal route. The morphologies of the composite nanoparticles were characterized with SEM and TEM. The particles have cores approximately ~15 nm in diameter SnO₂ shells doped with zinc and antimony of thickness~15-20 nm, respectively. The zinc and antimony dopant incorporation were confirmed by XPS measurements, and all of the zinc might be present as $ZnSnO_3$. The optical properties of the Au@SnO₂ nanoparticles exhibited a red shift on doping with zinc and antimony. The XRD pattern of Sb-doped Au@SnO₂ nanoparticles corresponds to polycrystalline SnO_2 with tetragonal rutile structure. No other phase was detected. The XRD pattern of the Zn-doped Au@SnO₂ nanoparticles showed the presence of two phases: of zinc stannate (ZnSnO₃) and SnO₂ with the tetragonal rutile structure. To improve the quality of these composite core-shell nanoparticles, other synthetic approaches are being considered and also further electrical conductivity experiments are planned because these composite core-shells are considered to potentially important to TCO applications.

4.6 References

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CHAPTER 5. Preparation and Characterization of Polymeric Thin Films Containing Gold Nanoshells via Electrostatic Layer-by-Layer Self Assembly

5.1 Abstract

This chapter describes the synthesis of gold shell/silica core particles ~200 nm in diameter with shells ~25 nm thick and their incorporation into organic polymeric thin films. The morphologies of the nanoparticles were characterized with scanning and transmission electron microscopy (SEM and TEM). Powder X-ray diffraction (XRD) demonstrated that the gold layers were well crystallized. Multilayered thin films containing the nanoparticles and polyethyleneimine (PEI) were generated using dip-coating techniques based on electrostatic layer-by-layer self-assembly methods. The resultant composite films containing uniformly dispersed nanoshells with minimal aggregation were imaged by SEM, and the optical properties were analyzed by absorption spectroscopy, which showed broad extinctions ranging from the visible to the near-IR spectral regions. X-ray photoelectron spectra (XPS) were also obtained to determine the elements present and the oxidation states of these elements.

5.2 Introduction

Metal nanoparticles (NPs) derived from noble metals have drawn wide interest because of their unique and tunable optical properties and their efficient photo-thermal effects.¹ The most notable optical feature of these NPs is the surface plasmon resonance (SPR), which arises from an interaction between an electromagnetic wave and the
conduction electrons present in the metal. Under the irradiation of light, the conduction of electrons on the surface of the metal NPs is driven by the electric field to oscillate collectively in response to optical excitation.² The SPR peak position of metal nanoparticles varies with the particle size, shape, and the refractive index of the surrounding medium.³⁻⁷ Recently, another related physical property, heat generation by NPs under illumination, has also attracted much interest.^{8,9} The heat generation from these NPs involves the absorption of incident photons and the conversion of photon energy into heat energy as well as heat transfer from the NPs to the surrounding matrix. The heating effect is especially strong for metal NPs because they have a high optical quantum yield (i.e., they are poor emitters of light). Efforts have been made to measure the temperature on the surface of Au NPs when optically excited.^{8,9}

For the last couple of decades, a new type of shell/core metal nanoparticle called a "nanoshell" has also drawn much interest.^{5,6,10,11} Gold nanoshells consist of a spherical dielectric core nanoparticle, such as silica or polystyrene, surrounded by a thin gold shell. Most metal NPs that exhibit SPR behavior generally adsorb or scatter light over the ultraviolet and visible regions of the electromagnetic spectrum. However, unlike simple metal NPs, the SPR of gold nanoshells can be tuned to a wide range of frequencies from the ultraviolet to the near-infrared regions of the electromagnetic spectrum. Gold nanoshells having SPRs in the near infrared region are well suited for biological applications because biological fluids and tissue are transparent over this range of the electromagnetic spectrum. Apart from their optical properties, gold nanoshells are biologically inert, and their surfaces can be readily functionalized with selective

biomolecular linkers for the purpose of targeting them to specific sites of interest. Some applications that rely on the optical and thermal properties of nanoshells include biological imaging and detection, drug delivery, and the photothermal treatment of various diseases, such as cancer.¹²⁻¹⁶ The most common synthetic approach for these gold nanoshells has been the "seeded growth" method.^{6,10} This route involves the synthesis of silica NPs and the functionalization of their surface with terminal amine groups to facilitate the attachment of small colloidal gold particles, which then serve as seeds to template the subsequent growth of a polycrystalline gold shell in a controlled manner.

To fabricate novel nanostructured devices, techniques for generating a wide range of nanoparticles with various sizes and properties, and the assembly of these NPs to produce various types of film, are necessary. A self-assembled monolayer (SAM) of nanoparticles to generate thin-film architectures is one such method that has many promising applications, including various functional layers in optoelectronic devices.¹⁷⁻²¹ Srinivasan et al.²¹ have reported the fabrication of multilayered Au NPs thin films on aminosilane functionalized quartz substrates. These researchers showed that the use of layer-by-layer (LBL) assembly with poly(allylamine hydrochloride) afforded tightly packed Au NPs; further, the NPs began to agglomerate and formed large clusters with an increase in the number of assembled layers. Separately, Shao-Horn and co-workers¹⁸ reported the fabrication of composite thin films comprised of gold nanoparticles and multiwall carbon nanotubes (MWNTs) using electrostatic LBL assembly. These researchers fabricated thin films by the assembly of positively charged 2aminoethanethiol-stabilized Au NPs together with negatively charged carboxylic acid functionalized-multiwall carbon nanotubes (MWNTs-COOH) on an organosilanemodified ITO electrode.

Here, we report a process for the fabrication of multilayered polymeric thin films containing gold nanoshells. These composite materials are being developed for use in solar-to-thermal fuel cells,²² which complements separate efforts that target the use of gold nanoshells for plasmon-enhanced dye-sensitized solar cells.²³ In the present study, gold nanoshells dispersed within poly(ethyleneimine) (PEI) multilayer films were prepared via electrostatic layer-by-layer assembly using simple dip-coating techniques. Specifically, a thin film of water-soluble PEI was adsorbed onto a glass slide, and then negatively charged gold nanoshells were absorbed electrostatically from aqueous solution onto the positively charged substrate surface. The process could be repeatedly cycled to increase the thickness of the film in a controlled manner. The use of PEI was particularly effective in particle dispersion since the polymer readily absorbed on the substrate and allowed only minimal aggregation of the nanoshells.

5. 3 Experimental Section

5.3.1 Synthesis of Silica Nanoparticles and Functionalization of the Surface with APTMS

Ammonia (3.0 mL, 30% NH_3 as NH_4OH assay) was added to ethanol (50.0 mL). The mixture was stirred vigorously, and 1.5 mL of tetraethyl orthosilicate (TEOS) was added dropwise. Over the course of 30 min, the solution changed from clear to opaque white. An excess of APTMS (~0.5 mL) was then added to the vigorously stirred SiO_2 nanoparticle solution, which was allowed to react for 2 h. The solution was gently refluxed for an additional 1 h to enhance covalent bonding of the APTMS groups to the silica nanoparticle surface. The APTMS-coated silica nanoparticles were centrifuged and re-dispersed in ethanol.

5.3.2 Preparation of a Solution of Colloidal Gold Nanoparticles

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) solution was prepared by adding 12 μ L of 80% THPC in water to 1 mL of HPLC grade water. An aliquot of 1M NaOH (0.5 mL) and 1 mL of THPC solution were added to 45 mL of HPLC grade water. The mixture was vigorously stirred for 5 min, and 2 mL of 1% HAuCl₄ solution (1 g HAuCl₄ in 100 mL of water) was quickly added to the stirred solution.

5.3.3 Addition of Colloidal Gold to the Functionalized Silica Nanoparticles

The colloidal gold NP solution prepared above was concentrated by rotary evaporation to a volume of 13 mL. In a 45 mL centrifuge tube, 1 mL of the APTMS-functionalized silica NP solution was added to an excess (10 mL) of the concentrated gold nanoparticle solution. The mixture was vigorously shaken, and kept overnight in the refrigerator. The solution was then centrifuged (3000 rpm, 1 h). Red-colored particles were observed to settle to the bottom of the tube. The colored particles were redispersed and sonicated in HPLC grade water. The solution was then centrifuged again (3000 rpm, 1h) and washed twice with HPLC grade water.

5.3.4 Preparation of a Reducible Gold Salt Solution (K-Gold)

In a 500 mL round-bottomed flask, potassium carbonate (0.1 g, K_2CO_3) was dissolved in 400 mL of HPLC grade water. After 10 min of stirring, 8 mL of 1% HAuCl₄ solution (1 g HAuCl₄ in 100 mL of water) was added. The solution initially appeared yellow and slowly became colorless.

5.3.5 Growth of Gold Nanoshells

The gold-seeded silica nanoparticle solution was injected into a vigorously stirred solution of gold salt (K-Gold). The thickness of the gold shell could be varied systematically by adjusting the amount of gold-seeded silica NP solution added. Then, 40 μ L of formaldehyde was slowly injected. Within 10 min, the solution changed from colorless to blue and dark red, which is characteristic of nanoshell formation.^{6,10} After 30 min, the nanoshells were centrifuged and re-dispersed in HPLC grade water.

5.3.6 Surface Functionalization of Gold Nanoshells

The aqueous gold nanoshells were mixed with 3-mercaptopropionic acid (MPA, 0.1 mol, 500:1 volume ratio of nanoshell solution:MPA) at room temperature to form a monolayer of MPA on the surface of the gold nanoshells. Excess MPA was then removed by two repetitive cycles of centrifugation (15 min, 1500 rpm) and re-dispersion of the nanoshells in deionized water. After removing the excess MPA, the MPA-functionalized gold nanoshell solution was concentrated (\times 15) by centrifugation.

5.3.7 Preparation of PEI Thin Films Containing Gold Nanoshells

A commercial solution of polyethyleneimine (PEI, 50 wt% in H_2O) was diluted by adding deionized water to prepare a solution having a low concentration of PEI (1 wt%). Glass microscope slides were cleaned by ultrasonication in soap, acetone, and Milli-Q water for 10 min each. The slides were immersed in PEI solution (1 wt%) for 1 h and then washed with water and allowed to dry. The PEI films were then immersed in the concentrated gold nanoshell solution for several hours.

5.3.8 Characterization

The surface morphology of the gold particles and overall uniformity of the composite films were examined by scanning electron microscopy (SEM). A JSM 6330F JEOL field emission scanning electron microscope was used at 15.0 kV. A variety of magnifications (×10,000-100,000) were employed to examine the product morphology. Extinction spectra were obtained using a Cary 50 Scan UV-vis spectrometer over the wavelength range of 300-1000 nm. Powder X-ray diffraction was performed with nickel-filtered Cu K_{α} radiation. The data were collected between scattering angles (2 θ) of 5° and 90° in steps of 0.02°. X-ray photoelectron spectroscopy (XPS) analyses were carried out using X-ray radiation from the aluminium K_{α} band. All spectra were recorded from 0 to 1100 eV and were internally calibrated by setting the Au_{4f 7/2} binding energy to 84.0 eV.

5.4 Results and Discussion

The purpose of this work was to develop a synthetic approach for fabricating the gold nanoshell thin films without particle aggregation or phase separation. The strategy for obtaining monolayer assembly of the nanoparticles involves the attachment of a functionalized (charged) polymer on a substrate and the subsequent exposure of the nanoshells to an oppositely charged polyelectrolyte, facilitating the attachment via electrostatic forces.

As a first step, scheme 5.1 shows the process that we used to synthesize the gold nanoshells.¹⁰ Silica (SiO₂) is a popular material used in shell/core particles because of its ease of synthesis, stability against coagulation, and versatile functionalization.²⁴ It is also chemically inert, optically transparent and does not affect redox reactions at core surfaces.²⁵ We prepared silica core particles via the hydrolysis and condensation of TEOS in the presence of ammonium hydroxide (NH₄OH) as catalyst. We then functionalized the surface of the silica NPs by grafting with APTMS to give a terminal amine group on the surface. In a separate process, we prepared a colloidal gold solution via reduction the of hydrogen tetrachloroaurate(III) $(HAuCl_4)$ with tetrakis(hydroxymethyl)phosphonium chloride (THPC). The solution was then aged for several days in the refrigerator to allow the size of the nanoparticles to stabilize before being seeded onto the surface functionalized silica core. The resultant gold nanoparticle seeds were consistently observed to be $\sim 2-3$ nm in diameter (data not shown). The aged THPC-gold seeds were then deposited onto the silica particles by simple mixing. To grow the gold layer on the gold-seeded silica NPs, we prepared a solution containing a reducible gold salt (K-Gold). Gold shells were grown by adding the gold-seeded silica nanoparticles to the K-Gold solution. Finally, gold nanoshells were successfully fabricated having a diameter of ~200 nm.

Scheme 5.1. Preparation of Gold Nanoshells Using the "Seeded Growth" Method.





Figure 5.1. SEM and TEM images of silica particles (a) and gold nanoshells (b-d).

The morphology of the silica particle cores and the gold nanoshells was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The images in figure 5.1 show that the silica NPs are quite uniform in size (approximately ~150 nm). Similarly, the micrographs show that the nanoshells are spherical, but their surface is rough on the nanometer scale. Based on the SEM and TEM images, we can estimate the dimensions of these shell/core particles. Given that the silica core and gold nanoshell diameters are \sim 150 nm and \sim 200 nm, respectively, we infer that the gold shells are \sim 25 nm thick. As a whole, the images in figure 5.1 provide direct evidence for the formation of gold nanoshells consisting of a silica core and a gold outer layer.



Figure 5.2. X-ray diffraction of the gold nanoshells and (111) reflection peak for the crystallite size calculation using the Scherrer formula.

We used X-ray diffraction (XRD) to examine further the gold nanoshells on the silica cores. The sharp peaks in figure 5.2 for shows that the outer layers are composed of crystalline gold, with $2^{\bullet} = 38.2^{\circ}$, 44.3° , 64.7° , 77.6° , and 81.8° , which correspond to

the (111), (200), (220), (311), and (222) lattice planes, respectively. The crystallite size of the gold shells was also determined from the (111) reflection in the XRD patterns using the Scherrer formula.²⁶ The gold cluster size calculated using the Scherrer equation was ~17 nm, which is in reasonably good agreement with the shell thicknesses determined from the SEM and TEM images in figure 5.1.

Scheme 5.2. Fabrication of Nanoshell Thin Films by Electrostatic Layer-by-Layer Assembly.



Modified Gold Nanoshells Colloids



Figure 5.3. The picture shows the gold nanoshells/PEI films on SiO₂ substrate via dipcoating process.

Scheme 5.2 shows the strategy we used to fabricate gold nanoshell thin films via electrostatic layer-by-layer (LBL) assembly using simple dip-coating methods. То provide negatively charged particles, the nanoshells were then functionalized by the addition of 3-mercaptopropionic acid (MPA). The thiol (headgroup) covalently attached to the nanoshell surface through the strong sulfur and gold interaction.²⁷ While the headgroups are bound to the gold, the negatively charged carboxylate tailgroups are exposed to the surrounding solution. The introduction of MPA enhances the stability of the gold nanoshells in aqueous solution, which enables the particles to be obtained in more highly concentrated nanoparticle solutions. After functionalization with MPA, no aggregation of the nanoshells was observed over several months. To give a positively charged surface, a thin film of PEI was adsorbed onto a glass substrate that had been thoroughly cleaned by ultrasonication. The cleaned substrate was immersed in 1 mol of PEI solution for 1 h, and then washed with water and dried under ambient conditions for several hours. The MPA-functionalized gold nanoshells were then adsorbed onto the PEI thin films. The negatively charged gold nanoshells readily adsorbed onto the positively charged PEI coated surface by electrostatic attraction. The desired nanoshell concentration on the surface was achieved simply by repeating the dipping process. The image in figure 5.3 shows the resultant gold nanoshell/PEI thin films generated via the strategy shown in scheme 5.2. The sample had the dimensions of $2 \text{ cm} \times 3 \text{ cm}$. The nanoshell/PEI thin films are optically transparent having gray color like window tinting film.



Figure 5.4. SEM images of the bare gold nanoshells (a-b) and nanoshell-dispersed PEI film; 1-dipping cycle (c-d), 3-dipping cycles (e-f) with different magnification. (Continue)



Figure 5.4. SEM images of the bare gold nanoshells (a-b) and nanoshell-dispersed PEI film; 1-dipping cycle (c-d), 3-dipping cycles (e-f) with different magnification.

Figure 5.4 shows representative SEM images of the nanoshell-dispersed PEI films and the bare gold nanoshells on the silicon substrate. The images of the samples suggest that the nanoshells were significantly aggregated when the bare gold nanoshells were dropped onto the substrate because the individual Au particles have a direct interaction with each other. The nanoshells were clustered together during the drying process, and as a consequence, some free space was produced on the surface. In contrast, using the water-soluble polymer PEI was effective for particle dispersion, as confirmed by the image in figure 5.4. The MPA-functionalized gold nanoshells-dispersed PEI films make possible the cyclic repetition of the dipping procedure. This feature can be used to build up multilayers of nanoshells intercalated with PEI. Figure 5.5 shows the schematic representation of the layer-by-layer assembled nanoshell films. The image of the sample generated via three dipping cycles of the nanoshell/PEI thin films showed the nanoshells were more packed on the surface of the substrate via LBL assembly and the particles partially look like agglomeration with each other with an increasing number of dipping cycles. However, there is a PEI layer between each successive nanoshell layer as shown a schematic figure 5.5. This probably is just because of viewing the system from the top (with particles appearing to be near each other but separated vertically).



Figure 5.5. Schematic representation of the layer-by-layer assembled nanoshell film.



Figure 5.6. UV-vis spectra of gold nanoshells in aqueous (a) and the nanoshell/PEI films depending on the dipping cycle (b).

Figure 5.6 shows the optical extinction spectra of the gold nanoshells in aqueous solution and the gold nanoshell/PEI thin films. The SPR properties of gold nanoshells

can be controlled by varying the core size and shell thickness.²⁸ The SPR peak of the aqueous gold nanoshells prepared by the procedure described above was 720 nm (figure 5.6 (a)). The extinction maximum for the nanoshell/PEI thin films was broadened and shifted to longer wavelength (800 nm). The red shift and broadening of the extinction band in the nanoshell film is consistent with the difference refractive index of surrounding medium between water (1.33) and air (1.00). In addition, when compared to dispersions in solution, the closer packing of the particles in the films can plausibly give rise to a broadening and red-shifting of the surface plasmon band.²⁹ The dipolar plasmons of the individual nanoshells strongly intermix to form a hybridized plasmon band, which disperses strongly to lower energies corresponding to higher wavelengths.²⁹ Therefore, the SPR peak position slightly red-shifted with an increase in the number of the dipping cycles as shown on figure 5.6 (b), which is consistent with a slight increase in closer packing of the particles in the films. The intensity of the band also increased with an increase in the number of dipping cycles. The peak extinction was directly proportional to the number of dipping cycles because of an increase in the number of nanoshell particles in the films.

Figure 5.7 shows the XPS spectra of the gold nanoshell film corresponding to the high-resolution core level data for the Au_{4f} and S_{2p} . After the introduction of MPA onto the surface of the nanoshells, the newly formed Au-S covalent bond was verified by analysis of the atomic binding energy. In particular, the S_{2p} region of the XPS spectra can be used to evaluate the bond formation of Au-S for the bound sulfur atom compared to the unbound sulfur atom: the binding energy of the S_{2p} 3/2 peak for S bound to Au

surfaces appears at ~162.1 eV; in contrast, the $S_{2p 3/2}$ peak for unbound thiols appears at ~163.6 eV.³⁰ As shown in figure 5.7 (b), the strong intensity of the $S_{2p 3/2}$ peak at ~162 eV for the bound thiol sulfur can be understood in the presence of covalent bond between the thiol and gold. Based on these facts, XPS confirmed the introduction of the MPA group on the surface of the gold nanoshells.



Figure 5.7. High-resolution XPS spectra of the gold nanoshell film; (a) Au_{4f} and (b) S_{2p} region.

5.5 Conclusions

We have demonstrated the synthesis of gold nanoshells via the "seeded growth" method and the fabrication of polymer-dispersed gold nanoshell thin films via electrostatic layer-by-layer assembly by way of simple dip-coating techniques. Negatively charged MPA-coated gold nanoshells were adsorbed electrostatically onto positively charged PEI-coated glass substrates. Multilayer films were formed by alternately dipping the glass slides in PEI solution and in a solution containing the modified gold nanoshells. The red shift and broadening of the maximum SPR band in the nanoshell film were observed because of difference of the refractive index of the surrounding medium between water and air. The extinction band in the film was affected by the doping concentration. This could explain that a slight increase in closer packing of the particles with increase in the number of dipping cycles can probably give rise to a red-shifting of the surface plasmon band because the dipolar plasmons of the nanoshells strongly intermix to form a hybridized plasmon band, which disperses strongly to lower energies corresponding to higher wavelengths. The intensity of the extinction peak was also directly proportional to the number of dipping cycles because of the increase in the concentration of the particles in the films. The SEM images verified that the gold nanoshells were well dispersed in the PEI films via electrostatic LBL assembly and made possible the cyclic repetition of the dipping procedure. Watersoluble PEI polymer was effective in the particle dispersion since it was adsorbed on the substrate and protected the nanoshells from coagulation.

5.6 References

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CHAPTER 6. Conclusions and Future Work

6.1 Conclusions

Coating a thin layer of a dielectric material onto gold nanoparticles provides improved chemical and colloidal stability thereby expanding the range of potential applications. The possible applications of core-shell nanoparticles are diverse and are found in catalysis, in sensors, in biomedical and environmental applications, and in optoelectronic devices. In this dissertation, approaches for the synthesis of various coreshell nanoparticles and thin films containing nanoparticles were presented, especially those with tin oxide (SnO_2) shells and gold (Au) cores. A comprehensive summary of the synthesis and the properties of core-shell nanoparticles with relevant literature references is presented in Chapter 1.

Only six prior reports¹⁻⁶ of Au@SnO₂ core-shell nanoparticles have been published concerning the particle synthesis and their application in a carbon monoxide (CO) gas sensor since the pioneering work by Mulvaney and co-workers in 2000.¹ The Au and SnO₂ nanocomposite core-shells can be potentially used in other applications such as plasmonic solar cells, selective gas sensors, and optoelectronic devices. In Chapter 2, we studied the stability of the Au@SnO₂ core-shell particle solutions over a wide pH range by visual monitoring and by UV-vis spectroscopy. The results were compared with Au@SiO₂ core-shell nanoparticles, which have been used in numerous biomedical and optoelectronic applications. Our results show that colloidal solutions composed of Au@SnO₂ nanoparticles are more stable under basic conditions (up to pH 14) than those composed of Au@SiO₂ nanoparticles. The Au@SiO₂ nanoparticle solution was unstable at high pH because of the dissolution of the SiO₂ coatings. Agglomeration at low pH for both SiO₂ and SnO₂-coated Au nanoparticles was observed due to the different isoelectric pH values of the oxides, called zero point of charge (ZPC) which are reported to be pH~2 (SiO₂, silica) and pH~4.5 (SnO₂), respectively. At this pH, there is no net surface charge on the particles so that interactions only come from attractive van der Waals forces; and hence, agglomeration and sedimentation can be predicted. The agglomeration at low pH, however, was reversible by neutralizing the solution changing the pH from 4 to 7.

Using the Au@SnO₂ core-shell nanoparticles, I demonstrated in Chapter 3 the fabrication of tin oxide (SnO₂) thin films with embedded Au nanoparticles using a solgel technique. Experimentally, dispersion of Au nanoparticles in SnO₂ films by direct mixing of the citrate-stabilized aqueous gold nanoparticles with an isopropanol-based SnO₂ sol solution is difficult because of rapid gelation of the tin isopropoxide, which leads to the rapid aggregation of the gold nanoparticles. To solve this problem, the gold nanoparticles were pre-coated with SnO₂ shells to prevent their direct interaction and to facilitate phase transfer into an isopropanol-based SnO₂ sol solution. The Au@SnO₂ core-shells were phase-transferred into a 2-propanol based SnO₂ sol without aggregation, which enables the preparation and ready manipulation of highly concentrated Au nanoparticle solutions. The nanoparticles were mixed homogeneously with a SnO₂ sol-gel precursor, and then deposited as a thin film by spin coating. The surface morphology of the film was characterized by SEM, which confirmed that the nanoparticles are well

dispersed in the SnO_2 thin films because the individual Au particles were pre-coated to prevent their direct interaction. The optical properties of the nanoparticles and the composite films were evaluated by UV-vis spectroscopy. The extinction maximum of the Au-doped SnO_2 films was red-shifted compared to that of Au nanoparticles due to the high refractive index of the sol-gel matrix. The approach enables the preparation of SnO_2 thin films with homogeneous distributions of embedded gold nanoparticles.

Tin oxide, SnO₂, is the basis of and important class of transparent conducting oxides (TCO), which possess high optical transparency in visible region and high dc electrical conductivity. The optical and electronic properties of SnO₂-based materials can be tuned by doping with oxides such as indium (ITO), antimony (ATO), zinc (ZTO), and fluorine (FTO). In Chapter 4, the synthesis of zinc- and antimony-doped Au@SnO₂ core-shell nanoparticles via a hydrothermal route is presented. The morphologies of the composite nanoparticles were characterized with SEM and TEM. Free oxide nanoparticles without Au core are also present in the samples, representing approximately ~40-50 % of the samples. The nanoparticles without Au core and nanoparticles with Au core have different sizes. The nanoparticles without Au core were composed of consistent size of ~20 nm in diameter while the core-shell shaped nanoparticles have a size of ~45 nm (Zn-doped Au@SnO₂) and ~55 nm (Sb-doped $Au@SnO_2$) in diameter. Incorporation of zinc and antimony into the composite particles was shown by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The optical properties of the composite nanoparticles were analyzed by UV-vis spectroscopy. A red shift of the plasmon resonance was observed on doping with zinc and antimony. To understand the effect of zinc and antimony addition on the $Au@SnO_2$ core-shells for TCO applications, further electrical conductivity experiments are planned.

The synthesis of gold shell/silica core particles (nanoshells) and their incorporation into organic polymeric thin films were described in Chapter 5. We have demonstrated the fabrication of polymer-dispersed gold nanoshell thin films via electrostatic layer-bylayer assembly. Negatively charged 3-mercaptopropionic acid (MPA)-coated gold nanoshells were adsorbed electrostatically onto positively charged polyethyleneimine (PEI)-coated glass substrates. The resultant composite films containing uniformly dispersed nanoshells with minimal aggregation were imaged by SEM and the optical properties were analyzed by absorption spectroscopy, which showed broad extinctions ranging from the visible to the near-IR spectral regions. The MPA-functionalized gold nanoshells-dispersed PEI films make possible the cyclic repetition of the dipping procedure. X-ray photoelectron spectra (XPS) were also obtained to determine the elements present and the oxidation states of these elements. The water-soluble PEI polymer was effective in the particle dispersion since it was adsorbed on the substrate and protected the nanoshells from coagulation.

In summary, we have studied gold and dielectric nanocomposite materials, especially shell/core nanoparticles and nanoparticle thin films. As described above, the shell/core nanoparticles that we have studied in this dissertation potentially can be formulated into wide range of surface-related applications and transparent conducting oxide materials, considering the solar cells, gas sensor, and other optoelectronic applications.

6.2 Future Work

The remaining issues in this research are the fabrication of monodisperse coreshells of Sb-doped and Zn-doped Au@SnO₂ by optimizing particle size distributions and composition because the free oxide particles without the Au cores were observed in the samples and they were smaller than core-shell particles. One method for further separating two particles is a centrifugation. The speed and time control of a centrifuge would be required to separate a mixture of two types of particles. Another method for the further separation is a membrane filtration. For example, the core-shell mixtures could filter using the high-purity alumina (Al₂O₃) membranes containing ~50 nm diameter pores. Large size of the core-shell particles will be accumulated during the filtration process on the top of the membrane while small sizes of the free oxide particles would be filtered out. The alumina membrane filter can be then dissolved away by base and neutralize the residue to obtain the homogeneous core-shell particles.

Moreover, the XRD pattern of the Zn-doped Au@SnO₂ nanoparticles showed the presence of two phases: of zinc stannate (ZnSnO₃) and SnO₂. To improve the quality of these composite core-shell nanoparticles, different approaches are being considered such as changing concentration of the Zn precursor. By using less concentration of Na₂ZnO₂, the formation of ZnSnO₃ would prevent because the ZnSnO₃ would form with a specific ratio of Zn²⁺/Sn⁴⁺/Na⁺ under hydrothermal conditions.

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