

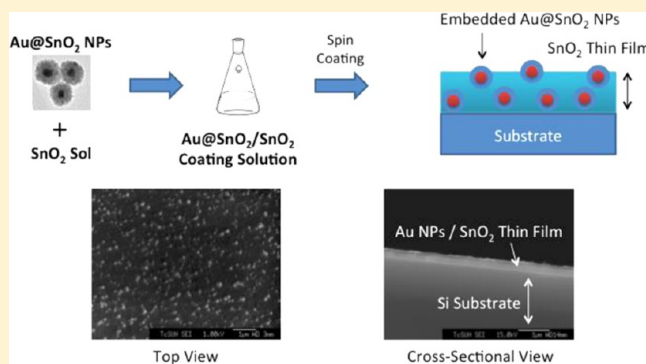
Transparent, Homogeneous Tin Oxide (SnO₂) Thin Films Containing SnO₂-Coated Gold Nanoparticles

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ABSTRACT: A sol–gel-based approach to the fabrication of tin oxide (SnO₂) 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.

KEYWORDS: tin oxide, SnO₂-coated nanoparticles, nanoparticle thin films, sol–gel



■ INTRODUCTION

With potential applications in nonlinear optics,^{1,2} plasmonic solar cells,³ photocatalytic degradation of pollutants,⁴ and gas sensing,^{5,6} efficient and reliable strategies for incorporating metal nanoparticles into dielectric metal oxide films are needed. To this end, a variety of synthetic processes for embedding metal nanoparticles within various metal oxide (e.g., SiO₂, TiO₂, SnO₂, ZnO, ZrO₂, MgO, WO₃, and ITO) thin films have been developed over the past decade.^{6–17} In most cases, metal salts or preformed metal nanoparticles are mixed with a dielectric material or a sol–gel precursor and deposited as a film via dip-coating or spin-coating.^{7,8,18} These efforts have been largely motivated by the desire to exploit the surface plasmon resonance (SPR) properties of the metal nanoparticles in optoelectronic nanocomposite thin-film devices.^{2,7} For example, highly dispersed metal nanoparticles incorporated in a dielectric metal oxide matrix, in the absence of substantial particle aggregation or phase separation, have shown promise for optical applications such as a system with enhanced third-order optical nonlinear susceptibility, $\chi^{(3)}$.^{2,19}

Tin oxide (SnO₂) is an attractive material for optical coatings because it is transparent for wavelengths 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 other optoelectronic devices because it possesses high photostability and good carrier mobility. Like titanium oxide (TiO₂) and zinc oxide (ZnO), SnO₂ is a large band gap semiconductor; consequently, much of the reported work

utilizes these films for solar energy conversion and for optoelectronic devices.²⁰

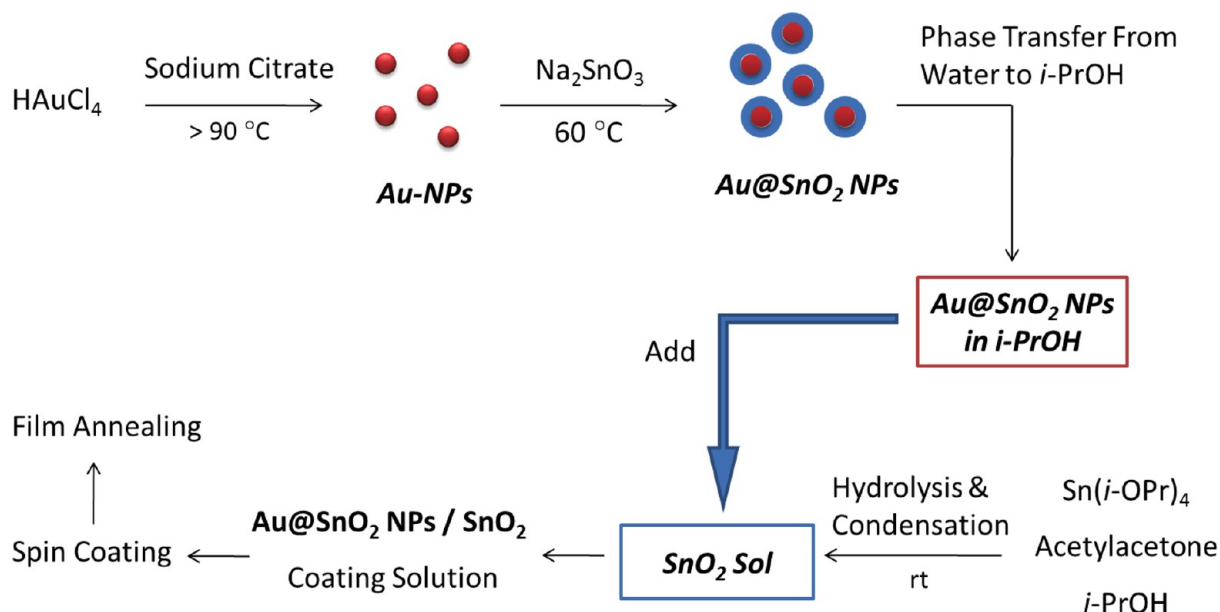
Tin oxide films can be fabricated using a variety of techniques, including chemical vapor deposition,²¹ sputtering,²² spray pyrolysis,²³ reactive evaporation,²⁴ and sol–gel methods.^{11,25} In general, sol–gel methods are more flexible and offer many advantages, such as excellent film homogeneity, well-defined film thickness, simple and low-cost processing, low-temperature processing, and most significantly, the ability to produce fine films.^{25,26}

The incorporation of metal nanoparticles into dielectric metal oxide films is most commonly accomplished using sol–gel methods in which the metal is introduced in the form of a soluble salt, and then reduced to form metal nanoparticles *in situ* through reductive annealing processes.^{11,18,27} Epifani et al.,¹¹ for example, 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 metal-doped SnO₂ sol. The tin precursor (SnCl₄) was first treated with propanol to generate a tin alkoxide, which was hydrolyzed and subsequently mixed with solutions of the metal dopants to prepare the composite sol solution. After deposition of the film and exposure to heat, Pd and Pt nanoparticles were formed within the SnO₂ matrix. This *in situ* method, however, offers limited control of the nucleation process and particle size, shape, and polydispersity.

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Scheme 1. Strategy Used to Prepare Tin Oxide Films Containing SnO₂-Coated Au Nanoparticles

In contrast, *ex-situ* synthesis offers greater flexibility in the design and fabrication of the nanoparticles embedded within the sol–gel matrix. Further, the features of the nanoparticles can be optimized before mixing with the sol–gel precursor, after which the resultant mixture is deposited as a film. Buso et. al.⁷ reported gold-nanoparticle-doped TiO₂ thin films using *ex-situ* sol–gel processing. To transfer the particles into ethanol, gold nanoparticles were first functionalized with mercaptoundecanoic acid, the particles were mixed with the sol–gel Ti butoxide solution (i.e., the TiO₂ precursor), and the mixture was deposited by spin coating. Subsequent annealing generated the final composite film.

In the present study, we report a new strategy for the fabrication of gold-nanoparticle-doped SnO₂ thin films. To incorporate Au nanoparticles homogeneously in the SnO₂ sol and ultimately the thin films, the Au nanoparticles were precoated with SnO₂ to enhance their miscibility and to prevent aggregation, which occurred readily with uncoated Au nanoparticles during sol formation. The SnO₂-coated Au nanoparticles were mixed with a tin oxide sol, which was subjected to spin-coating methods to obtain SnO₂ thin films doped with discrete, uniformly dispersed Au nanoparticles. We also report the optical properties of the SnO₂-coated gold nanoparticles prior to and after incorporation into the thin films. Importantly, this *ex-situ* synthesis method can be readily extended to other nanoparticles and dielectric metal-oxide thin films that have the potential to serve as optical materials in plasmonic devices and solar energy conversion systems.

EXPERIMENTAL SECTION

Synthesis of Citrate-Stabilized Au Nanoparticles. In a 250-mL beaker, a solution containing 1% HAuCl₄ (0.5 mL) was diluted with H₂O (to 150 mL) and then heated to boiling with stirring. An aliquot of a 1.0 wt % sodium citrate solution (10 mL) was added quickly to the hot HAuCl₄ solution. The solution changed color within an hour from light yellow to dark red.

Synthesis of SnO₂-Coated Au Nanoparticles.²⁸ A 150-mL aliquot of the citrate-stabilized gold nanoparticles was placed in a warm water bath (60 °C) and stirred vigorously, followed by the rapid addition of sodium stannate trihydrate (5.0 mL, Na₂SnO₃·3H₂O 95%,

40 mM, Aldrich). A purple colloidal solution was obtained, consistent with the formation of SnO₂-coated gold nanoparticles.²⁸ 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).

Preparation of SnO₂ Sol Solution Containing SnO₂-Coated Au Nanoparticles. A SnO₂-based mixture containing the core–shell nanoparticles was prepared using sol–gel techniques. An aliquot of (tetrakis(isopropoxide)tin, Sn(*i*-OPr)₄, (1.0 mL, 10% in isopropanol, Alfa Aesar) was diluted in isopropanol (2.0 mL) and stirred for 30 min. An aliquot of the complexing agent acetylacetone (2.0 mL) was then added to stabilize the products of Sn(*i*-OPr)₄ hydrolysis. To facilitate the dispersion of the SnO₂-coated Au nanoparticles in the sol–gel solution, the aqueous nanoparticle solution was centrifuged and redispersed into a minimum volume of isopropanol and then added to the acetylacetone-stabilized SnO₂ sol. After stirring at room temperature for 24 h, a dark-purple transparent sol solution containing SnO₂-coated Au nanoparticles was obtained.

Fabrication of SnO₂ Thin Films Containing SnO₂-Coated Au Nanoparticles. Nanocrystalline SnO₂ thin films containing the SnO₂-coated Au nanoparticles were fabricated by spin coating the sol on either glass slides or silicon wafers by gradually increasing the rotation to 1500 rpm and then spinning for 20 s. The process was repeated up to five times per sample until the desired film thickness was achieved on the substrate. After spin coating, the gel film was dried in air for 1 h and then annealed (200 °C for 1 h).

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. FE-SEM analysis of the composite films by energy-dispersive X-ray spectroscopy (EDX) was used 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. A Siemens D-5000 powder X-ray diffraction (XRD) equipped with a monochromatic Cu K_α ($\lambda = 1.540562$ Å) radiation was used to analyze the samples over the 2θ range 20°–90° in steps of 0.02°.

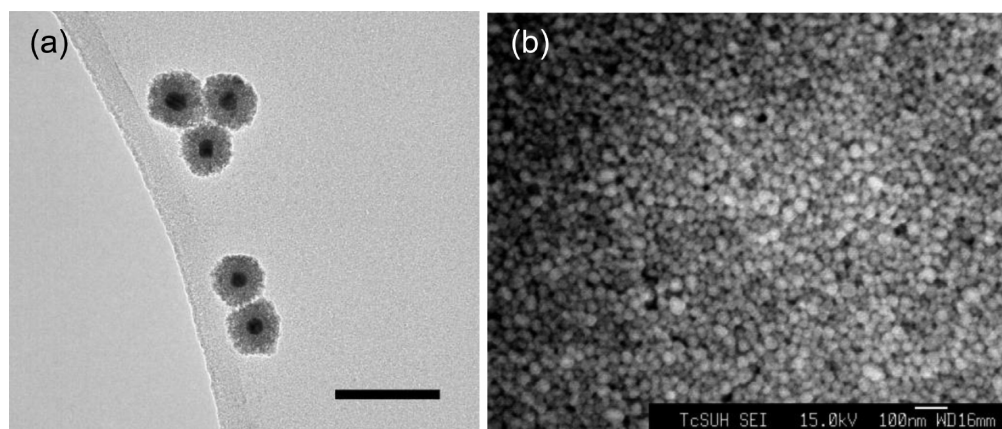


Figure 1. (a) TEM and (b) SEM images of SnO_2 -coated Au nanoparticles. Scale bars are 100 nm.

RESULTS AND DISCUSSION

The goal of this work was to develop a reliable 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 $\text{Sn}(i\text{-OPr})_4$, acetylacetone, and isopropanol. Attempts to disperse the Au nanoparticles in SnO_2 films by direct mixing of the citrate-stabilized 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 extensive aggregation of the gold nanoparticles. A key step in solving this problem was the encapsulation of the gold nanoparticles within a tin oxide shell, which allowed their phase-transfer into isopropanol without aggregation, enabling the preparation and facile manipulation of these highly concentrated Au nanoparticle solutions.

There are a limited number of reports of SnO_2 -coated gold nanoparticles,^{29–35} including our recent investigation of the unique stability of these core–shell particles.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 ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$) via a simple hydrothermal process. Importantly, gold nanoparticles coated with tin oxide layers are resistant to coagulation because the tin oxide coatings have negative surface charges, leading to repulsion between the like-charged particles.³⁶

To facilitate the phase transfer of the particles into isopropanol, the synthesized SnO_2 -coated Au nanoparticles were centrifuged and washed with deionized water to remove any unreacted species and impurities and then redispersed into a minimum volume of isopropanol, where the SnO_2 -coated Au nanoparticles showed no obvious signs of aggregation. The composite nanoparticles were then added to the acetylacetone-stabilized SnO_2 precursor solution. No precipitation was observed visually in the composite solution. Importantly, this strategy circumvented the need to add compatibilizing agents, such as polyvinyl alcohol or polyvinylpyrrolidone. Nanocrystalline SnO_2 thin films containing the SnO_2 -coated Au nanoparticles were fabricated on silicon wafers and glass slides by spin coating and subsequent drying and annealing as described in the Experimental Section. Scheme 1 illustrates the overall synthetic procedure used to obtain nanocrystalline SnO_2 thin films with homogeneously embedded SnO_2 -coated Au nanoparticles.

Figure 1 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 ± 5 nm, giving an overall diameter of 55 ± 10 nm for the composite particles. Free SnO_2 nanoparticles with no Au cores are also present in the sample, representing approximately $\sim 10\%$ of the nanoparticles present. As a whole, the images show that the nanoparticles are uniform in both size and shape.

Figure 2 shows the room-temperature powder X-ray diffraction (XRD) pattern of the SnO_2 -coated nanoparticles.

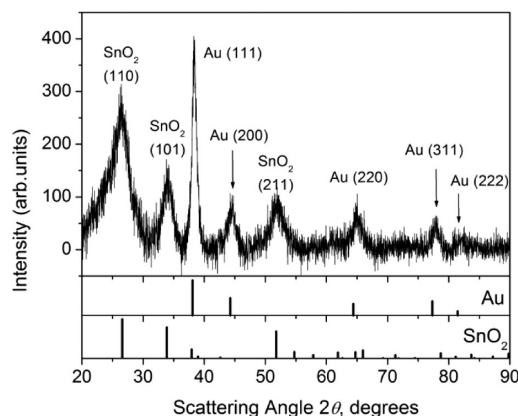


Figure 2. Powder X-ray diffraction pattern of SnO_2 -coated Au nanoparticles. Calculated patterns for Au (*fcc* structure) and SnO_2 (rutile structure) are presented for reference.

All of the peaks correspond to either tin oxide or gold. The peaks at $2\theta = 38.08^\circ$, 44.26° , 64.38° , 77.31° , and 81.45° correspond respectively 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° correspond respectively 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 SnO_2 (101) diffraction peaks using the Scherrer equation,³⁷ $D = 0.94 \cdot \lambda / \beta \cdot \cos\theta$, where λ is the wavelength of the X-ray source, β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle in the diffraction pattern. From this analysis, we estimate that the diameter of the Au nanoparticles is ~ 10 nm and that the mean grain SnO_2 size of the shell is ~ 4 nm from the values of $\lambda = 0.15406$ nm, $2\theta =$

38.41° (Au), $2\theta = 34.08^\circ$ (SnO_2), $\beta = 0.84^\circ$ (Au), and $\beta = 2.01^\circ$ (SnO_2), indicating that the spherical SnO_2 shells consist of small particles, which is consistent with the morphology observed by TEM (see Figure 1).

Figure 3 shows the optical absorption spectra of the gold nanoparticles, SnO_2 -coated gold nanoparticles, and the latter

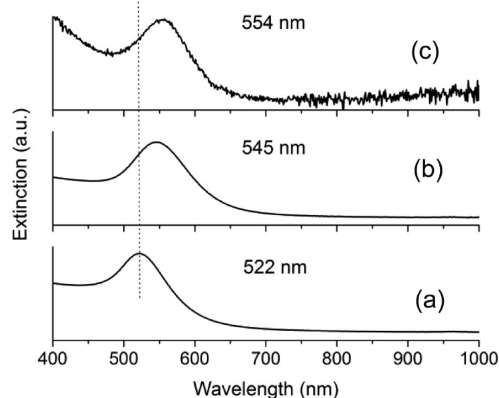


Figure 3. Extinction spectra of (a) Au nanoparticles, (b) SnO_2 -coated Au nanoparticles, and (c) core-shell nanoparticles embedded in a thin film of SnO_2 .

particles embedded in the SnO_2 film. The surface plasmon resonance (SPR) of the gold nanoparticles in aqueous solution was centered at 522 nm. Coating the particles with SnO_2 shifted the SPR to a longer wavelength (545 nm). The red shift of the extinction band is consistent with coating the nanoparticles with a high refractive index material;³⁸ the refractive index of SnO_2 is ~ 2.2 , which is greater than that of water (~ 1.3).²⁹ The SPR band of the core-shell nanoparticles embedded in the SnO_2 film is further red-shifted to 554 nm. This additional red shift might arise due to the decrease in the average interparticle distance within the nanoparticle film compared to that in solution. With the decrease of the interparticle distance, the absorption peak begins to red-shift due to interparticle plasmon coupling.³⁹ Notably, the initial SnO_2 coating prevents the gold cores from aggregating in the film environment (vide infra). Additionally, the presence of a continuous SnO_2 medium might also contribute to the red-shift to 554 nm, given that the refractive index of a metal oxide material is related to the degree of porosity.⁴⁰ The porosity (void space or a second material with a different refractive index) and the effective refractive index are directly related by the Bruggemann effective medium approximation. If the porosity present in a metal oxide is air, then the effective refractive index for the material is lowered. Further, the effective refractive index of the SnO_2 shell surrounding the Au nanoparticles is likely lower than that of a continuous SnO_2 film. In summary, the further red-shift to 554 nm of the SPR band of the composite films might also reflect a change in the effective refractive index for the adjacent SnO_2 material.

Uncoated gold nanoparticles are prone to aggregation in high ionic strength solutions due to their strong van der Waals attraction;⁴¹ this type of aggregation typically broadens and red-shifts the SPR band. Figure 4a shows, however, that in our system, the position of the SPR band does not vary with the number of the layers. More specifically, the position of the extinction maximum is unaffected by the increasing amount of Au nanoparticle dopant. This invariance would be expected

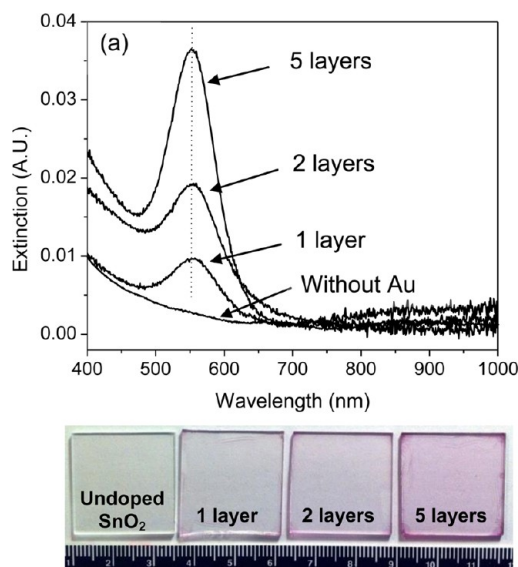


Figure 4. (a) Extinction spectra of spin-coated SnO_2 thin films with and without embedded SnO_2 -coated Au nanoparticles; (b) photograph of the composite films deposited on glass substrates. The scale bar is in centimeters.

when the individual gold nanoparticles are prevented from direct interaction owing to an effective encapsulation of the particles. During the application of the films on the substrate, the gold nanoparticles experienced no increase in aggregation beyond that which occurred during the initial mixing, and with each layer, the relative nanoparticle density within the film plausibly remains constant. This model is further supported by the fact that only the intensity of the SPR band increases with an increasing number of coating layers. The photograph in Figure 4b shows four samples: a tin oxide film with no Au nanoparticles and a series of films with embedded SnO_2 -coated Au nanoparticles in which the number of spin-coated layers is increased from 1 to 5. The sample dimensions can be deduced from the scale bar. Importantly, 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.

The Au-doped SnO_2 films fabricated by spin coating on silicon wafers and glass slides were examined by scanning electron microscopy. As shown in Figure 5a, analysis of the films by EDX confirms the presence of Sn, O, and Au. Cross-sectional views of the films in Figures 5b and 5c indicate a uniform SnO_2 film thickness of ~ 200 nm; moreover, individual Au nanoparticles can be discerned in these images (particularly Figure 5c, where the magnification is greatest). The gold nanoparticles appear as white spheres randomly distributed within the ~ 200 nm thick SnO_2 films. The SEM images in Figures 5d and 5e confirm the existence of well-dispersed core-shell nanoparticles in the SnO_2 thin film, with no evidence of large-scale aggregation. The observation of well-dispersed particles is consistent with the extinction spectra in Figure 4.

CONCLUSIONS

We have demonstrated the fabrication of nanocrystalline tin oxide (SnO_2) thin films in which SnO_2 -coated Au nanoparticles are embedded and uniformly dispersed. The gold nanoparticles

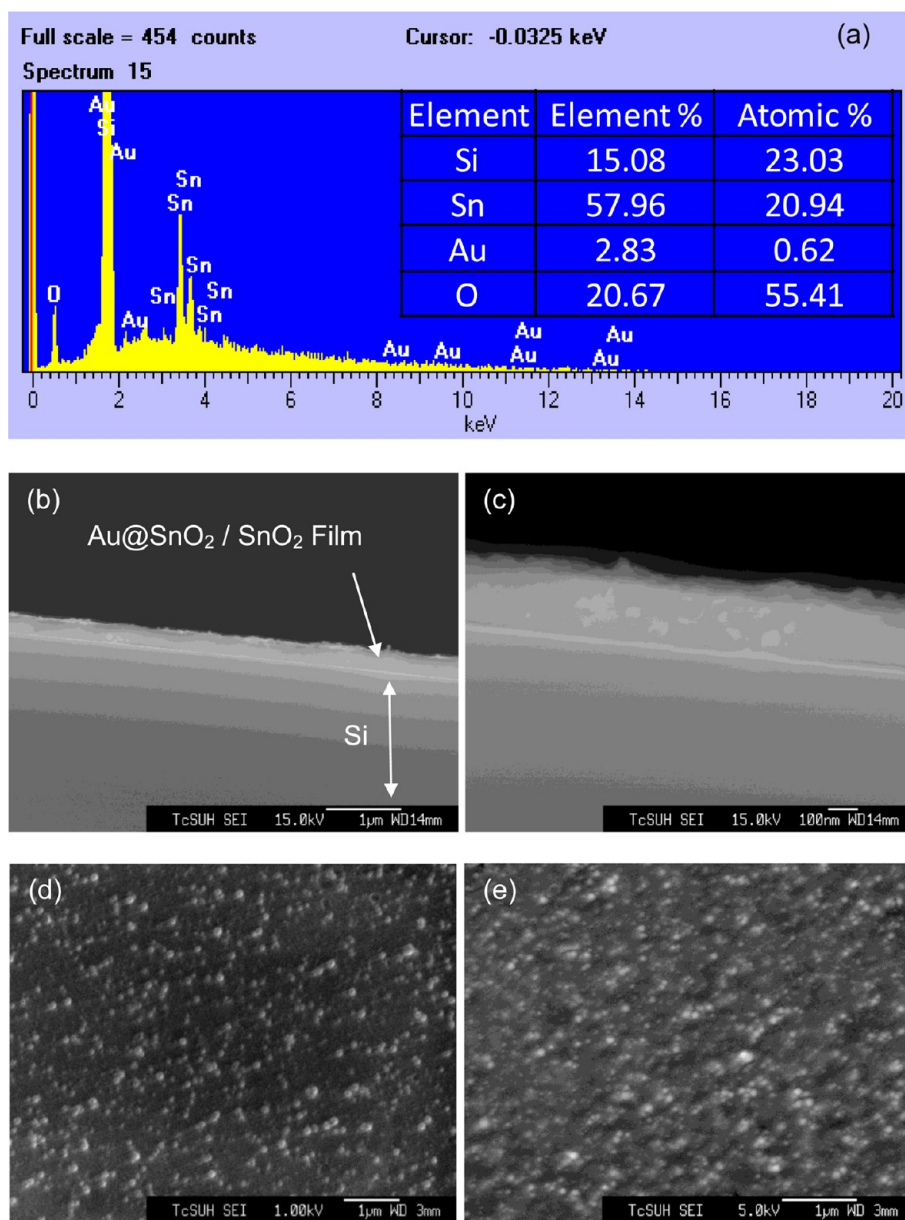


Figure 5. (a) EDX spectrum of SnO₂ thin films containing SnO₂-coated Au nanoparticles. (b and c) SEM images showing cross-sectional views of a film generated by spin coating one sol aliquot on a silicon wafer. (d and e) SEM images showing top views of films on silicon generated by treatment with one and five aliquots of the film precursor solution, respectively.

were encapsulated within SnO₂ shells to prevent their direct interaction and to facilitate phase transfer into an isopropanol-based SnO₂ 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 SnO₂ thin films, a proposed consequence of coating the Au particles with SnO₂. The extinction maximum of the Au-doped SnO₂ films was red-shifted compared to that of Au nanoparticles in aqueous solution due to the high refractive index of the sol-gel derived matrix. This *ex-situ* synthesis and doping strategy allows the fabrication of SnO₂ thin films with homogeneous distributions of embedded metal nanoparticles.

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Notes

The authors declare no competing financial interest.

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