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Preparation of ITO/Ag nanohybrid particles by a reverse micellar layer-by-layer coating

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Abstract

Silver (Ag) nanoparticles were adsorbed preferentially on indium tin oxide (ITO) surface to form composite particles using a reverse micellar layer-by-layer deposition. The micellar process stabilized the Ag particles by an anionic sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant in isooctane solvent. The ITO particles surface was mediated by a cationic poly(allylamine hydrochloride) (PAH) polyelectrolyte. The heterogeneous deposition was rendered by both electrostatic attraction and hydrophilic/hydrophobic interaction, and was carried out in multiple coating cycles. The resulting hybrid particles were characterized by zeta-potential measurement, electron microscopy, X-ray diffractometry, and inductively coupled plasma analysis, respectively. Optical transmittance of the ITO/Ag composite films was found to decrease substantially with the Ag deposition over the visible wavelengths range, arising mainly from scattering induced by the Ag nanoparticles.

Keywords: Indium tin oxide; ITO; Silver; Ag; Composite; Micelle

1. Introduction

Transparent conducting oxides (TCOs) have attracted much attention over the years owing mainly to their unique characteristics in providing a high optical transparency in the visible wavelength region, a high reflectance in the infrared region, and a nearly metallic electrical conductivity. The valuable electrical and optical properties enable TCOs to find wide application in displays, solar cells, and energy-saving devices [1,2]. Meanwhile, noble metal nanoparticles with tailored size, shape, particle-size distribution, and surface functionality have been embedded in the host TCO matrix. The hybrid composites show interesting optical, catalytic, electrical, thermal, antibacterial, photocatalytic, photo/electrochromic, photoluminescent, and surface plasmon resonance properties [3–11]. Houng [4], in particular, was the first to report a successful preparation of TCO thin films with silver (Ag) metal embedded in indium tin oxide (ITO) via a sol–gel route. The ITO/Ag films showed a reduced electrical resistivity as low as 8.2×10^{-5} Ω cm, due mainly to the formation of interconnected conductive paths from the Ag particles [5] in the composite films, while maintaining a reasonable optical transmission in the visible wavelength range. In addition to the sol–gel method [4,6], ITO/Ag thin films have also been prepared via a preferential attachment of dispersed Ag nanoparticles on the ITO surface by seed-mediated growth [8], double pulse method [10], and self-assembly of the Ag nanoparticles by use of poly-L-lysine solution as a surface modifier for the ITO surface [11], respectively. The presence of Ag nanoparticles on the electrically conducting ITO surface was found to promote the electron transfer reactions so that the composite films can be used as an electrode in electrochemical cells [8,11,12].

In contrast to the vast interest of ITO/Ag thin films, synthesis of ITO/Ag hybrid *particles* has received less attention, despite technological interests in using the composite particles as a raw material for film-forming techniques such as inkjet printing with advantages of attaining hierarchically structured multilayer free-forms in a cost-effective way without the need of prior mold tooling [13]. In this regard, Yang et al. [14] have reported the synthesis of ITO/Ag/ITO particulate films on silica

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fibers via an electrostatic layer-by-layer (LbL) route. The surface of the coating particles was tailored to bear an opposite charge in comparison to the targeting surface so that multilayer deposition of the charged particles can be made sequentially. The successful preparation of ITO/Ag hybrid particles requires a stabilized dispersion of the ITO nanoparticles in liquids [15,16] before a preferential deposition of Ag nuclei or nanoparticles can be implemented. In this study, a reverse micellar process has been carried out for the synthesis of particulate ITO/Ag composites. The process is featured with an additional hydrophilic/hydrophobic interaction in addition to the electrostatic attraction so that the nanoparticle buildup can be facilitated [17]. Structure of the resulting ITO/Ag particles was characterized upon completion of every adsorption cycle, and a total of up to five coating cycles was performed. This micellar LbL process has been used on synthesis of several core–shell composite particles recently [17–19]. To the author's knowledge, this is the first time to apply this route to the synthesis of ITO/Ag nanohybrid particles.

2. Experimental procedure

2.1. Materials

ITO particles (Shinwei Technology Co., Taiwan) with an average diameter about 150 nm, purity $> 99\%$, and In:Sn molar ratio = 9:1 (vendor specification) were used as the starting material. The as-received ITO particles were yellowish in color, about spherical in shape, and were apparently agglomerated (Fig. 1). X-ray diffractometry (XRD, MXP3, Mac Science, Japan) revealed a majority of cubic In_2O_3 structure (JCPDS 06-416) with a minor SnO_2 phase (JCPDS 41-1445).

Reagent-grade silver nitrate ($AgNO_3$, 99.7 wt.%, J. T. Baker, USA), ethanol (EtOH, Fluka, Switzerland), ammonia solution (NH_4OH, 28 wt.% NH_3 in water, Osaka Chemical, Japan), sodium chloride (NaCl, 99.8%, Riedelde Haën, Germany), sodium bis(2-ethylhexyl) sulfosuccinate (AOT, $C_{20}H_{37}NaO_7S$, 98%, Alfa, USA), sodium borohydride ($NaBH_4$, Riedelde Haën, Germany), and poly(allylamine hydrochloride) (PAH, MW $\sim$ 60,000, Alfa, USA) were purchased commercially and used without further purification. De-ionized water (18.2 MΩ) was from a Millipore Milli Q filtration system.

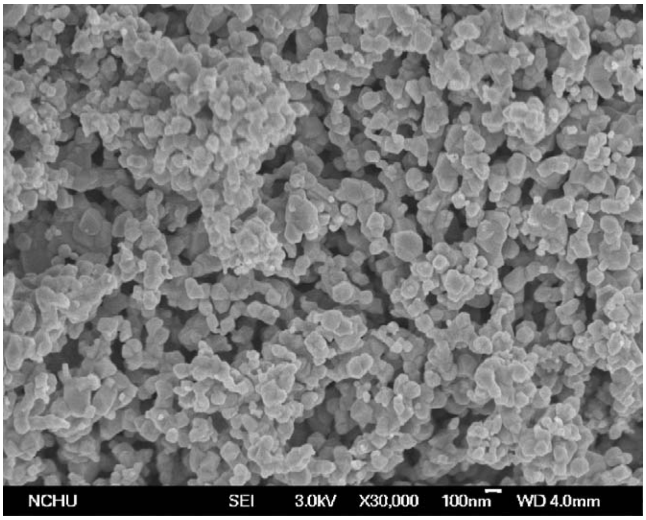

Fig. 1. Morphology of the as-received ITO particles. The particles are apparently agglomerated.

2.2. Synthesis

The ITO particles (0.2 g) were dispersed in a PAH solution consisting of 0.1 g PAH dissolved in 100 ml 0.5 M NaCl aqueous solution. The solution pH was at about 6.5, and the colloidal solution was magnetically stirred for 30 min, followed by the collection of the surface-mediated particles through centrifugation (Universal 320, Hettich, Germany).

Reverse micellar synthesis of Ag nanoparticle was obtained from mixing of two ionic solutions. One of the solutions consists of 0.034 g $AgNO_3$ dissolved in isooctane–water mixture (49.1 and 0.9 ml, respectively) with 2.175 g AOT (equivalent to 0.1 M). The $AgNO_3$ serves as the precursor for the Ag nanoparticles. The other solution containing a reducing agent for Ag was prepared by mixing 0.038 g $NaBH_4$ in the AOT-added isooctane–water mixtures. Ag nanoparticles were formed by mixing the two ionic solutions under vigorous stirring at 25 °C for 30 min, and the particles were stabilized from the encapsulation of AOT reverse micelles [17].

The ITO/Ag hybrid particles were prepared by slowly re-dispersing the PAH-mediated ITO particles in the Ag-containing AOT micellar solution by continuous magnetic stirring for 30 min. The resulting hybrid particles were centrifuged, rinsed in ethanol repeatedly for three times to complete one adsorption cycle. Multiple Ag depositions were prepared by repeated mixing of the PAH-modified composite particles with the Ag-containing AOT micellar solution, followed by the same centrifuge and rinsing process to remove the loosely anchored surfactant molecules on the nanoparticle surface. Up to five deposition cycles were performed sequentially in the study. The resulting ITO/Ag composite particles were calcined at 400 °C in ambient air to remove the low-melting organic surfactants and solvents.

2.3. Characterization

Zeta (ζ) potential of the ITO and the ITO/Ag hybrid particles was determined from diluted colloids ($\sim$0.005 in volumetric concentration) by dynamic light-scattering spectroscopy (Zetasizer NS, Malvern Instruments, U.K.). The pH was adjusted with HNO_3 and NH_4OH. Particle morphology and composite structure were examined by field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan) and by transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). Structure of the composite particles was characterized by XRD using Cu Kα radiation with a characteristic wavelength of 1.5406 Å. For preparing the coating samples, particles were mixed with ethanol via ultrasonication. A few drops of the dispersions were then placed onto electrically conductive glass plates by a pipette before being dried ready for the UV–vis spectrophotometry (Lambda 800, Perkin Elmer, U.S.A.) over wavelengths ranging from 300 to 800 nm. In addition, chemical composition of the particles was determined quantitatively by an inductively coupled plasma atomic emission spectrometer (ICP-AES, ICAP 9000, Jarrell-Ash, USA).

3. Results and discussion

The ITO particles show an isoelectric point (pH_{IEP}) at ~4.6 (Fig. 2), at which, the surface charge changes from positive to negative when the solution pH was raised above the pH_{IEP}. In the literature, the pH_{IEP} of ITO particles varies from 4.9 to 8.5 [15,16,20], presumably due to the different physical and chemical properties at the surface of the various ITO particles prepared. In Fig. 3, the surface potential of the ITO particles changes pronouncedly from negative to positive, i.e., ζ potential increased from −22 to +62 mV, as the adsorption of cationic PAH polyelectrolyte occurs. This surface charge promotes preferential adsorption of the Ag nanoparticles (negative ζ potential) on the PAH-modified ITO (positive ζ potential) in the isooctane mixture by the electrostatic interaction. An additional hydrophilic/hydrophobic interaction is rendered since the PAH molecules and the head group of AOT surfactants are both hydrophilic while the tail group of the AOT and the suspending solvent (i.e., isooctane) are hydrophobic [17]. The Ag adsorption is then confirmed by a resulting shift of the ζ potential, i.e., from +62 to −16 mV, upon completion of one adsorption cycle. Further repeating the deposition process shows a cyclic ζ change on the composite surface, and this variation in the ζ potential is quite consistent, revealing that multiple Ag adsorptions occur as the deposition cycle proceeds. Similar results were observed for the preparation of SiO_2/Ag and TiO_2/Ag composite particles via this reverse micellar LbL route [18,19].

XRD result (Fig. 4) shows existence of Ag on the ITO/Ag composites. The diffracted intensity from Ag is not strong; yet, appears to increase as the adsorption cycle proceeds, suggesting an increased Ag concentration along with the cyclic deposition. The preferential adsorption of Ag is further confirmed by the ICP-AES measurement. The atomic Ag/In ratio is found to increase from 0.20 to 1.13%, equivalent to a calculated Ag concentration of 0.17 to 0.93 wt.% respectively in the In_2O_3 matrix, as the deposition cycle increases from one to three. This finding is in good agreement with the XRD result; from which, the diffracted intensity from Ag is relatively lower compared to the ITO phase, reflecting the low Ag concentration. This further reveals that the ζ-potential measurement in Fig. 3 is a surface-sensitive property, so that a moderate Ag adsorption on the ITO particles suffices to alter the surface chemistry in the given carrier liquid.

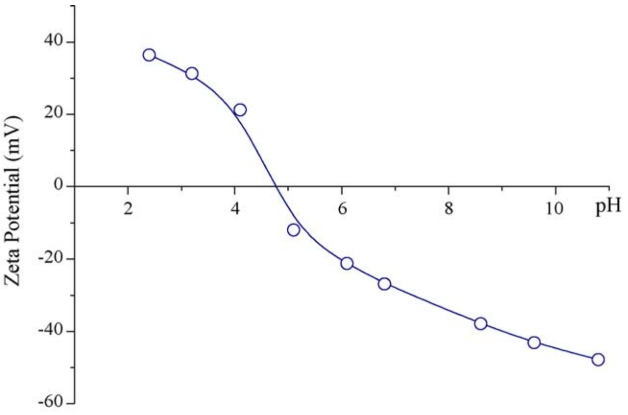

Fig. 2. Variation of the ζ potential of the ITO particles with solution pH.

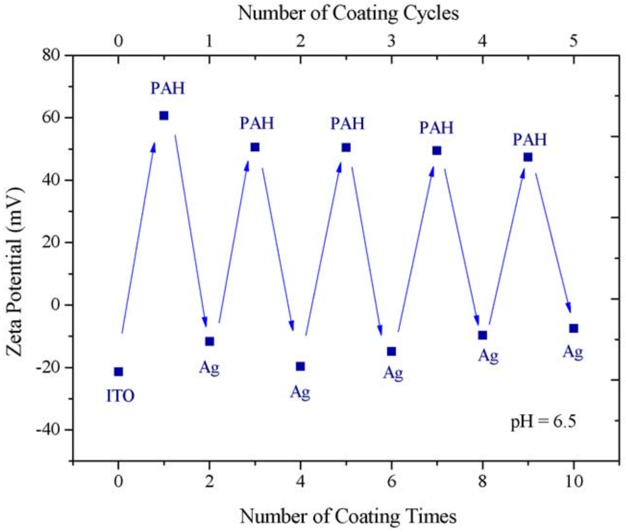

Fig. 3. Cyclic ζ-potential profile of the ITO/Ag composite particles when the deposition of PAH molecules and micellar AOT-encapsulated Ag were proceeded sequentially.

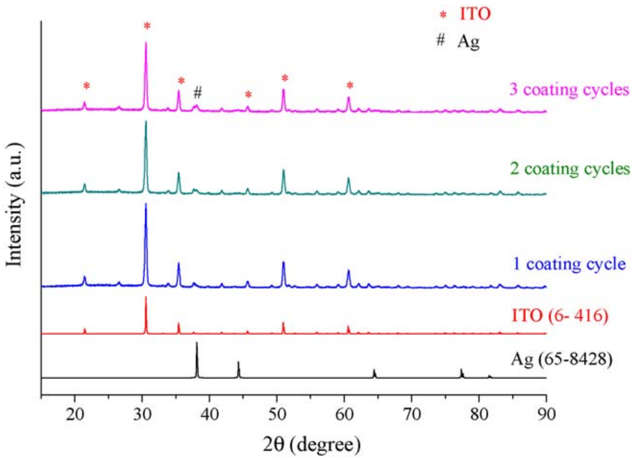

Fig. 4. XRD patterns for the ITO/Ag composite particles with deposition cycles up to three times.

Fig. 5 shows typical SEM and TEM microstructures of the ITO/Ag composite particles. The primary Ag particles present a mean diameter lower than 10 nm, and are easily distinguishable from the submicrometer ITO particles (~150 nm in diameter). The nanoparticles appear to distribute discretely on the ITO surface. In addition, the Ag nanoparticles did not form a complete coating layer around the ITO particles regardless of the increase in the deposition cycle up to 5 cycles. Even though a uniform core–shell structure was not obtained, the Ag

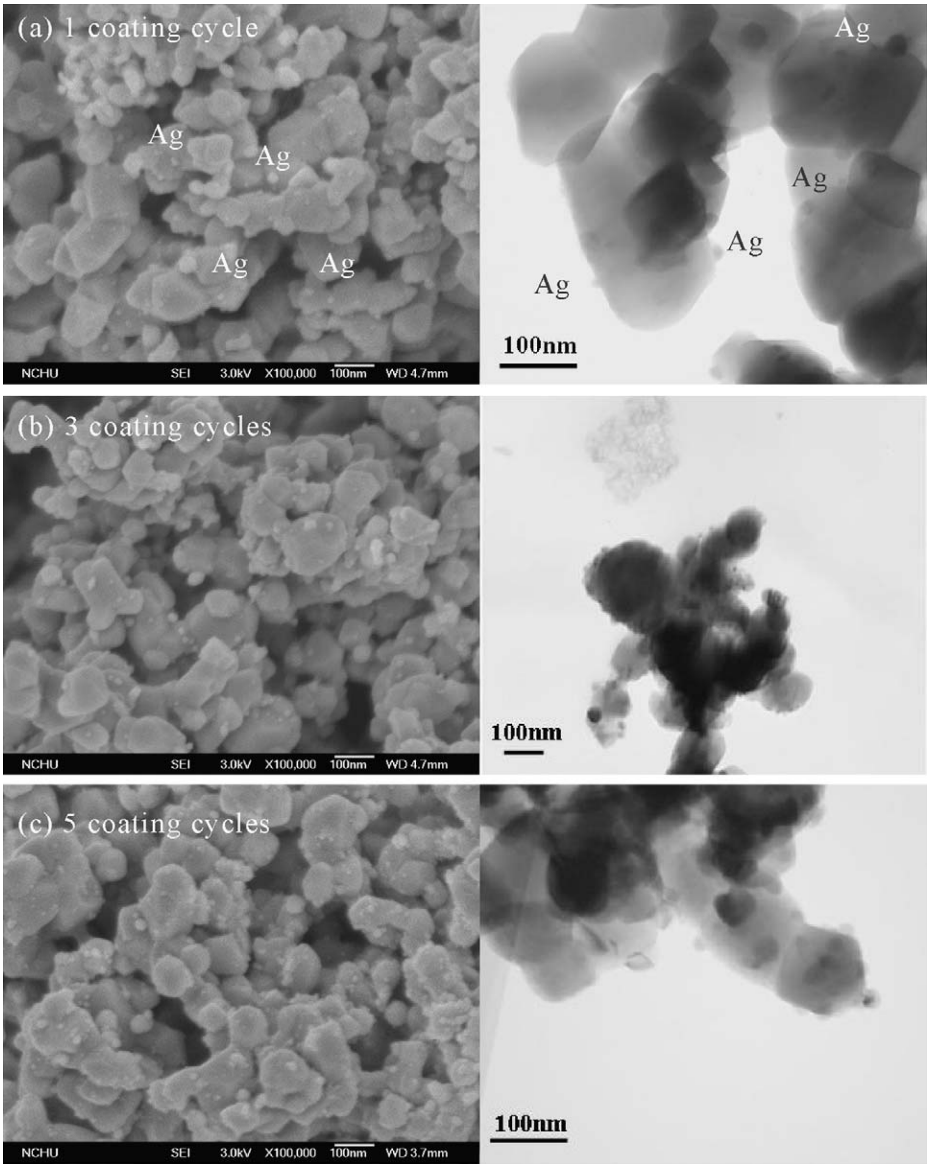

Fig. 5. SEM and TEM micrographs of the ITO/Ag composite particles with various deposition cycles.

coverage increases apparently in its concentration as the multiple deposition proceeds.

The discrete distribution of the Ag nanoparticles on the ITO particle surface does not significantly alter the electrical property of the bare ITO particle assemblies. A resistance measured by a four-point probe shows a sheet resistivity decreasing slightly to 1.8 Ω cm after 3 coating cycles when compared to that of the bare ITO powdered films (2.7 Ω cm). Note that the measurement was carried out on the particulate films without sintering; therefore, the conductivity is substantially greater than that of dense ITO films (2×10^{-4} Ω cm). The existence of Ag nanoparticles on the ITO surface shows a pronounced reduction in the optical transmittance of the particulate films. As shown in Fig. 6, the optical transmittance of the hybrid composite films with one deposition cycle is reduced by more than half of the bare ITO particulate films, despite only a minor Ag content (equivalent to a calculated 0.17 wt.%) was detected from the ICP-AES measurement. The transmittance further reduces as the deposition cycle increases to three (0.93 wt.% of Ag). Both reveal a strong scattering induced by the Ag nanoparticles, so that the transmittance of the ITO/Ag hybrid films is substantially reduced.

4. Conclusion

Ag nanoparticles (~10 nm) were preferentially adsorbed on submicrometer ITO particles (~150 nm) via a successive layer-by-layer deposition process involving both electrostatic and hydrophilic/hydrophobic interactions. A cyclic change on zeta potential of the composite particles was found as the deposition cycle proceeds. The Ag coverage was not of a uniform film on the particulate ITO surface, but of discrete particles that

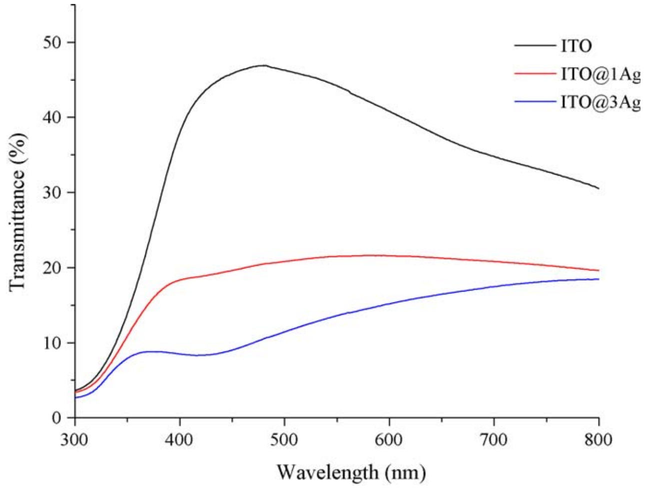

Fig. 6. Transmittance spectrum of the particulate ITO and ITO/Ag composite films over the visible wavelengths.

anchored specifically on the ITO surface because of the presence of organic polymers, e.g., PAH and AOT molecules, that serve as a bridge between the different phases. The deposition of Ag nanoparticles appeared to scatter the incoming visible light substantially despite of their low doping concentration (ca. 0.17–0.93 wt.%). This together with the zeta-potential property showed that the preferential adsorption of Ag nanoparticles on the ITO particles is critically important to the surface-prone properties of the hybrid particles.

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