Hybrid nanocomposite based on cellulose and tin oxide: growth, structure, tensile and electrical characteristics

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Abstract
A highly flexible nanocomposite was developed by coating a regenerated cellulose film with a thin layer of tin oxide (SnO$_2$) by liquid-phase deposition. Tin oxide was crystallized in solution and formed nanocrystal coatings on regenerated cellulose. The nanocrystalline layers did not exfoliate from cellulose. Transmission electron microscopy and energy dispersive x-ray spectroscopy suggest that SnO$_2$ was not only deposited over the cellulose surface, but also nucleated and grew inside the cellulose film. Current–voltage characteristics of the nanocomposite revealed that its electrical resistivity decreases with deposition time, with the lowest value obtained for 24 h of deposition. The cellulose–SnO$_2$ hybrid nanocomposite can be used for biodegradable and disposable chemical, humidity and biosensors.

Keywords: electrical resistivity/conductivity, growth, nanocomposite, SnO$_2$, cellulose

1. Introduction

Hybrid inorganic–organic nanocomposites are a new class of functional nanomaterials that show improved optical, thermal and mechanical properties because of the synergistic effect resulting from physical or chemical interactions between the inorganic and organic components [1]. These nanocomposites offer advantages of flexibility, light weight, low cost and high impact resistance. They have a wide range of applications, including flexible sensors, displays and dye-sensitized solar cells. Many reports have been published recently on the preparation of mineral nanoparticle-reinforced and nanofiber-reinforced polymer matrix nanocomposites as well as hybrid nanocomposites based on natural cellulose [2–7]. Marqueus et al [1] and Goncalves et al [8] have prepared a cellulose–TiO$_2$ composite by coating cellulose fibers using surface modification and acid hydrolysis of TiO$_2$. Coating cellulose fibers with SiO$_2$ via polyelectrolyte assembly was reported by Pinto et al [2]. ZnO has been grown on cellulose fibers by mineralization and liquid-phase deposition [3, 4]. Although these newly developed materials possess excellent physical and optical properties, they require post-processing into hand sheets or regenerated films for flexible electronics and sensor applications. Such post-processing might disrupt the association between cellulose and metal oxide nanoparticles, thereby deteriorating the physical, optical and electrical properties of the composite. Therefore, synthesizing a very thin and uniform nanocrystalline metal oxide layer on a cellulose film can be advantageous in applying this material to flexible electronic devices, disposable sensors and biosensors.

Here, we report a flexible and biodegradable hybrid nanocomposite based on cellulose and tin oxide (SnO$_2$). We use a regenerated cellulose membrane as a base material because of its biodegradability, biocompatibility, flexibility and low price. A thin layer of SnO$_2$ was introduced onto the cellulose surface via liquid-phase deposition. We chose SnO$_2$ because it is an electrical conductor that is optically transparent in the visible spectrum with a wide band gap of 3.6 eV at room temperature. SnO$_2$ has been widely used in gas sensors [9, 10], optical devices [11], lithium batteries [12, 13] and so on. Thus, a hybrid nanocomposite of cellulose and SnO$_2$ can combine the natural polymer properties of cellulose with the electrical conductivity of SnO$_2$. These
unique characteristics of the cellulose–SnO\textsubscript{2} nanocomposite can be capitalized to design flexible, biodegradable and disposable chemical, humidity and biosensors.

2. Experimental approach

2.1. Preparation of regenerated cellulose

Cellulose regeneration from \(N,N\)-dimethylacetamide (DMAc)/lithium chloride (LiCl) solvent system has been well documented in the literature \cite{14} and the same method was employed. In brief, cotton cellulose pulp (MVE, DPW 4580 purchased from Buckeye Technologies Co, Tennessee, USA) and LiCl (extra pure, Junsei Chemicals Co, Japan) were heated under reduced pressure at 110°C for 1 h and LiCl was dissolved in DMAc. Then, the pulp was mixed with the LiCl–DMAc solution and heated to 155°C followed by cooling to 40°C for 2 h. An optically transparent cellulose solution was obtained from this process. The transparent cellulose solution was deposited on a silicon substrate using a spin coater (Laurrell, EDC2-100) followed by curing with a mixture of isopropyl alcohol and deionized water, which resulted in a film of wet regenerated cellulose.

2.2. Fabrication of cellulose–SnO\textsubscript{2} nanocomposite

Tin(II) fluoride (SnF\textsubscript{2}) of 99% purity from Aldrich was used as received. Deionized water (200 ml) was kept at 90°C in a polypropylene bottle with a cap containing a hole; 870.6 mg of SnF\textsubscript{2} was dissolved in the bottle to obtain 5 mM concentration \cite{5}. A wet regenerated cellulose film was then immersed in the solution at 90°C for 3, 6, 12 18 or 24 h under stirring. The solution was changed every 6 h. During this process, SnO\textsubscript{2} was deposited and grown continuously and uniformly throughout the surface of the cellulose film. The SnO\textsubscript{2}-coated cellulose film was then washed with running water and dried under ambient conditions.

2.3. Characterization of cellulose–SnO\textsubscript{2} nanocomposite

The deposition and growth of SnO\textsubscript{2} layers over cellulose films were characterized by scanning electron microscopy (SEM, Hitachi S4300) and transmission electron microscopy (TEM, Philips CM200 equipped with Multiscan CCD camera). X-ray diffraction (XRD) patterns were recorded with a thin-film x-ray diffractometer using CuK\(\alpha\) radiation at 40 kV and 50 mA and a scanning rate of 0.015° min\(^{-1}\). The diffraction angle ranged from 5 to 40°.

X-ray photoelectron spectroscopy (XPS) measurements were conducted using the Thermo Scientific K-ALPHA spectrometer equipped with a microfocused and monochromated Al K\(\alpha\) x-ray source (spot size 400 µm). The chemical elements present in the samples were identified from the survey spectra. The surface scans started at 1400 eV and ended at 0 eV, with 1 eV step and a dwell time of 200 ms. The effect of SnO\textsubscript{2} deposition on the electrical conductivity of the cellulose films was evaluated by measuring their current–voltage (I–V) characteristics.

The thermal behavior of the cellulose–SnO\textsubscript{2} nanocomposite was analyzed by thermogravimetry and differential thermal analysis (TG-DTA, NETZSCH, STA 409 PC). Weight loss was measured in air, by heating 10–15 mg samples to 600°C at a rate of 10°C min\(^{-1}\). Tensile tests were conducted in accordance with the ASTM D-882-97 standard using a universal testing machine, under ambient conditions and a pulling rate of 0.02 mm s\(^{-1}\). Two ends of the specimen were fixed between the upper and lower fixtures of the instrument with a gauge length of 50 mm. Four samples were tested for each measurement and average values were used.

3. Results and discussion

3.1. Growth mechanism of tin oxide on cellulose film

The synthesis of nanocrystalline SnO\textsubscript{2} from SnF\textsubscript{2} in aqueous solutions is considered to proceed through the formation of SnF(OH) and its subsequent conversion into tin(II) hydroxide, followed by thermal hydrolysis into nanocrystalline tin oxide \cite{15, 16}. Thus the growth of tin oxide on cellulose may proceed through either of two mechanisms: (i) tin oxide nanocrystals are formed in the solution and then attach to cellulose or (ii) SnF(OH) is synthesized at the nucleation sites of the cellulose surface and then transformed into tin oxide via thermal hydrolysis. To reveal which mechanism takes place, we carried out two simple experiments.

(a) Delayed immersion test. SnF\textsubscript{2} was introduced into deionized water maintained at 90°C for about 3 h until the formation of SnO\textsubscript{2} nanoparticles (yellowish-white suspension) was completed. Then a wet cellulose membrane was introduced in the reaction vessel and kept there for 6 h.

(b) Instant immersion test. A wet cellulose membrane was introduced in the reaction vessel right after SnF\textsubscript{2}. After 6 h, the membrane was removed and washed with running water.

In the first test, the film color remained unchanged as shown in figure 1(a). However, in the second case, the film turned blue-green as shown in figure 1(b), indicating the formation of a SnO\textsubscript{2} layer. This result implies that, upon introduction of the wet cellulose into a mixture of SnF\textsubscript{2} and deionized water at 90°C, stannous fluoride converted to SnF(OH), nucleated on the cellulose surface via inter- and intramolecular hydrogen bonding and then hydrolyzed to SnO and SnO\textsubscript{2}. Figure 1(c) depicts the mechanism of tin oxide growth on cellulose.

3.2. Morphology

The growth and deposition of SnO\textsubscript{2} on cellulose were analyzed by SEM, TEM and XRD. Figure 2 shows the SEM images of the cellulose surface coated with SnO\textsubscript{2} for different deposition times. The pristine cellulose has a very smooth surface, and after 3 h of deposition, many SnO\textsubscript{2} particles appear randomly all over the surface. As the deposition time was increased, the density of the SnO\textsubscript{2} particles increased...
Figure 1. Photographs of cellulose samples after immersion in the reaction vessel for 6 h: (a) delayed immersion and (b) instant immersion; (c) is a schematic of the growth mechanism of tin oxide on cellulose.

Figure 2. Surface SEM images of the cellulose–SnO$_2$ nanocomposite as a function of deposition time: (a) pristine cellulose, (b) 3 h, (c) 6 h, (d) 12 h, (e) 18 h and (f) 24 h.

until they coalesced into a continuous layer, which might consist of assemblies of SnO$_2$ nanosheets. Note that the size of the SnO$_2$ particles and the layer thickness increased with the deposition time. A uniform SnO$_2$ coating is one of the advantages of the solution process. It is worth noting that, unlike the SnO$_2$ coating on Teflon [5], the SnO$_2$ coating on cellulose cannot be exfoliated by scratching with a metal spatula.
Figure 3. (a) TEM image, (b) EDS spectra and (c) tin oxide distribution profile in cellulose–SnO$_2$ nanocomposite after 18 h of deposition, (d) cross-sectional SEM image of the cellulose–SnO$_2$ nanocomposite after 24 h of deposition.

Figure 3(a) shows a TEM image of the cellulose–SnO$_2$ nanocomposite after 18 h of deposition. Energy dispersive x-ray spectroscopy (EDS) analysis of the coating in figure 3(b) suggests the existence of a SnO$_2$ layer. It was repeated at different locations normal to the cellulose–SnO$_2$ interface. The result is plotted in figure 3(c) as the Sn/O atomic ratio vs. the distance from the top surface. The Sn/O ratio is almost constant up to 2.6 $\mu$m; it decreases sharply between 2.6 and 3.9 $\mu$m and then saturates. This observation suggests that a 1.3 $\mu$m thick layer of SnO$_2$ was deposited inside cellulose (SnO$_2$-rich cellulose) and capped by a 2.6 $\mu$m layer, i.e. SnO$_2$ not only deposited on the cellulose film, but also nucleated and grew inside it. This intergrowth might explain why the SnO$_2$ coating on cellulose could be exfoliated by scratching. Thus, figures 3(c) and (d) reveal a uniform and homogeneous deposition of SnO$_2$ on cellulose. Pristine cellulose has a compact layer-by-layer structure with abundant nanopores all over its surface [17]. When the wet cellulose film was immersed in the reaction vessel containing a metal precursor (SnF$_2$) and deionized water at 90 $^\circ$C, the coating reaction first created nucleation sites of SnO$_2$ on the cellulose surface. As time progressed and the condensation reaction continued, the nucleation sites merged to form a continuous coating [6]. Thus, the nucleation occurred simultaneously in the solution and on the cellulose surface, in agreement with the observation of a yellowish-white suspension in the reaction vessel. Direct crystallization of SnO$_2$ on the cellulose films resulted in a high adhesion strength, which is required for sensor and solar cell applications. The thicknesses of both the SnO$_2$ coating and SnO$_2$-rich cellulose layer appear to increase with the deposition time. After 24 h of deposition, the SnO$_2$ coating was 4.3 $\mu$m thick.

3.3. XRD

Figure 4 shows the XRD patterns of cellulose–SnO$_2$ nanocomposites after different deposition times. Raw cotton cellulose pulp has a highly crystalline cellulose I structure with reflections from the (110), (1–10) and (200) planes at 15, 16.8 and 23$^\circ$, respectively [18]. However, upon dissolution and regeneration in the DMAc/LiCl solvent, it transforms into the more disordered cellulose II structure [19]. The pristine cellulose film showed a characteristic peak at 2$\theta$ = 20.9$^\circ$ and weak SnO$_2$ peaks appeared at 26.7, 32.3 and 52$^\circ$ in the cellulose–SnO$_2$ nanocomposite after 3 h of deposition. The intensity of these 3 peaks increased with deposition time. After 24 h of deposition, the increase rate accelerated and a new peak appeared at 37.2$^\circ$. Meanwhile, the cellulose signal remained unchanged, suggesting that cellulose was not altered by the SnO$_2$ deposition. Peaks at 2$\theta$ = 26.7, 32.3, 37.2 and 52$^\circ$ were assigned to the (110), (002), (200) and (211) diffraction peaks from SnO$_2$ and SnO [5, 7], respectively. Their large width is consistent with the small crystallite size. Thus, XRD analysis suggests that the coating indeed consists of SnO$_2$ and SnO.
Figure 4. XRD patterns of cellulose–SnO$_2$ nanocomposites for different deposition times.

Figure 5. XPS survey of the cellulose–SnO$_2$ hybrid nanocomposite (24 h of deposition).

3.4. XPS analysis

XPS was used to characterize the chemical state of the SnO$_2$ coating. Figure 5 shows the XPS survey spectrum of the cellulose–SnO$_2$ nanocomposite after 24 h of deposition. All the SnO$_2$-coated cellulose films showed signals of tin, oxygen and fluorine. Sn3d$_{5/2}$ and Sn3d$_{3/2}$ peaks were observed at 487.1 and 495.4 eV, respectively [6], as shown in figure 6(a). The binding energy of 487.1 eV is similar to the values for SnO$_2$ (486.3 and 486.6 eV) and higher than those of Sn metal (484.8, 484.9 and 485 eV). The slight shift compared with the SnO$_2$ energies suggests that tin atoms in the coating were positively charged by forming direct bonds with oxygen [5].

The O1s spectrum in figure 6(b) shows the main peak at 530.6 eV with a shoulder at 532.1 eV, which were attributed to lattice oxygen and oxygen in absorbed hydroxyl groups [20]. The chemical compositions of the coatings deposited for 12, 18 and 24 h were estimated as Sn : O : F : C = 13.7 : 16.0 : 2.1 : 36.0, 24.7 : 29.5 : 4.5 : 22.1 and 27.7 : 29.5 : 5.1 : 16.6, respectively, revealing that the amount of SnO$_2$ increased with the deposition time.

3.5. TGA analysis

Figure 7 shows thermogravimetry curves of pristine cellulose and SnO$_2$ and of the cellulose–SnO$_2$ nanocomposites. Pristine tin oxide is stable over a broad temperature range, whereas cellulose decomposes in two steps at 350 and 550 °C [21]. After the deposition of SnO$_2$ on cellulose, the first step progressively shifts to lower temperatures, from 330 °C for 6 h to 308 °C for 24 h of deposition. The residues left after heating to 600 °C are 2.2, 6.3, 28.1, 61.2 and 65.3% for deposition times of 0, 6, 12, 18 and 24 h, from which the amounts of SnO$_2$ deposited on cellulose were estimated as 0, 3.6, 25.4, 58.5 and 63.1%, respectively. Despite these large amounts of SnO$_2$, the nanocomposite still possessed excellent flexibility, as shown in figure 8.

3.6. Tensile properties

Figure 9 shows the stress-strain behavior of cellulose–SnO$_2$ nanocomposites. Note that tensile properties such as tensile strength, yield strength and strain at break decrease with SnO$_2$ deposition time. For example, the respective values of tensile strength, yield strength and strain at break of pristine cellulose decrease from 74.7 MPa, 32 MPa and 18.1% to 10.8 MPa, 10.6 MPa and 1.52% after 24 h deposition. The tensile properties of metal oxide–polymer composites depend...
Figure 6. XPS survey of the cellulose–SnO$_2$ hybrid nanocomposite after 24 h of deposition: (a) Sn3d and (b) O1s spectra.

Figure 7. Thermogravimetry curves of the cellulose–SnO$_2$ hybrid nanocomposites for different deposition times, as well as of pristine cellulose and tin oxide.

Figure 8. Photograph of the cellulose–SnO$_2$ hybrid nanocomposite (24 h of deposition) demonstrating its excellent flexibility.

Figure 9. Stress–strain curves of cellulose–SnO$_2$ hybrid nanocomposites for different deposition times.

on several factors such as the distribution of metal oxide nanoparticles, amount of metal oxide loading, interaction between metal oxide and polymer and so on [22]. XRD and TGA analyses reveal that the amount of SnO$_2$ on cellulose increases with deposition time, reaching 63.1% after 24 h. This increase induces the transformation from ductile to brittle behavior as evidenced by the reduction in the strain at break. Also, as mentioned in section 3.1, the nucleation and growth of tin oxide on cellulose disrupt the inter- and intramolecular hydrogen bonds of cellulose chains that partly accounts for the inferior tensile properties of cellulose–SnO$_2$ nanocomposites. Note that a similar reduction in tensile strength with the amount of inorganic component was reported previously for cellulose–TiO$_2$ [1] and bacterial cellulose–silica [23] nanocomposites.

3.7. I–V characteristics

To study the effect of SnO$_2$ coating on the electrical properties of cellulose, the electrical conductivity of the
cellulose–SnO$_2$ nanocomposites was measured under ambient condition using a semiconductor parameter analyzer. Prior to the measurement, rectangular gold electrodes with a gap of 50 $\mu$m were fabricated using a lift-off process. The voltage $V$ was scanned between $-2$ and $+2$ V and the induced dc current $I$ was measured. Figure 10 shows the typical $I$–$V$ curves of the nanocomposites as a function of the SnO$_2$ deposition time. After deposition for 3 or 6 h, the sample behaved as an insulator with no detectable current. When the deposition time was extended to 12 h, a conductivity of $3.97 \times 10^{-8}$ S cm$^{-1}$ was detected; it further increased to $4.76 \times 10^{-3}$ S cm$^{-1}$ after 24 h of deposition, which can be attributed to a higher amount of deposited SnO$_2$.

This result suggests that the deposition time of 24 h is suitable for the fabrication of a SnO$_2$ layer on cellulose. The produced nanocomposite can be used for developing low-cost, disposable gas, chemical and biosensors. Recently, we have reported a glucose and urea sensor based on a cellulose–SnO$_2$ nanocomposite [24, 25]. Experiments are underway to demonstrate the application of this nanocomposite as pH, gas and chemical vapor sensors, and the results will be reported in the future.

4. Conclusions

A highly flexible hybrid nanocomposite of regenerated cellulose film and SnO$_2$ was prepared by coating cellulose with a thin SnO$_2$ layer via liquid-phase deposition. TEM-EDS analysis revealed that SnO$_2$ nucleated and grew not only on but also in the cellulose films. The thickness of the SnO$_2$ layer increased with deposition time, reaching 4.3 $\mu$m after 24 h. XRD analysis suggested that the coating is a mixture of SnO$_2$ and SnO. The electrical conductivity of the composite increased with deposition time up to $4.76 \times 10^{-3}$ S cm$^{-1}$ after 24 h. The cellulose–SnO$_2$ nanocomposite can be used for sensors of urea, glucose, chemical vapors and humidity.

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