Composites of Polyvinyl Alcohol and Carbon Nanotubes Decorated with Silver Nanoparticles

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Abstract: A simple method to decorate carbon nanotubes (CNTs) with silver nanoparticles was developed to enhance the electrical conductivity of CNTs. The acid-treated CNTs were suspended in the silver acetate solution, ammonia solution was then added, and the CNTs decorated with silver nanoparticles (Ag@CNTs) were produced. The Ag@CNTs were dispersed in polyvinyl alcohol (PVA) to fabricate electrically conducting polymer composites. The electrical, thermal and mechanical properties of the composites were measured. The electrical conductivity of the composites containing 0.8 % (o.w.f.) Ag@CNTs was more than four orders of magnitude higher than those of pristine and functionalized CNTs respectively, which confirmed the effectiveness of the Ag@CNTs as conducting filler. However, the improved electrical conductivity led to somewhat decrease of mechanical properties of PVA/Ag@CNTs composites.

Keywords: Ag nanoparticle, Carbon nanotube, Composite, PVA

Introduction

Since their discovery in 1991, CNTs have been extensively studied due to their large aspect ratios that provide them with a unique combination of mechanical, electrical, and thermal properties [1,2]. Among the numerous CNTs chemistry developed in the past, the integration of one-dimensional nanotubes with zero-dimensional nanoparticles into hybrid structures, especially the noble metal nanoparticles/CNTs composites, has received increasing interests [3-9]. Among all of the noble metal nanoparticles, Ag nanoparticles have been paid much more attention due to their potential utility as electrocatalysts [10,11], electrode materials [12], biosensors [13], broad-band optical limiters [14], and anode materials in lithium-ion batteries [15]. Several approaches have been proposed to prepare the silver nanoparticles/CNTs composites, such as chemical deposition [16], solution-phase synthetic method [17], and photochemical deposition method [18]. Nevertheless, the relatively complicated processes limited their utilizations in industry. Therefore, to search for a simple approach to modify CNTs combined with the Ag nanoparticles is still a research focus.

PVA-based CNTs composites have been extensively investigated in view of their potential application in the packing and anti-electrostatic clothes because of their excellent properties [19,20], especially their electrical conductivity and the mechanical properties. Though increase of CNTs content could enhance electrical conductivity of composites [21], processing techniques for improving the conductivity became crucial.

Ag nanoparticles decoration would have a beneficial effect on the electrical conductivity of CNTs because the inherent electrical conductivity of Ag (σ_{Ag}=6.30×10^5 S/cm)

is much higher than that of the CNTs without Ag. Ma *et al.* used Ag@CNTs prepared by the reducing reaction of silver ions (Ag^+) using *N, N*-dimethylformamide as conducting filler in epoxy resin to fabricate electrically conducting polymer composites. As expected, the electrical conductivity of composites containing Ag@CNTs was much more higher than those containing pristine CNTs (p-CNTs) and functionalized CNTs (f-CNTs). So far, PVA composites containing Ag@CNTs has not been studied yet. As a odorless and nontoxic polymer, the high conductivity PVA composites will have more extensive applications.

In this paper, a simple approach different from that described in literature [22] was proposed to decorate CNTs with Ag nanoparticles (Ag@CNTs), aiming at enhancing the electrical conductivity of CNTs. The Ag@CNTs were incorporated into PVA as conducting fillers to prepare electrically conducting composites PVA/Ag@CNTs. Several methods were employed to characterize the morphology, structure and the related properties of Ag@CNTs and the composite of PVA containing Ag@CNTs.

Experimental

Instrumentation

Transmission electron microscopy (TEM) images were obtained with an FEI TecnaiG 200 transmission electron microscope using samples deposited on carbon coated copper grids. XRD studies were performed in a powder XRD system (PANalytical, Holland). Surface morphologies of the samples were obtained using scanning electron microscope (SEM, Hitachi S-570). Bulk electrical conductivity was measured using a broad band dielectric spectrometer (Nanocontrol Gmbh). Mechanical properties of the composites were analyzed using a universal material testing machine (INSTRON 3365).

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Chemicals

Silver acetate, ammonia water 25 % (o.w.f.), concentrated sulfuric acid 98 % (o.w.f.), concentrated nitric acid 65 % (o.w.f.), and polyvinyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). p-CNTs were from Chengdu Organic Chemicals Co., Ltd. (China).

CNTs Decoration with Ag nanoparticles

The p-CNTs were multi-walled CNTs and they were synthesized by a chemical vapor deposition method. Their electric conductivities were more than 100 s/cm. The diameter and length of the CNTs ranged between 20-30 nm and 30-40 μm, respectively. In order to functionalize the p-CNTs, they were treated according to literature [23]. 1 g p-CNTs were added to 150 ml mixed solvent composed of concentrated nitric acid and concentrated sulfuric acid (HNO_3:H_2SO_4= 1:3 V/V), the solution was ultrasonicated for 1 h at room temperature, and then heated for 8 h at 90 °C. The solution was cooled to room temperature, and functionalized nanotubes were obtained through filtering the solution using microhole filter membrane. The nanotubes were washed repeatedly by deionized water till the water pH was near 7, and then dried in vacuum for 12 h at 50 °C. Meanwhile, 10 mg CH_3COOAg was dissolved in 5 ml deionized water, then 0.1 ml $NH_3 \cdot H_2O$ 25 % (o.w.f.) solution was added to form precursor solution, in which 10 mg dried f-CNTs were soaked for 24 h. After the f-CNTs centrifugally separated from the solution were dried at 70 °C in vacuum, and calcined at 300 °C in the presence of N_2 for 2 h, Ag@CNTs were prepared.

Preparation of Composites

PVA ($M_w \approx 100000$ g/mol) was dissolved in distilled water at 90 °C to give 15 % (o.w.f.) aqueous solution. The three CNTs including p-CNTs, f-CNTs and Ag@CNTs were ultrasonicated for 20 min in deionized water. Then the CNTs solutions were mixed with the PVA solution by continuously stirring to obtain 10 % (o.w.f.) PVA solution with CNTs concentration of 0.2, 0.4, 0.6, or 0.8 % (o.w.f.) with respect to PVA weight. After that, the resulting mixed solutions were cast into dishes, and dried in air at ambient temperature. Blank experiments without adding CNTs were performed under the same conditions.

Results and Discussion

CNTs Decoration with Ag Nanoparticles

The process of the modification of CNTs should be multistep, in which various chemical reactions occurred. It is difficult to illustrate all the exact chemical reactions, but the chief formation route can be inferred on the basis of analysis of the results shown in this paper. As shown in Figure 1, p-CNTs were treated to give carboxylic group and became f-CNTs. Meanwhile, $NH_3 \cdot H_2O$ was added into Ag^+ solution to form $[Ag(NH_3)_2]^+$, in which f-CNTs were soaked. Owing to

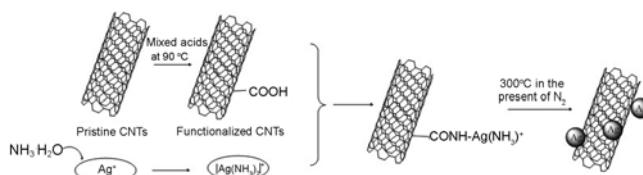**Figure 1.** Schematic presentation for formation of Ag@CNTs.

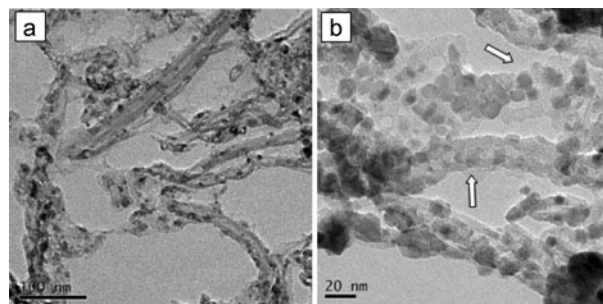**Figure 2.** TEM images of Ag@CNTs at (a) low and (b) high magnification.

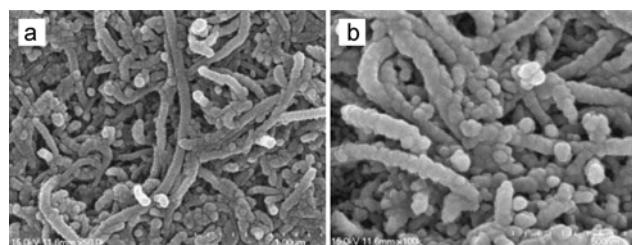**Figure 3.** SEM images of Ag@CNTs at (a) low and (b) high magnification.

the electrostatic attraction, the $[Ag(NH_3)_2]^+$ diffused to the surface of f-CNTs in the solution. Subsequently, the intermediate product f-CNTs-CONH-Ag(NH_3)^+ was separated from the solution. Finally, the product was converted to the Ag@CNTs via calcinations treatment in the presence of N_2.

Typical TEM images of Ag@CNTs are shown in Figure 2 in low and high magnifications, respectively. Figure 2(a) shows the morphology of Ag@CNTs in general. It can be seen that Ag nanoparticles are homogeneously dispersed on the CNTs surface. A close look at Ag@CNTs as shown in Figure 2(b) tells us that the Ag nanoparticle size is estimated to be around 20 nm. The white arrows in the Figure 2(b) point out the typical Ag nanoparticles which are attached on the outer surface of CNTs and have a near round shape. The results suggest that the Ag nanoparticles grow closely on the nanotubes' surface rather than loose attachment.

Figure 3 shows the representative SEM micrographs of the Ag@CNTs. In low magnification as shown in Figure 3(a), most silver nanoparticles distribute almost uniformly on the sidewalls of the nanotubes. In high magnification as shown in Figure 3(b), it is obviously seen that Ag nanoparticles
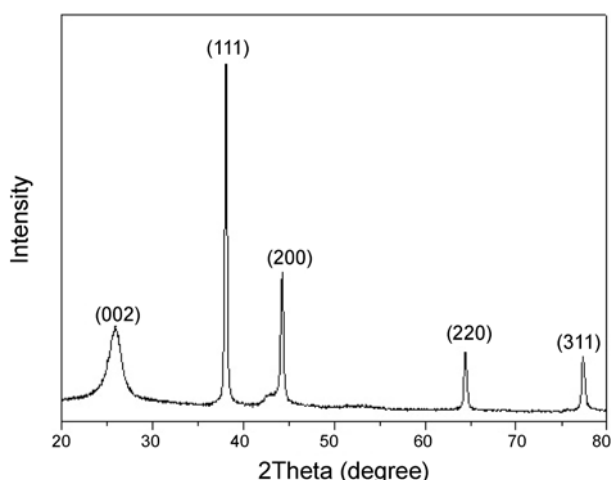
Figure 4. XRD pattern of Ag@CNTs.

with the particle size of about 20 nm are homogeneously combined on the surface of CNTs and intimately attached to the CNTs, in agreement with the observation of TEM images as shown in Figure 2.

Figure 4 shows XRD patterns of the Ag@CNTs. A peak at 26.4° corresponds to a typical (002) reflection of CNTs, whereas diffraction peaks at 38.0, 44.2, 64.3, and 77.2 correspond to Ag (111), (200), (220), and (311) reflections, respectively, indicating the formation of Ag nanocrystals and the 0-valence nature of the Ag nanoparticles. The average size of the Ag nanoparticles is about 20 nm calculated by Scherrer equation, which accords well with the average size estimated in terms of TEM and SEM images.

CNTs Dispersion in PVA Matrix

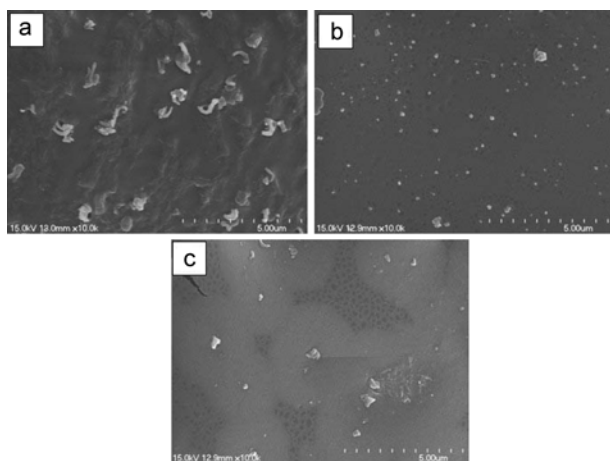The morphologies of PVA/CNTs composites are shown in Figure 5, providing some insight into the CNTs dispersion

state. Large CNTs agglomerates are seen for the composite containing p-CNTs (Figure 5(a)), while these agglomerates are almost absent for that containing f-CNTs and Ag@CNTs (Figures 5(b) and 5(c)). This phenomenon can be explained in terms of improved interactions between CNTs and PVA, or CNTs and Ag because of the functionalization of CNTs in f-CNTs and Ag@CNTs [24]. On the one hand, this functionalization prevents the f-CNTs from agglomeration, resulting in easier dispersion of the f-CNTs in PVA, on the other hand, the functional groups like carboxyl on the surface of CNTs facilitate Ag decoration onto f-CNTs [25-27].

Electrical Conductivity of Composites

The electrical conductivity of the composites (PVA/p-CNTs, PVA/f-CNTs, and PVA/Ag@CNTs) is plotted as a function of CNTs content as shown in Figure 6. Conductivity of the composites containing different CNTs rises with the increase of the CNTs content. The incorporation of 0.8 % (o.w.f.) p-CNTs with PVA increases the conductivity of PVA/p-CNTs by about two orders of magnitude over that of pure PVA, while PVA/Ag@CNTs exhibit a more pronounced enhancement in electrical conductivity than p-CNTs at the same CNTs content. A remarkable difference of electrical conductivity-about four orders of magnitude-is observed between PVA/Ag@CNTs and PVA/p-CNTs, showing that Ag@CNTs acts as an effective conducting filler to improve the conductivity of the composites. However, the composites containing f-CNTs exhibit consistently lower conductivities than those containing p-CNTs and Ag@CNTs. Zhang *et al.* [28] reported that CNTs length along with the degree of CNTs dispersion determined electrical conductivity of CNTs-polymer composites. f-CNTs dispersion in PVA is not a problem as shown in Figure 5, but their lengths can be reduced after the acid-treatment [29], which weakens electrical conductivity of the composites. Compared to the p-CNTs,
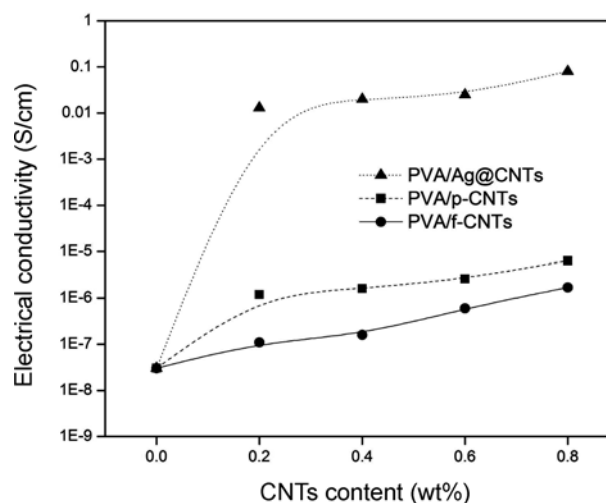

Figure 5. Surface morphologies of PVA/CNTs composites. (a) PVA/p-CNTs, (b) PVA/f-CNTs, and (c) PVA/Ag@CNTs. CNTs content: 0.8 % (o.w.f.).

Figure 6. Variation of electrical conductivity of PVA/CNTs composites with CNTs content.
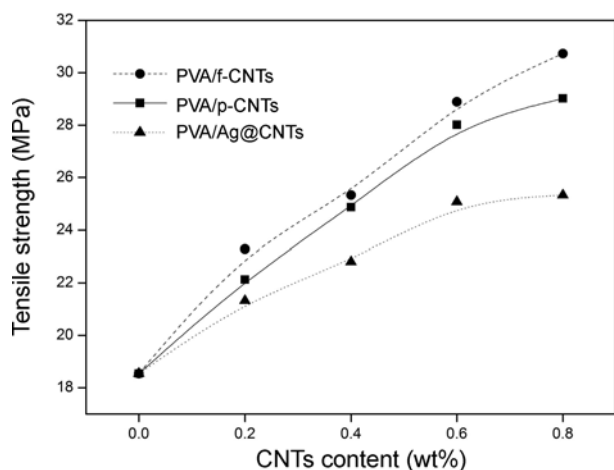
Figure 7. Effect of CNTs content on the tensile strength of PVA composites.

Ag@CNTs is shorter in lengths. Nevertheless, the conductivity of Ag is much higher than that of the CNTs, so Ag nanoparticles that are tightly attached onto the CNTs surface in PVA/Ag@CNTs as shown in Figure 2(b) will compensate the weakening effect.

Tensile Properties of Composites

Figure 7 shows the relationships between tensile strength of the composites and CNTs content. The tensile strengths for all three composites increase with increasing CNTs content, particularly PVA/f-CNTs exhibits much higher strength than PVA/p-CNTs and PVA/Ag@CNTs. This can be explained by the dispersion of CNTs in PVA as well as the interfacial interactions between CNTs and PVA matrix as reported by some researchers [30-34]. On the one hand, as shown in Figure 5, dispersion of f-CNTs in PVA is better than p-CNTs. On the other hand, -COOH on f-CNTs can form hydrogen bond with -OH on PVA main chain. Nevertheless, as we know, p-CNTs tend to agglomerate to form thick ropes, and these ropes tend to agglomerate into larger domains, which can contain a number of nanotubes that are not in contact with the PVA and only bonds to each other between nanotubes by weak interactions, leading to weak tensile strength. Although there are f-CNTs in PVA/Ag@CNTs, surprisingly the strength of PVA/Ag@CNTs is lower than PVA/p-CNTs and PVA/f-CNTs. The existence of Ag particles somewhat sacrifices the reinforcement effect of CNTs in the composites. It may be explained that Ag particles prevent CNTs to contact PVA, so only poor combination between Ag@CNTs and PVA matrix can be formed, which weakens the strength of the composites. As for this point, we will study it further.

Conclusion

A simple method is established to fabricate Ag@CNTs,

and PVA-based composites containing CNTs with Ag nanoparticles PVA/Ag@CNTs were prepared. The incorporation of a small fraction of CNTs in the PVA matrix can result in a significantly increase in electrical conductivity for the composites stated in this paper, especially, Ag@CNTs are effective conducting filler of PVA. However, the tensile strength of PVA/Ag@CNTs is lower than that of PVA/f-CNTs and PVA/p-CNTs, which possibly ascribe to poor combination between CNTs and PVA due to existence of Ag nanoparticles.

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