

Photochemical deposition of Ag nanoparticles on multiwalled carbon nanotubes

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Abstract

A simple method for preparation of Ag nanoparticle (NP)/multiwalled carbon nanotube (MWCNT) composites using laser irradiation without a reducing agent is presented. Ag NPs were grown on MWCNTs by laser-induced photoreduction of $[\text{Ag}(\text{NH}_3)_2]^+$. The larger the initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentration, the bigger the average particle size. XRD investigations revealed the well-crystallized structure of the nanoparticles.

Silver nanoparticle (NP)/carbon nanotube (CNT) composites have attracted much attention due to their potential utility as conducting fillers to make conductive polymers [1], anode materials in lithium-ion batteries [2], sensors of DNA hybridization [3] and electrocatalysts [4]. Several methods have been proposed to prepare these composites, such as electroless plating [5], electrochemical deposition [6,7], solid-state reaction [8] and chemical deposition [9]. During the deposition, aggregation might occur. To obtain highly dispersed nanoparticles on CNTs, a monolayer-grafting method has been proposed [10].

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Nanoparticles have attracted much interest due to their inherent size- and shape-dependent properties and their important potential technological applications. In this letter, we present a simple method for preparation of Ag NP/multiwalled carbon nanotube (MWCNT) composites using laser irradiation without a reducing agent. Ag NPs were grown on MWCNTs by laser-induced photoreduction of $[\text{Ag}(\text{NH}_3)_2]^+$. As the initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentration increases, the particle size becomes larger. XRD investigations revealed the well-crystallized structure of the nanoparticles.

A 1 mL of 10% aqueous NaOH solution was mixed with 50 mL of 5% aqueous AgNO_3 solution to precipitate Ag_2O ; then 2% aqueous NH_3 solution was added to produce a $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ $[\text{Ag}(\text{NH}_3)_2]^+$ stock solution. The solution was further diluted to the concentrations of 3.0×10^{-4} (sample A), 1.0×10^{-3} (sample B) and 1.0×10^{-2} (sample C) mol dm^{-3} . A mass of 1 mg of MWCNT (Showa Denko VGCF-S, diameter 80 nm, length 10–20 μm) was dispersed in 10 mL of the $[\text{Ag}(\text{NH}_3)_2]^+$ solution. The dispersions, while being stirred, were irradiated by the fundamental of a Nd:YAG laser (Spectra Physics, Quanta-Ray INDI 40, repetition rate 20 Hz) for 5 min (samples A and B) or 1 min (sample C) at $17.7 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ sufficiently low fluence for prevention of MWCNTs damage [11]. The Ag NPs deposited on the MWCNT surfaces were filtered using a 0.5 μm pore size acetate membrane filter, and rinsed with deionized water. The Ag NP/MWCNT composites were dried at 373 K for 2 h. The deposition was examined using a field emission-scanning electron microscope (FE-SEM) (JEOL JSM-7000F). The X-ray powder diffraction (XRD) measurement was performed on a Rigaku, RINT 2200V/PC-SV X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$, $U = 40 \text{ kV}$, $I = 20 \text{ mA}$) at a scanning rate of $2.0 \text{ degree min}^{-1}$ in the 2θ range from 20 to 80 degrees. A three-electrode electrochemical cell configuration was applied to measure the rest potential with a potentiostat/galvanostat (Hokuto

Denko HA-151). The working electrode was a Pt plated ITO glass; the counter electrode was a Pt wire, and an Ag/AgCl electrode was used as the reference.

Fig. 1 shows SEM images of Ag NP/MWCNT composites prepared with different initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentrations of (a) 3.0×10^{-4} , (b) 1.0×10^{-3} and (c) $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. It is evident that as the initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentration increases, the particle size becomes larger. The photoreduction of the more concentrated $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ condition of $[\text{Ag}(\text{NH}_3)_2]^+$ was initiated instantaneously; the tube color changed to gray within 2 min and a Ag mirror grew on the glass wall (not shown). The XRD pattern of Ag NPs on MWCNTs prepared from the $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{Ag}(\text{NH}_3)_2]^+$ solution showed major diffraction peaks for Ag nanoparticles and MWCNTs (Fig. 2). The MWCNTs show a typical (002) reflection peak at 26.4 degrees. The peaks at 38.1, 44.3, 64.5 and 77.4 degrees can be assigned to (111), (200), (220) and (311) reflections, respectively, of the face-centered cubic lattice of Ag (JCPDS 04-0783). The average size of the Ag particles was estimated to be about 21 nm from the full width at half maximum of the (111) diffraction peak using the Scherrer equation. This value is in good agreement with the result obtained by the SEM image (Fig. 1(b)). For a better understanding of the phenomena observed under laser irradiation, we measured the change in the rest potential of MWCNTs in aqueous dispersion without Ag ion. Fig. 3 shows the change in the rest potential of a 1 mg MWCNTs/10 mL aqueous dispersion. The rest potential rapidly shifted in the negative direction upon laser irradiation. Cationic species are known to be adsorbed efficiently on the CNTs in water [12,13]. Therefore, we expect this to be the case for $[\text{Ag}(\text{NH}_3)_2]^+$. The deposited $[\text{Ag}(\text{NH}_3)_2]^+$ should be reduced by the electron transfer from the photoexcited MWCNTs. Considered scheme is as follows: $\text{MWCNT} + [\text{Ag}(\text{NH}_3)_2]^+(\text{ad}) + (n)h\nu \rightarrow \text{MWCNT}^+ + \text{Ag}(\text{ad}) + 2\text{NH}_3$. MWCNT^+ will be reduced by abundant OH^- . The produced Ag particles serve as seeds for nucleation. This mechanism is supported by the previous work where DNA-wrapped single walled carbon

nanotubes photoreduced the Ag^+ to form Ag NPs in solution [14]. During the laser irradiation, the change in solution color was not observed for dilute solution, indicating the direct growth of Ag NPs on MWCNTs. In case of the most concentrated solution, when the potential reached the reduction potential of $[\text{Ag}(\text{NH}_3)_2]^+$ (+0.373 V vs. SHE), Ag particles were generated in solution and deposited on the glass to form a silver mirror.

We have developed a facile synthesis of Ag NP/MWCNT composites via a burst nucleation of Ag crystals upon laser irradiation. The MWCNTs were used not only as supports, but also as sensitizers. The method may be applicable for preparation of other metal NP/carbon nanotube composites, though this depends on the reduction potential of the metal ion.

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Figures

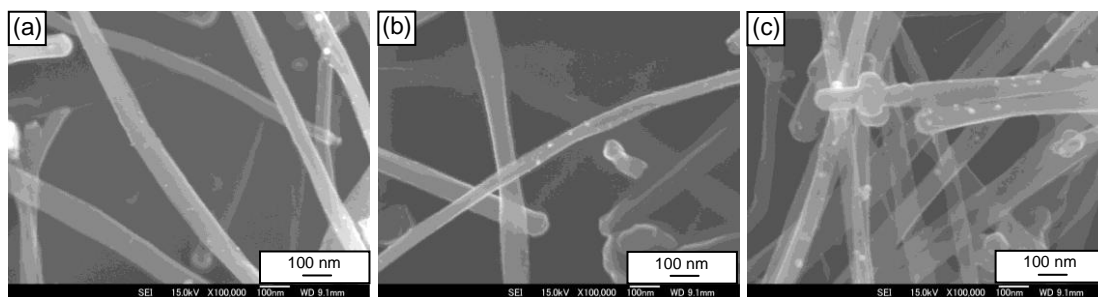


Fig. 1–SEM images of Ag NP/MWCNT composites with different initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentrations: (a) 3.0×10^{-4} , (b) 1.0×10^{-3} and (c) $1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

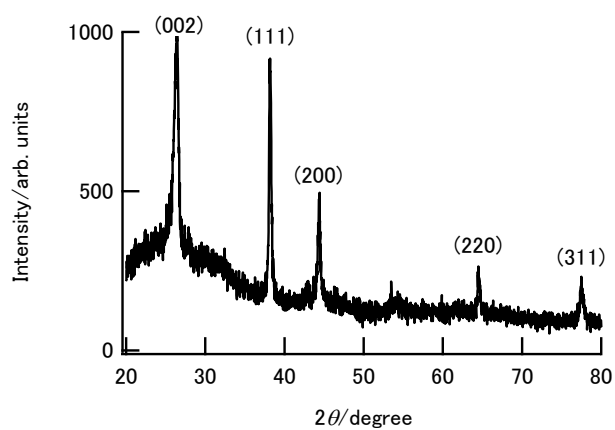


Fig. 2–XRD pattern of the Ag NP/MWCNT composites with initial $[\text{Ag}(\text{NH}_3)_2]^+$ concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$.

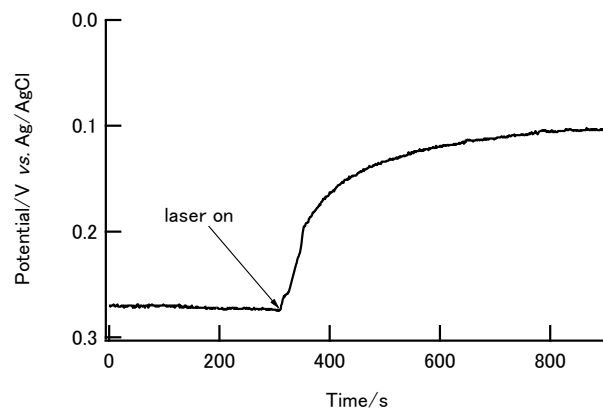


Fig. 3—Change in the rest potential of 1 mg MWCNTs/10 mL aqueous dispersion.