

Ultrasound irradiation induced Ag NP/MWCNT composites preparation

超音波照射による銀ナノ粒子担持多層カーボンナノチューブ
複合体の作製

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1. Introduction

Ultrasound irradiation leads to the cavitation, that is, the formation, growth and collapse of bubbles in the liquid [1]. Caused by the collapse of the bubbles, the liquid microjets and shock waves are generated. They cause the nanoparticles to adhere strongly to the solid surface [2] and/or to penetrate the substrate [3]. Cavitation is also known to create local high pressure and temperature which leads to the particle size reduction [4]. The ultrasound irradiation has been proven to be an effective method for the deposition of nanoparticles onto the CNFs supports [5].

Silver nanoparticle (NP)/carbon nanotube (CNT) composites have attracted much attention due to their potential utility as conducting fillers to make conductive polymers [6], anode materials in lithium-ion batteries [7], sensors of DNA hybridization and electrocatalysts. Several methods have been proposed to prepare these composites, such as electroless plating [8], electrochemical deposition [9], solid-state reaction, chemical deposition [10] and photochemical deposition [11]. During the deposition, aggregation might occur. To obtain highly dispersed nanoparticles on CNTs, a monolayer-grafting method has been proposed.

In this paper, we report the preparation of the Ag NPs highly dispersed MWCNTs composite. We use *N,N*-dimethylformamide (DMF) as a solvent and reducing reagent of Ag ion. Just dissolving of AgNO₃ into DMF brings about the Ag nanoparticle formation. However, nanoparticles continue to grow to the submicrometer size particles and are difficult to stay with nanometer order size. Therefore, it is of great interest to control the diameter of the nanoparticles by the ultrasound irradiation. We compare the effect of ultrasound irradiation on the particle size and deposition amount by following procedures: (1) After grown in DMF, Ag NPs were deposited on MWCNTs without ultrasound irradiation. (2)

Ultrasound irradiation was conducted after the MWCNTs/DMF dispersion was added into the Ag colloid. The surface morphology and the qualitative analysis of the composites were examined.

2. Experimental

A 4.3 mg of AgNO₃ was dissolved in 25 mL of *N,N*-dimethylformamide (DMF, Wako Pure Chemical) to prepare a 1.0×10^{-3} mol dm⁻³ solution. UV-VIS spectra of the solution were measured by UV-VIS spectrophotometer (Shimadzu MultiSpec-1500) to monitor growth of Ag particles. A mass of 2.0 mg of MWCNT (Showa Denko VGCF-S, diameter 80 nm, length 10–20 μm) was dispersed in 20 mL of DMF. After 5 min ultrasound irradiation, the dispersion was mixed with the Ag colloid. The dispersions were sonicated for 0 to 180 min by the ultrasonic cleaner (TGK FU-6H, 38 kHz, 150 W) for procedure 2. The Ag NPs deposited MWCNTs were filtrated using a 0.5 μm pore size membrane filter and rinsed with DMF. The Ag NP/MWCNT composites were dried at 373 K for 2 h. The composites were examined using a field emission-scanning electron microscope (FE-SEM, JEOL JSM-7000F), a transmission electron microscope (TEM, JEOL JEM-2010) and an electron probe micro analyzer (EPMA, Shimadzu EPMA-1610) with analyzing crystals of LIF, PET, RAP and PBST.

3. Results and discussion

Fig. 1 shows time development of the UV-VIS spectra of AgNO₃/DMF solution. For a time range from 0 to 60 min after the dissolving, the absorbance due to Ag plasmon at around 405 nm increased. Through several hours the profile was unchanged indicating the Ag nanoparticles stayed stabilized. The measurement at 11 h showed the peak absorbance slight decrease and the peak wavelength red-shift indicative of size growth of the nanoparticles. Based on the above results, MWCNTs were added to the Ag colloid 90 min

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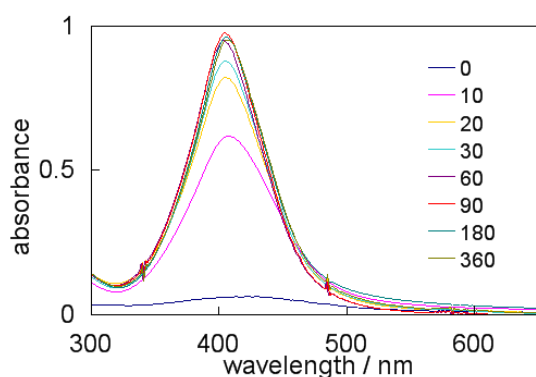


Fig. 1 Changes in UV-VIS spectra of AgNO_3/DMF solution.

after dissolving of AgNO_3 in DMF for procedure 1. As the standing time increased, the diameter of Ag NPs on the MWCNTs surface increased by the FE-SEM measurement. Contrary to this for the Ag NP/MWCNT composites prepared by the procedure 2 it is evident that as the ultrasound irradiation time increased, the particle size became smaller.

Fig. 2 shows the TEM images taken after (a) 0 and (b) 180 min ultrasound irradiation. Without irradiation the particle size is relatively large (20–50 nm) and aggregation between adjacent particles was shown. With irradiation NPs are highly dispersed on the surface and the particle size is measured to be 2–9 nm.

To confirm the NPs to be Ag, EPMA

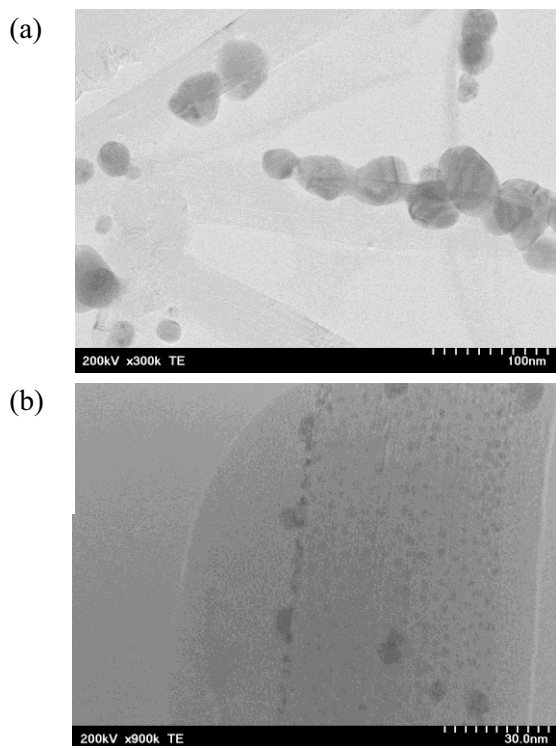


Fig. 2 TEM image of Ag NP/MWCNT composites prepared (a) without and (b) with ultrasound irradiation.

measurements were conducted. The spectra are composed of strong bands at 0.4154 and 4.470 nm attributed to Ag L_α and C K_α transitions, respectively, accompanying other weak bands due to the other transitions of Ag. Elemental composition of the composite was obtained by the EPMA analysis to be 95.5 mol% of C and 4.5 mol% of Ag.

4. Conclusions

In summary, Ag NP well dispersed MWCNT composites have been synthesized by the ultrasound irradiation of the mixture of the Ag colloid and the MWCNTs/DMF dispersion. The obtained Ag NPs are spherical and have a nanometer order size based on the TEM measurements. The composites can be used in catalytic and electric applications. The EPMA measurement confirmed the deposition to be Ag NPs.

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