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Silver nanoparticle assembly on carbon nanotubes triggered by reductive surfactant coating

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ABSTRACT

A conceptually new strategy has been developed for the deposition of Ag nanoparticles (AgNp) on multiwalled carbon nanotubes (MWCNT). The approach was based on the dispersion of MWCNT using cetylpyridinium chloride (CC), reaction with potassium borohydride (KBH_4) and synthesis of uniform cetylpyridinium borohydride (CBH_4) coatings on MWCNT. The CBH_4 coating material provided good suspension stability and served as a reducing agent and a template for controlled Ag^+ reduction and synthesis of AgNp. The AgNp-MWCNT hybrid material showed a high electrocatalytic activity towards the reduction of hydrogen peroxide, which was ascribed to the uniform dispersion of AgNp on MWCNT surface. The method offers a versatile strategy for the synthesis and assembly of other nanomaterials on MWCNT.

1. Introduction

Silver nanoparticles (AgNp) are widely used for various applications due to their catalytic, electrical and antimicrobial properties [1–3]. Many investigations were focused on the development of advanced reducing and capping agents for the synthesis of AgNp [1,2]. Considerable attention has been given to the deposition of AgNp on carbon nanotubes (CNT) [4–6] for catalytic applications. The use of CNT as a support for catalytic AgNp offers the advantages of high surface area and electrical conductivity. It was found that AgNp of controlled size can be formed on the surfaces of pristine and modified CNT [4,7]. The fabrication of AgNp on the CNT surface by chemical reduction of Ag^+ in $AgNO_3$ solutions is an attractive method for the fabrication of AgNp-CNT hybrid materials for catalysis [4].

The fabrication of AgNp-CNT materials requires good dispersion of CNT in the solutions and controlled synthesis of AgNp on the CNT surface [4]. Various techniques have been developed for the dispersion of CNT, such as chemical functionalization and surfactant based methods [8]. Chemical functionalization [9] can damage the CNT structure, leading to reduced mechanical and electrical properties. On the basis of this consideration, many efforts have been made to disperse CNT using ionic surfactants [10,11]. However, relatively high concentration of the surfactants is required for the CNT dispersion [10,11]. It was found that the formation of the surfactant micelles promoted depletion-induced aggregation of CNT [10,11].

The goal of this investigation was the development of AgNp-multiwalled carbon nanotubes (MWCNT) hybrid using a new approach, based on the use of coated MWCNT. The cetylpyridinium borohydride (CBH_4) coating material combined properties of dispersant for MWCNT and reducing agent for Ag^+. We report that CBH_4 coated MWCNT could be used as a template for the synthesis of AgNp on MWCNT. The obtained AgNp-MWCNT hybrid material showed a promising electrocatalytic performance.

2. Experimental procedures

Cetylpyridinium chloride (CC), silver nitrate ($AgNO_3$), potassium borohydride (KBH_4), potassium hydroxide (KOH), Nafion (5 wt% ethanol solution) and hydrogen peroxide (H_2O_2) were purchased from Sigma-Aldrich company. MWCNT was provided by Arkerma company. The proof of concept studies involved the fabrication of stoichiometric CBH_4 material by mixing equimolar solutions of 0.15 M CC and 0.15 M KBH_4. The pH of the mixture was controlled at pH=11 during the reaction using KOH. For the fabrication of CBH_4 coated MWCNT, firstly, a 200 mL of 5 g L^{-1} MWCNT suspension was prepared by adding 0.5 g CC as a dispersant and ultrasonicated for 0.5 h, then 50 mL of 0.15 mM KBH_4 solution (pH=11) was added to the suspension. The reactions were carried out at 4 °C for 20 h. The obtained powders were

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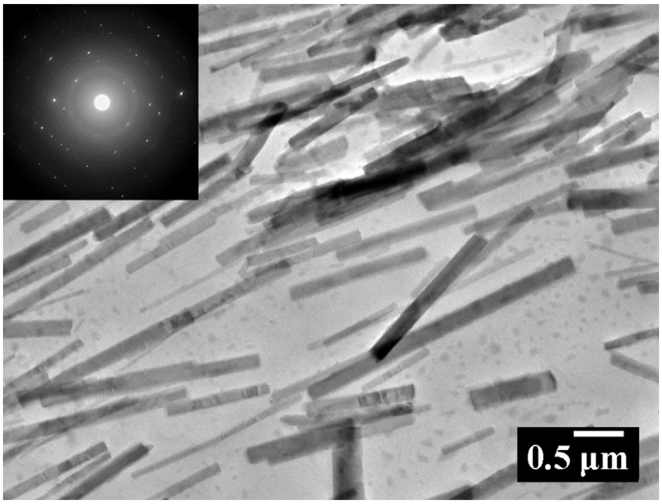

Fig. 1. TEM image with selected-area electron diffraction pattern (inset) of CBH_4 nano-crystals.

washed with deionized water and collected using vacuum filtration process. CBH_4 coated MWCNT were dispersed in water and formed a stable suspension. AgNp-MWCNT were prepared by adding 50 mL of 0.03 mM $AgNO_3$ solution to 50 mL of 5 g L^{-1} CBH_4 coated MWCNT. The reaction was performed at 4 °C for 20 h.

The obtained materials were studied by the X-ray diffraction (XRD) method, using powder diffractometer (Nicolet I2, monochromatized CuK-α radiation). The microstructure was investigated using JEOL JSM-7000 F scanning electron microscope (SEM). Transmission electron microscopy was conducted using a FEI Tecnai Osiris TEM. High angle annular dark field (HAADF) microscopy with ChemiSTEM energy dispersive X-ray (EDX) spectroscopy was used for the chemical analysis. Cyclic voltammetry(CV) was performed using a potentiostat (PARSTAT 2273, Princeton Applied Research). The CV studies were conducted using a conventional three-electrode cell, which included a platinum gauze as the counter electrode, standard calomel electrode (SCE) as the reference electrode and a bare or modified glassy carbon electrode (GCE) as the working electrode. The modified GCE was fabricated by drop-casting 2 µL of a suspension, containing 5 mg L^{-1} AgNp-MWCNT in Nafion solution. The electrochemical tests were performed in 20 mM $K_4[Fe(CN)_6]$ and 0.2 M phosphate buffer solution (PBS, pH 7.0) in the absence and presence of H_2O_2 as the electrolyte.

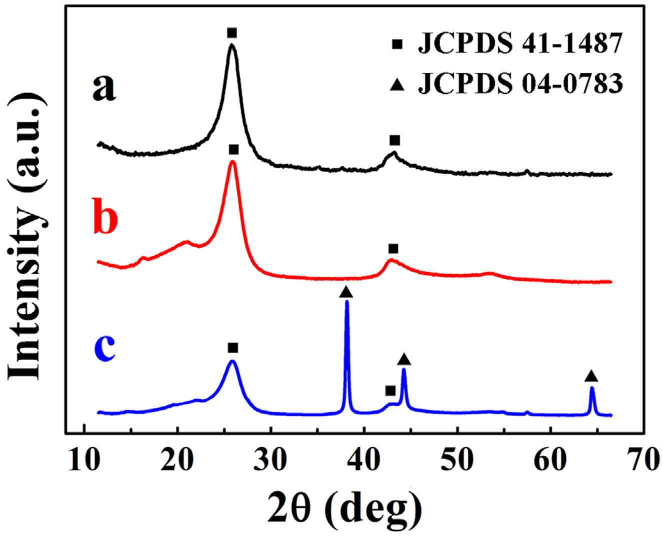

Fig. 3. X-ray diffraction patterns of (a) MWCNT, (b) CBH_4 coated MWCNT and (c) AgNp-MWCNT.

3. Results and discussion

Our strategy involved two major steps: the fabrication of CBH_4 coated MWCNT and their use as a template for the controlled synthesis of AgNp-MWCNT hybrid material. In the proof of concept studies we found that CBH_4 can be formed by a chemical precipitation by mixing CC and KBH_4 solutions in a molar ratio of 1:1. Fig. 1 shows a TEM image of the precipitated material, which mainly contained rod-like particles with a typical diameter of 0.1–0.3 µm and length of 1–5 µm. In addition to the rod-like particles, the precipitate contained small amount of nanoparticles with the typical size in the range of 30–100 nm. The electron diffraction studies revealed that the CBH_4 material was crystalline (Fig. 1, inset). The CBH_4 powder was added to the $AgNO_3$ solution and the formation of AgNp with particles size of 2–40 nm was observed as a result of Ag^+ reduction (Fig. S1, Supporting information). Therefore, CBH_4 can be used as a reducing agent for the fabrication of AgNp. These results paved the way for the fabrication of CBH_4 coatings on MWCNT.

The procedure for the fabrication of CBH_4 coated MWCNT involved the dispersion of MWCNT in water using CC surfactant, which adsorbed on MWCNT and allowed for the electrosteric dispersion. The addition of KBH_4 resulted in the reaction of the

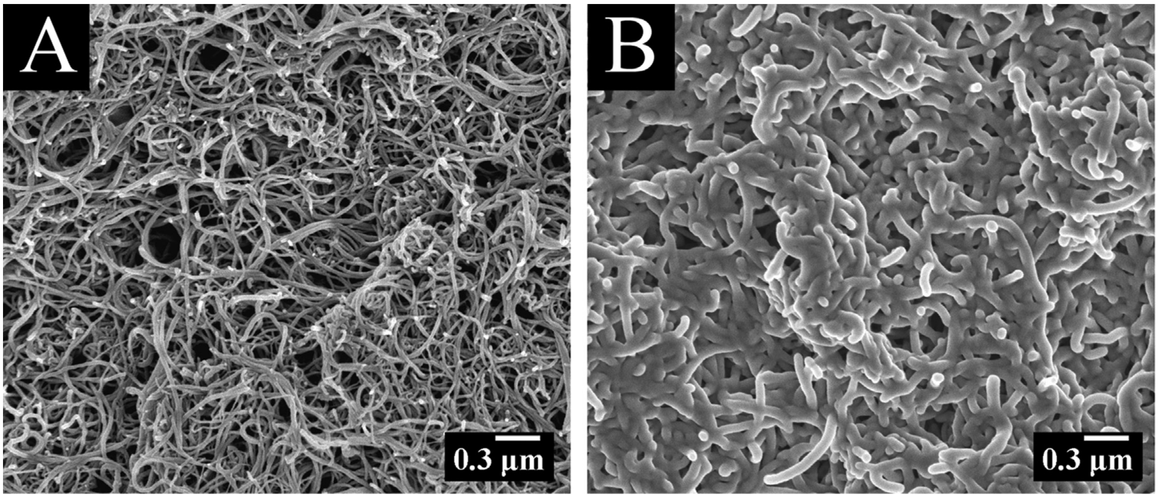

Fig. 2. SEM images of (A) pristine MWCNT and (B) CBH_4 coated MWCNT.