Research Article

A Facile Strategy for the Functionalization of Boron Nitride Nanotubes with Pd Nanoparticles

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A facile *in situ* fabrication of palladium nanoparticles decorated boron nitride nanotubes (Pd-BNNTs) is described. The decoration of BNNTs was carried out by the self-regulated reduction of palladium chloride (PdCl_2) with the aid of sodium dodecyl sulfate (SDS). During the preparation process, the surfactant SDS plays a dual role: it aids the dispersibility of BNNTs and produces the reductant of $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$. Then the $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ can reduce Pd^{2+} to form Pd nanoparticles on the surface of BNNTs. The as-prepared Pd-BNNTs were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray energy dispersive spectroscopy, and Fourier transform infrared spectroscopy. The results show that the Pd nanocrystalline particles can be deposited onto the BNNTs surface *via* this simple route. This approach constitutes a basis for the assembly and integration of nanoscale materials onto BNNTs and puts a light on the potential application of the BNNTs in electronic, catalysis, and hydrogen storage fields.

1. Introduction

Boron nitride nanotubes (BNNTs) have recently attracted increased attention due to their various potential applications in electronic, mechanical, and optical devices. Structurally similar to carbon nanotubes (CNTs), BNNTs exhibit excellent mechanical [1–3] and thermal [4–6] properties. Despite these similarities, BNNTs exhibit excellent chemical stability and high resistance to oxidation at high temperature [7]. BNNTs are uniform semiconductors with a bandgap of 5.5 eV, basically independent of tube chirality and diameters [8], while CNTs exhibit variable metallic and semiconducting characteristics. In addition, recent research has also demonstrated that BNNTs can be used as room temperature hydrogen storage media [9], humidity sensor devices [10], and oil/water separation materials [11]. Considering the above-mentioned properties, BNNTs have become very attractive for innovative applications in various fields of science and technology, especially in hazardous and high temperature environments. However, the insolubility in common solvents and good insulating property also limit their applications. Further modification of BNNTs is therefore necessary for

the utilization of BNNT-based materials for novel sensory, electronic, catalytic, and biomedical applications. For example, the multiwalled BNNTs modified with long alkyl chains are soluble in many organic solvents [12]. And subsequent cathodoluminescence and UV-Vis absorption tests show that long alkyl chains can induce drastic changes in the band structure of BNNTs [12]. The Au decoration on the surface of BNNTs significantly enhanced their field emission current densities [13]. Additionally, the introduction of rare-earth element into the walls of BNNTs can result in broad and tunable light emission [14, 15], making them a potential candidate in nanosized lighting sources and nanospectroscopy. Yet it is difficult to directly decorate the BNNTs with metal nanoparticles by chemical route due to the good chemical inertness of the BNNTs. At present, the synthesis of metal nanoparticles decorated BNNTs is mainly realized by physical vapour deposition (PVD) [13] or a complicated chemical route [16]. Although metal nanoparticles with uniform size can be obtained by PVD, the deposition only occurs on the top surface of bulk BNNTs samples facing the metal target. And, for previous chemical route, the surface of the BNNTs and metal nanoparticles needs to be functionalized with

organic molecules, which is fairly complicated. Therefore, simpler and effective methods are required to prepare these metal nanoparticles decorated BNNTs.

In this work, a facile *in situ* preparation of Pd-BNNTs is developed. The process was carried out by self-regulated reduction of PdCl_2 with the aid of SDS. The method provides a basis for the assembly and integration of nanoscale materials onto the BNNTs. In addition, Pd is an important transition metal in catalysis due to their high hydrogen solubility, diffusivity, and corrosion resistance [17, 18] and it can also be used as hydrogen storage media [19] for its high affinity for hydrogen. That is, the introduction of Pd may improve the catalytic activity and hydrogen adsorption property of the BNNTs, making them potential candidate in these fields.

2. Experimental Procedure

The BNNTs were synthesized by a ball milling and subsequent high temperature annealing process [13–15]. Typically, the amorphous boron powder was first milled in a planetary mill with a stainless steel bowl and several balls for 50 h at a rotation speed of 300 rpm. The weight ratio of the milling balls to the boron powder was 50 : 1. Then, the milled boron powder was annealed in a tube furnace at 1100°C for 2 h under a H_2/N_2 (15% H_2) gas flow (100 mL/min). Then, 0.5 mg of as-synthesized BNNTs was suspended in 2 mL of 0.05 M aqueous SDS solution and ultrasonicated for 30 min. Subsequently, 1 mL of PdCl_2 saturated solution (20°C) was added to the BNNTs/SDS dispersion and the mixture was refluxed for 6 h at $130 \pm 1^\circ\text{C}$. After cooling down to room temperature naturally, the reaction mixture was filtered with $0.45\ \mu\text{m}$ membrane filter, washed several times with distilled water to remove the excess surfactant, and then redissolved in ethanol.

Zeiss UltraPlus analytical field emission scanning electron microscopy (FESEM) was used for morphology investigation. X-ray energy dispersive spectroscopy (EDS) attached to the Zeiss UltraPlus analytical FESEM was used to examine the components. Philips CM300 high-resolution transmission electron microscopy (HRTEM) was employed to probe the interior construction of the as-prepared BNNTs and Pd-BNNTs. The X-ray diffraction spectrum was collected with BRUKER-AXS X-ray diffractometer (XRD) with monochromatic $\text{Cu K}\alpha$ radiation. The bonding information of BNNTs was identified with PerkinElmer Fourier transform infrared spectroscopy (FTIR).

3. Results and Discussion

As shown in Figure 1(a), the typical XRD pattern of the as-prepared BNNTs shows three peaks (marked with black rhombus “ $\blacklozenge$ ”) at the d-spacing of 3.36, 2.15, and 2.06 which can be assigned to (002), (100), and (101) planes of hexagonal boron nitride structure (JCPDF card number 73-2095) [20]. The rest peak marked with hollow rhombus “ $\diamond$ ” can be identified as (110) plane of α -Fe, which was introduced in the ball milling process and used as catalyst in the BNNTs growth process. In addition, two IR absorption regions can

be obviously distinguished at $805\ \text{cm}^{-1}$ and $1385\ \text{cm}^{-1}$ in the FTIR spectrum (Figure 1(b)), corresponding to the out-of-plane radial buckling (R) mode where boron and nitrogen atoms are moving radially inward or outward and transverse optical (TO) mode of h-BN sheets that vibrate along the longitudinal or tube axis of BNNTs, respectively [21, 22]. Figures 1(c) and 1(d) show the typical FESEM and TEM images and EDS spectrum of the as-prepared BNNTs. The FESEM image (Figure 1(c)) reveals that pure products were formed on the sample surfaces, which possess a high density of one-dimensional structures with relatively uniform diameters in the range of 100–300 nm. The inset EDS spectrum confirms that the main components composed of the nanotubes are boron and nitride. Further examination carried out by TEM analysis (Figure 1(d)) indicates that the BNNTs are formed by repeated cup-like structures with void interior. The intrinsic plane spacing of the walls is determined to be 0.34 nm in terms of the HRTEM images (inset in Figure 1(d)), which is well matched with that of h-BN (002) plane.

As described in Figure 2, the *in situ* decoration of BNNTs with Pd nanoparticles is realized by refluxing a dispersion of BNNTs in an aqueous solution of SDS/ PdCl_2 for 6 h (details can be seen in Experimental Procedure section). During the whole preparation process, the surfactant SDS plays a dual role. Firstly, as the surfactant, a great deal of SDS molecules will be absorbed on the surface of the BNNTs thus aiding the dispersion of BNNTs in water as shown in Figure 2. Secondly, SDS acts as a reactant to participate in the oxidation-reduction reaction. During the reflux process, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ was generated by the reaction of SDS with H_2O (reaction (1) in Figure 3), and then the Pd^{2+} ions that had diffused into the core of the micelle were reduced by the $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ to form Pd atoms (reaction (2) in Figure 3) [23]. With the increase in the reduced Pd atoms, they agglomerated together on the BNNTs' surface to form Pd nanoparticles. After separating and carefully rinsing, the residual organic was removed and Pd-BNNTs were achieved. Figure 4(a) shows a typical SEM image of the Pd nanoparticles decorated BNNT, where Pd nanoparticles can be clearly seen attached on the surface of BNNT. EDS analysis (inset in Figure 4(a)) confirmed that the attached nanoparticles are indeed palladium. Figures 4(b) and 4(c) present the TEM micrographs of pristine and Pd nanoparticles decorated BNNTs, respectively. Comparing Figure 4(c) with Figure 4(b), the dark spots particles can be clearly seen on the surface of Pd nanoparticles decorated BNNT. Inset in Figure 4(c) is a typical HRTEM image of the Pd nanoparticles attached on the surface of BNNTs. The lattice constant of the nanoparticles is calculated to be 0.197 nm, which is the same as the (200) plane distance of the cubic Pd crystal structure [24], demonstrating that the Pd nanoparticles are successfully deposited on the surface of the BNNTs.

4. Conclusions

It has been demonstrated that Pd-BNNTs can be prepared by the self-regulated reduction of PdCl_2 with the aid of SDS.

FIGURE 1: (a) The XRD pattern and (b) the FTIR spectrum of the BNNTs; (c) and (d) the FESEM image (inset is the EDS spectrum) and the TEM image (inset is the HRTEM image) of the as-synthesized BNNTs.

FIGURE 2: The process for the decoration of BNNTs with Pd nanoparticles.

FIGURE 3: The reactions during the reflux process.

FIGURE 4: (a) FESEM image of the Pd-BNNTs (inset is the corresponding EDS spectrum); (b) and (c) the typical TEM images of pristine BNNTs and BNNTs with Pd nanoparticles (inset is the HRTEM image).

During the preparation process, the surfactant SDS plays a very important role in the dispersibility of BNNTs and reduction of Pd^{2+} to form Pd nanoparticles. The characterization results indicate that Pd nanocrystalline particles can be successfully deposited on the BNNTs surface *via* this simple wet chemical route, which constitutes a basis for the assembly and integration of nanoscale materials onto the BNNTs. The good activity catalysis of Pd combined with the excellent properties of BNNTs may make the Pd-BNNTs be potential candidate in the application of electronic and catalysis fields.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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