Fabrication of metal nanoparticles on highly dispersed pristine carbon nanotubes

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A convenient approach to fabricate metal (i.e. gold, platinum, and palladium) nanoparticles on highly dispersed pristine carbon nanotubes (CNTs) was developed using a conjugated block copolymer of poly(3-hexylthiophene)-b-poly(vinylpyrrolidone) (P3HT-b-PVP). P3HT-b-PVP not only provides a stable dispersion of pristine CNTs through the π–π interactions between P3HT block and CNTs, but also introduces PVP groups on CNT surfaces to induce the heterogeneous nucleation of metal nanoparticles and protect them from aggregating. The density of metal nanoparticles on CNT surfaces was controlled by the metal salt/CNT feed ratio. The simple processing procedure, versatility in synthesizing various metal nanoparticles, high metal nanoparticle loading capacity, and excellent dispersibility and processability of the product make this approach a promising method to fabricate metal nanoparticles on CNTs.

Keywords: metal nanoparticle; carbon nanotube; composite

1. Introduction

Carbon nanotubes (CNTs) possess numerous attractive properties, including large surface area [1], excellent mechanical properties [2,3], high thermal and electrical conductivities [4,5] and extraordinary chemical and thermal stability [6–9]. All these properties make CNTs ideal candidates as support materials, enabling the production of CNT-supported nanoparticle systems with extensive applications in energy storage devices, including supercapacitors [10–14], and power generation devices such as fuel cells [15–18]. In addition, CNT-supported metal nanoparticles have been widely used in heterogeneous catalytic systems [19–21], electrochemical sensors [22,23], hydrogen storage absorbents [24] and surface-enhanced Raman scattering substrates [25]. To fabricate CNT-supported metal nanoparticles, various approaches including electron beam deposition [26,27] electroless/electrochemical deposition [28,29], chemical deposition [30] and physical absorption [31–33] have been investigated. However, some of these approaches involve time-consuming invasive treatments of CNTs, which deteriorates their electrical and mechanical properties. Therefore, convenient approaches to fabricate highly processable pristine CNT-supported metal nanoparticles are highly desirable. Recently, we developed a non-invasive approach to disperse and functionalize pristine CNTs in one step using conjugated block copolymers [34–36]. The conjugated block copolymer contains...
two blocks, a conjugated block of poly(3-hexylthiophene) (P3HT) and a functional non-conjugated block. By sonicating pristine CNTs with the block copolymers, the P3HT block bonds to the CNT surface through non-covalent \( \pi-\pi \) interactions, and stabilizes the de-bundled CNTs in the dispersion. The functional non-conjugated block is located at the outer surface of the CNTs, and provides the desired functionalities. By varying the composition of the functional block, dispersed pristine CNTs with different functionalities and applications were obtained [36]. Such conjugated block copolymer/CNT systems are expected to offer a non-invasive approach to produce metal nanoparticles on CNT surfaces, providing ideal supports for metal nanoparticles combined with the high processability and superior properties of the pristine CNTs. To synthesize metal nanoparticles onto CNT surfaces, the functional block is required to possess high affinity to the metal nanoparticles in order to induce the heterogeneous nucleation of metal nanoparticle on CNT surface. Poly(vinylpyrrolidone) (PVP), with its high affinity to various metal nanoparticles, has been applied to stabilize fine nanoparticles [37–40]. In this study, a conjugated block copolymer of poly(3-hexylthiophene)-b-poly(vinylpyrrolidone) (P3HT-b-PVP) was synthesized and used to disperse multi-walled carbon nanotubes (MWCNTs). The resulting P3HT-b-PVP-dispersed MWCNTs were employed as the support for various metal nanoparticles, including gold nanoparticles (AuNPs), platinum nanoparticles (PtNPs) and palladium nanoparticles (PdNPs).

2. Experimental section

MWCNTs with a diameter of 10–20 nm and a length of 5–20 \( \mu \)m were purchased from Nanolab (Newton, MA). Chloroauric acid (HAuCl\(_4\)), chloroplatinic acid (HPtCl\(_6\)), and ammonium tetrachloropalladate(II) ((NH\(_4\))\(_2\)PdCl\(_4\)) were obtained from Strem Chemical Inc. (Newburyport, MA). Sodium borohydride was purchased from Sigma-Aldrich (St. Louis, MO). All chemicals and materials were used as received.

P3HT-b-PVP (Scheme 1) was synthesized through a reversible addition-fragmentation chain transfer (RAFT) polymerization of 1-vinyl-2-pyrrolidinone using P3HT thio-carbonate compound [41] as the macroinitiator. P3HT thio-carbonate compound (0.1 g, 0.013 mmol), 1-vinyl-2-pyrrolidinone (1 g, 9 mmol), trichlorobenzene (3 ml), \( N,N \)-dimethylformamide (DMF, 3 ml), and azobisisobutyronitrile (AIBN, 1.2 mg, 0.007 mmol) were mixed in a 25 ml flask. After being degassed by three cycles of freeze-pump-thaw, the polymerization was carried out at 90\(^\circ\)C. The product was precipitated in methanol three times and then dried under vacuum at 60\(^\circ\)C. \(^1\)H NMR (CDCl\(_3\)): 6.98 (s, 4\(^{\prime}\) proton on thio- phene), 3.0–3.4 (s, \( CH_2-N-C=O \)), 2.78 (s, thiophene-\( CH_2\)). The molecular weight of P3HT-b-PVP was determined by gel permeation chromatography (GPC, \( M_n \), polystyrene standard) to be 11,200 with the polydispersity of 1.4, and the composition was estimated by \(^1\)H NMR to contain 54.8 wt % and 45.2 wt % of P3HT and PVP, respectively.

Scheme 1 illustrates the procedure for synthesis of metal nanoparticles on pristine MWCNTs. A typical process is described as following. Pristine MWCNTs (5 mg) were dispersed by P3HT-b-PVP (10 mg) in chloroform (10 ml) with 30 min sonication with the water bath temperature maintained at 18–20\(^\circ\)C. The excess P3HT-b-PVP in the dispersion was eliminated by centrifuging and re-dispersing in 10 ml chloroform. After diluting with 30 ml methanol, the dispersion was incubated with HAuCl\(_4\) (10 mg) for 2 h; PVP forms a complex with AuCl\(_4^-\) via coordinative bonding [42]. Freshly prepared NaBH\(_4\) methanol solution was then added to the dispersion to reduce AuCl\(_4^-\) to AuNPs. After being purified for three cycles of centrifugation and redispersion, the AuNP/MWCNT was finally dispersed in methanol with a brief sonication.
Scheme 1. Procedure for synthesis of metal nanoparticles on pristine CNTs and the chemical structure of P3HT-b-PVP.

The morphology of the metal nanoparticle on MWCNTs was investigated by transmission electron microscopy (TEM, JEOL 1011). UV–visible measurements were carried out on a Cary 300 UV–visible spectrophotometer. An X-ray photoelectron spectroscopy (XPS) investigation was conducted on a VG ESCALAB 220i XPS system.

3. Results and discussion

According to the mechanism of dispersing CNTs by conjugated block copolymers [34–36], when P3HT-b-PVP is sonicated with MWCNTs in chloroform, the P3HT block attaches to the CNT surface through $\pi-\pi$ interactions, and the PVP block is located at the outer surface of the MWCNTs. The PVP plays a key role in fabricating AuNPs on MWCNT surfaces. First, by forming the complex with $\text{AuCl}_4^-$, the PVP induces the heterogeneous nucleation of AuNPs on the MWCNT surface. Second, the PVP stabilizes the formed AuNPs, and prevents them from aggregating [37–40]. In our experiment, some free AuNPs also formed in the dispersion by homogeneous nucleation. They were removed by three cycles of centrifugation and redispersion. The AuNPs on MWCNTs were investigated by TEM. As shown in Figure 1a, the sample prepared with HAuCl$_4$ to MWCNT weight ratio of 2:1 shows uniform distribution of AuNPs on the MWCNT surface and no free AuNPs were observed. The particle size was characterized to be 2.9±1.1 nm (statistical result from more than 200 AuNPs).

To investigate the influence of HAuCl$_4$ to MWCNT feed ratio on the product properties, two samples with the HAuCl$_4$ to MWCNT feed ratios of 4:1 and 6:1 were synthesized. Their TEM images (Figures 1b and 1c) indicate that, with increasing HAuCl$_4$ feed ratio, the density of AuNPs on MWCNT increases. The increasing AuNP density was also verified by the UV–visible spectra. Three MWCNT/AuNP samples with HAuCl$_4$ to MWCNT feed ratios of 2:1, 4:1 and 6:1 were prepared to have the same concentration of MWCNT by equalizing their absorption intensity at 800 nm since AuNPs do not have absorption at 800 nm [43]. As shown in Figure 2, the absorption around 500 nm assigned to AuNPs [43] increases with increasing HAuCl$_4$ feed ratio, signifying increasing density of AuNPs on the MWCNTs. TEM images of the three samples also indicate that the
size of AuNPs size was influenced by the HAuCl₄ to MWCNT feed ratio. As shown in Figure 1d, 2:1 and 4:1 particles samples have a size of ∼3 nm with a narrow size distribution, whereas the size of the 6:1 sample increases dramatically to ∼7 nm with a broadening of the particles size distribution. The increase of AuNP size was also indicated in the UV–visible spectra; 2:1 and 4:1 samples show the AuNP absorption at 489 nm, whereas the absorption of 6:1 sample red shifts to 499 nm, indicating the increased AuNP
particle size. The increasing particle size with the increment of HAuCl₄ to MWCNT feed ratio is due to the limited number of PVP nucleation sites on MWCNT surface. When the excess amount of HAuCl₄ is reduced, the reduced gold atoms, instead of forming new particles, will grow on the already formed AuNPs to increase the particle size. We assume that, by increasing the PVP content on the MWCNT surface to increase the nucleation site for AuNPs, AuNPs with small particle size can be fabricated at high HAuCl₄ feed ratio. To prove this hypothesis, we synthesized another P3HT-b-PVP block copolymer with same P3HT RAFT reagent but longer PVP block. The molecular weight was determined to be 15,800, and the composition was estimated to contain 35.7 wt % and 64.3 wt % of P3HT and PVP, respectively. When this P3HT-b-PVP was applied to mediate the synthesis of AuNPs on MWCNT surface with the HAuCl₄ to MWCNT ratio of 6:1, uniform densely grafted AuNPs with a particle size of ∼3 nm formed on the MWCNT surface (Figure 1e).

The density of AuNPs on the MWCNT surface was further analyzed quantitatively by XPS. Figure 3 shows the survey spectrum of the 6:1 sample, which clearly reveals the signals of C 1s and Au 4f. By comparing the normalized area of Au 4f and C 1s, the Au/C ratio of the samples with HAuCl₄ to MWCNT feed ratios of 2:1, 4:1, and 6:1 were characterized to be 0.72:1, 1.53:1, and 2.07:1, respectively. These XPS results show lower Au/C ratios than the theoretical values of 0.98:1, 1.96:1, and 2.94:1 calculated from the reactants weight ratio. The deviation from the theoretical value is attributed to the purification step during which free AuNPs are removed. These results demonstrate that uniform AuNPs can be fabricated on MWCNTs with controlled density up to two times the weight of MWCNTs.

Since PVP has a high affinity to various metal nanoparticles, such as AuNPs [44], PtNPs [45] and PdNPs [46], other metal nanoparticles besides AuNPs can also be fabricated on P3HT-b-PVP-dispersed MWCNT surfaces. Using the same fabrication procedure as for AuNP/MWCNT, PtNP/MWCNT and PdNP/MWCNT (incubation time of 24 h required to form the complex of PVP with (NH₄)₂PdCl₄) were also synthesized. As shown in Figures 4a and 4b, PtNPs and PdNPs on MWCNT surfaces have a similar particle size. The PtNPs particle size was in the range 1.1–2.2 nm, which is substantially smaller than that of AuNPs, whereas PdNPs had a comparable particle size of 2.4–4.2 nm. All these
results indicate that our approach is versatile to fabricate various metal nanoparticles on MWCNTs.

In contrast to other reported pristine CNT/metal nanoparticle composites, which are insoluble in solvents and unprocessable, fabricating metal nanoparticles on P3HT-\(b\)-PVP-dispersed MWCNTs is a versatile and convenient method that leads to highly processable products. As shown in the inset of Figure 2, the AuNPs on MWCNTs are highly dispersible in methanol, making them suitable for various applications. Additionally, the metal nanoparticle/MWCNT composites are robust. As shown in Figure 5, no detachment of nanoparticles from MWCNTs was observed after the metal nanoparticle/MWCNT was sonicated for 30 min.

4. Conclusions

Various metal (i.e. gold, platinum, and palladium) nanoparticles were synthesized on pristine MWCNTs mediated by P3HT-\(b\)-PVP. P3HT-\(b\)-PVP not only provides a stable suspension of pristine MWCNTs in solvents through the \(\pi-\pi\) interactions between P3HT and CNTs, but also introduces PVP on the CNT surface for the subsequent metal nanoparticle
Figure 5. A TEM image of AuNP on MWCNTs (2:1) after being sonicated for 30 min.

fabrication. P3HT-\textit{b}-PVP-dispersed CNTs can support and stabilize various metal nanoparticles with $\sim$3 nm diameter as high as twice of their own weight. This approach provides a non-invasive and versatile method to fabricate metal nanoparticles on pristine CNTs with undisrupted electrical and mechanical properties. The processability of the obtained products, such as high dispersity in methanol, overcomes one of the major challenges for the applications of CNT-supported metal nanoparticles.

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