

In Situ Synthesis and Characterization of Multiwalled Carbon Nanotube/Au Nanoparticle Composite Materials

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An effective and facile in situ reduction approach for the fabrication of carbon nanotube-supported Au nanoparticle (CNT/Au NP) composite nanomaterials is demonstrated in this article. Linear polyethyleneimine (PEI) is ingeniously used as both a functionalizing agent for the multiwalled carbon nanotubes (MWNTs) and a reducing agent for the formation of Au NPs. This method involves a simple mixing process followed by a mild heating process. This approach does not need the exhaustive surface oxidation process of CNTs. The coverage of Au NPs on CNTs is tunable by varying the experimental parameters, such as the initial molar ratio of PEI to HAuCl₄, the relative concentration of PEI and HAuCl₄ to MWNTs, and the temperature and duration of the heat treatment. More importantly, even the heterogeneous CNT/Au composite nanowires are obtainable through this method. TEM, XPS, and XRD are all used to characterize the CNT/Au composite materials. In addition, the optical and electrocatalytic properties are investigated.

Introduction

Recently, functionalized carbon nanotubes (CNTs) have been of great interest because of their potential applications in creating next generation electronic devices and networks.¹ To optimize the potential applications of CNTs, it is essential to modify the CNTs with functional groups to integrate the CNTs into desired structures or attach suitable nanostructures on the nanotubes.^{2–10} Among them, metal–nanotube interactions are especially attractive for the development of low-resistance ohmic contacts to these structures.¹¹ The attachment of gold NPs to CNTs' sidewalls is particularly promising for novel, highly efficient photoelectrochemical cells and sensor devices. The gold or platinum nanoparticles (NPs) attached CNTs are primarily based on the self-assembly of NPs on the prefunctioned CNTs by polyelectrolytes^{5,12,13} and DNA.¹⁴ Besides, assemblies of CNTs and gold NPs have been reported by virtue of hydrophobic and hydrogen bonding interactions and electrostatic interactions as well as by the formation of pseudorotaxane.^{8,12,15–18} Although the attachment of NPs on CNTs has been extensively studied, most of the methods involve a tedious assembly process and usually require multistep reactions. Furthermore, the amount of NPs loaded on CNTs by assembly is greatly limited, and this fact limits many practical applications.¹⁹ Up to the present, the investigation of direct chemical synthesis of CNT/metal N composites is mainly concentrated on the CNT/Pt catalysts,^{20–22} which are fabricated by reduction of K₂PtCl₄ in the presence of ethylene glycol and are based on prior oxidation of MWNTs. In all of these articles, the extensive oxidization treatment of CNTs is prerequisite. To our knowledge, the one-step attachment of gold NPs onto unoxidized CNTs with high NP coverage has been rarely reported.

In recent years, polyethyleneimine (PEI), an amino-rich cationic polyelectrolyte, has been known to effectively interact with CNTs via physisorption on the CNTs' sidewalls^{23–28} and has been demonstrated to cause significant changes in the

electrical conductance of *sem*-SWNT.^{24,29–31} More recently, linear PEI has been used both as reducing agent and protecting agent for preparation of gold NPs and gold nanoplates.³² Combining the two functions of PEI, one can prepare CNT/Au NP composites through in-situ reduction of HAuCl₄ by PEI adsorbed on the sidewalls of CNTs.

In this article, we report a simple in situ chemical reduction route to coat MWNTs with controllable coverage of gold NPs. This approach involves noncovalent functionalization of purified MWNTs with PEI and in situ reduction of HAuCl₄ without the additional step of introducing other reducing agents and oxidizing of MWNTs. The novel method is expected to be applicable for preparation of other metal/CNT composites and finds use in applications for electronic nanodevices.

Experimental Section

Reagents. PEI ($M_n = 423$) and HAuCl₄·3H₂O were all purchased from Aldrich and were used as received without further purification. MWNTs (95% purity, Nanotech Port Ltd. Co. Shenzhen, China) were purified using literature techniques.^{2,33} Ultrapure water purified with Milli-Q plus system (Millipore Co.) was exclusively used in all aqueous solutions and rinsing procedures. Its resistivity was over 18 MΩ·cm.

Synthesis of CNT/Au NP Composites. The purified MWNTs (0.4 mg) were dispersed in 15 mL water with the help of ultrasonic treatment. Eight samples 1–8 were prepared according to the following procedure: First, 1.5 mL as-prepared MWNT solution was placed in a vial, followed by addition of various amounts of 1.0 M PEI aqueous solution. They were thoroughly mixed by a combination of vigorous stirring and sonication. To the eight respective mixed solutions, 0.2 mL of HAuCl₄ (24.3 mM) with initial molar ratios of 400:1, 200:1, 98:1, 40:1, 9.8:1, 8:1, 4:1, and 2:1 of PEI to gold (repeating unit) (corresponding to samples 1–8, respectively) was added. Another sample (sample 9) was prepared by doubling the concentration of PEI and HAuCl₄ in sample 4 with the molar ratio of PEI to HAuCl₄ unchanged. All the resulting solutions

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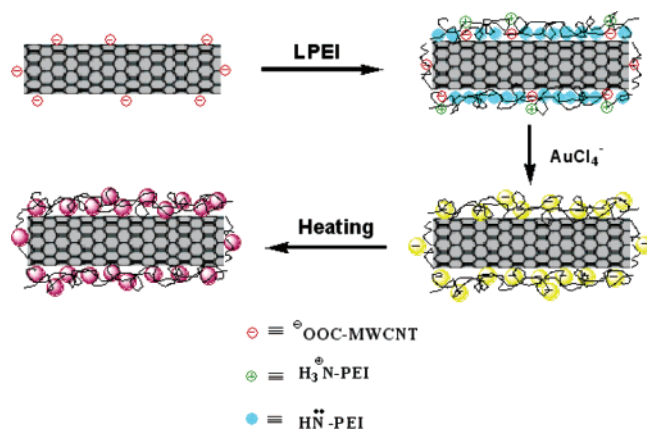


Figure 1. Schematic illustration of the experimental procedure in which PEI possibly interacts with acid-functionalized MWNTs through electrostatic interaction and physisorption process.

were heated at 60 °C for 20 min. After washing and centrifugation for two cycles, the resulted products were dispersed in 1 mL water, respectively. As for the higher temperature reaction, the mixed solution was put into an autoclave and was heated in an oven.

Preparation of the CNT/Au NP Composites Modified Electrode. One-and-a-half milliliters of the as-prepared CNT/Au NP composite solution was centrifuged and washed with water twice, followed by dispersion in 0.5 mL water with the aid of ultrasonic agitation. The glassy carbon (GC) electrode was carefully polished with 1.0 and 0.3 μm $\alpha\text{-Al}_2\text{O}_3$ powders successively and then was cleaned ultrasonically in water for a few minutes. The clean GC electrode was coated by casting a suspension (15 μL) of the CNT/Au NP composites in water and was dried in air for more than 12 h. The modified electrode was then thoroughly rinsed and scanned in 0.1 M H_2SO_4 in the range of -0.4 to 0.2 V.

Instrumentations. TEM measurements were made on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. Optical spectra were acquired using a Cary 500 UV–visible NTR spectrometer (Varian, United States). XRD analysis of the resulting precipitates was carried out on a D/MAX 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation. XPS measurements were conducted with an ESCLAB MK II spectrometer (VG Co.) with Mg KR radiation as the X-ray source. Electrochemical experiments were performed with a CHI 660 electrochemical workstation in a conventional three-electrode electrochemical cell using GCE (3-mm diameter) as the working electrode, Pt foil as the auxiliary electrode, and Ag/AgCl as a reference electrode.

Results and Discussions

Figure 1 represents the schematic procedure of the preparation of CNT/Au NP composites. Purified MWNTs are slightly coated by a small quantity of carboxylic groups. Cationic PEI is coated onto MWNTs by virtue of electrostatic interaction. More importantly, it has been reported that amines possess high affinity for physisorption along the CNTs' sidewalls.^{23–31} So, in this article, the driving force involved in the functionalization of PEI on CNTs' sidewalls is a combination of the electrostatic interaction between the oppositely charged CNTs and the PEI and the physisorption process which is analogous to the polymer wrapping process.^{8,34} PEI has a high density of imino- groups, which can serve as primers for the adsorption of anionic AuCl_4^- followed by reduction of AuCl_4^- .³² By combination of the multifunctions of PEI, the attachment of gold particles on the

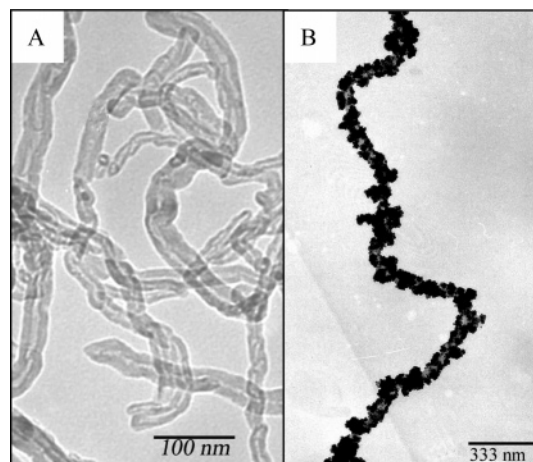


Figure 2. Typical TEM images of MWNTs before (A) and after (B) attachment with gold NPs.

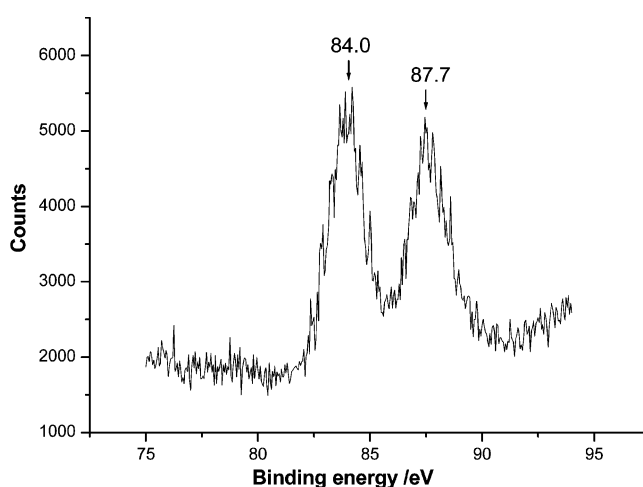


Figure 3. XPS spectrum of Au 4f of the as-prepared CNT/Au NP composites deposited on a glass slide.

sidewalls of CNTs is achieved. The contribution of the physisorption interactions is quite significant because even the pristine MWNTs which had no functional groups on their surfaces were also coated by PEI and then the resulted CNT/Au NP composites were also obtained, indicating the physisorption interactions played an important role in the functionalization of CNTs. Therefore, this method does not need an additional process of oxidizing the surfaces of CNTs by sonicating in the mixed $\text{H}_2\text{SO}_4\text{--HNO}_3$ solution. The reason for the use of purified MWNTs instead of pristine MWNTs in this article is that the convenience for further application is desired by purifying the MWNTs.

The formation of gold NPs attached CNTs is confirmed by the TEM images (Figure 2). Figure 2A shows the TEM image of the MWNTs before modification with gold particles. It can be seen that the MWNTs are endless with a rather smooth surface. Figure 2B shows a representative image for the gold particle attached CNTs. It is interesting to see that the gold particles preferentially adhere to the surfaces of CNTs rather than to other regions without CNTs. We assume that the presence of CNTs catalyzes the reduction of HAuCl_4 to Au^0 , which makes the reduction of HAuCl_4 prefer to occur on the surfaces of CNTs. Therefore, the gold NPs are selectively present at the sidewalls of CNTs and are not found at the areas without CNTs. To demonstrate the reductive effect of PEI in the formation of CNT/Au NP composites, a control experiment was performed. We examined samples obtained from a mild-

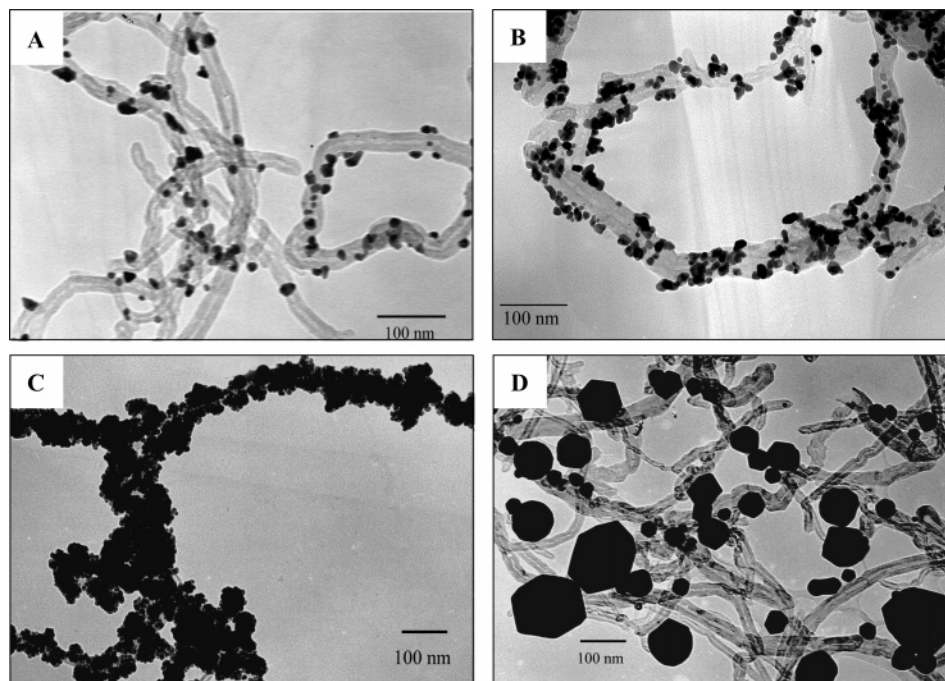


Figure 4. TEM images of CNT/Au NP composites prepared at molar ratio 400:1 (A), 98:1 (B), 9.8:1 (C), and 2:1 (D) of PEI to HAuCl_4 (repeating unit).

heated solution of HAuCl_4 and MWNTs in the absence of PEI. In this case, scarcely any gold NPs attachment on CNTs is observed (data not shown). Therefore, the presence of PEI plays an important role in the formation of CNT/Au NP composite materials.

The oxidation state of gold in the NPs attached on CNTs is determined by X-ray photoelectron spectroscopy as shown in Figure 3. The XPS spectrum of the as-prepared CNT/Au NP composites shows the Au $4f_{7/2}$ and $4f_{5/2}$ doublet with the binding energies of 84.0 and 87.7 eV, respectively. These are typical values for Au^0 ,³⁵ indicating the formation of gold NPs on the sidewalls of CNTs. The precipitates were also characterized by XRD. The four characteristic peaks of a Au crystal indicated the formation of crystalline gold³⁶ on CNTs (data not shown).

To gain further insight into the factors which can influence the coverage of gold NPs on CNTs, a series of control experiments were performed. Eight samples 1–8 with corresponding initial molar ratios of 400:1, 200:1, 98:1, 40:1, 9.8:1, 8:1, 4:1, and 2:1 of PEI to HAuCl_4 (repeating unit) were prepared to examine the influence of initial molar ratio on morphology of the composites. Figure 4 shows typical TEM images of sample 1 (A), 3 (B), 5 (C), and 8 (D). At the molar ratio of 400:1, a small quantity of gold NPs is decorated on CNTs (Figure 4A). The gold NPs with average diameter of 15 nm dispersedly adhere to the sidewalls of CNTs, and the aggregation of gold NPs is rarely seen. The packing density of the attached gold NPs exhibits an increase with the initial molar ratio of PEI to HAuCl_4 decreasing (Figure 4A–C). At the molar ratio of 98:1, the loading of NPs on CNTs is markedly increased (Figure 4B). The gold NPs with average diameter of 12 nm are not well defined in shape, including round and irregular shapes. Further decreasing the molar ratio to 9.8:1, the gold NPs are densely attached on the CNTs. The close-packed gold NPs form aggregates and are likely to further form CNT/Au heterogeneous nanowires.

At the molar ratios of 4:1 and 2:1, the expected CNT/Au heterogeneous nanowires are not obtained. However, the well-shaped NPs with large size distribution around the CNTs are

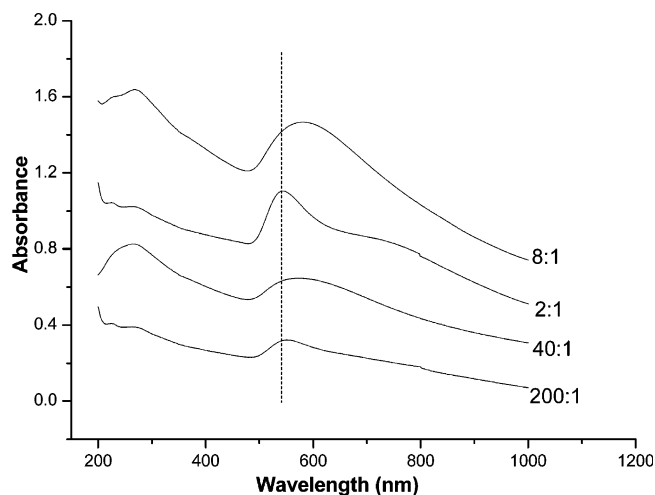


Figure 5. UV–vis absorption spectra of CNT/Au NP composites with initial molar ratio 2:1, 8:1, 40:1, and 200:1 of PEI to HAuCl_4 (repeating unit).

produced. The NPs have diameters in the range of 28–158 nm with shapes of hexagon, pentagon, and sphere (Figure 4D). The NPs are well dispersed without any aggregation. Although the NPs have a larger dimension relative to the MWNTs, we are sure that the NPs are certainly bound stably to the surfaces of CNTs through some linking sites because they can resist extensive washing and sonication. It is considered that the lower PEI concentration makes the confining ability of PEI to Au NPs weaker. As a result, the Au NPs can grow bigger. In addition, a relative less amount of PEI is present, less nucleation site is available, and the following deposition of gold atoms is confined to the preformed nucleation centers resulting in the larger size of NPs.

The UV–visible spectra of these various constructions are shown in Figure 5. The spectra show characteristic absorption bands at about 265 and 550 nm corresponding to the absorption bands of CNTs and Au NPs, respectively. The variation in the molar ratio of PEI to HAuCl_4 allows rough tuning of the position

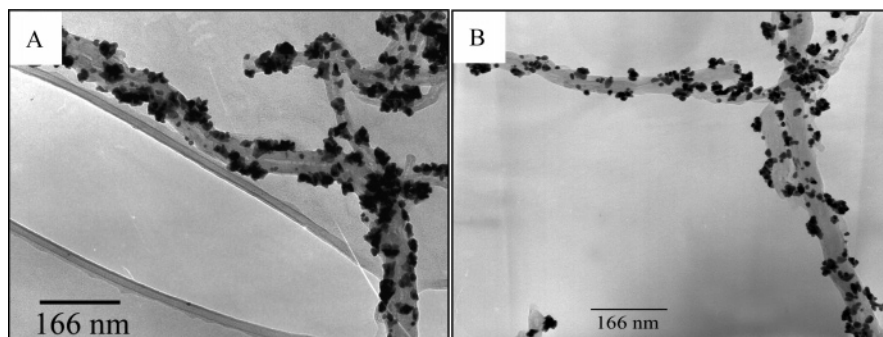


Figure 6. Contrastive TEM images of sample 9 (A) and sample 4 (B). Sample 9 is prepared by doubling the concentration of PEI and HAuCl_4 in sample 4.

and the shape of the absorption band of Au NPs. At the molar ratio 2:1, the weak absorption band at about 740 nm is attributed to the existence of hexagonal and pentagonal NPs. The strong and narrow absorption at 540 nm is due to the absence of aggregates. In the other three cases, the absorption bands are wider and stronger with the molar ratio decreasing, which is due to the high coverage of gold NPs and the formation of aggregates.

Though the CNT/Au NP composite materials have been successfully fabricated, the pursuit of higher coverage of gold NPs on sidewalls of CNTs is still attractive. The coverage of gold NPs on sidewalls of CNTs is expected to also correlate with the relative concentration of PEI and HAuCl_4 to CNTs. Sample 9 was prepared by doubling the concentration of PEI and HAuCl_4 in sample 4 while keeping the concentration of MWNTs unchanged. The higher coverage of Au NPs on MWNTs is obtained at a higher concentration of sample 9 (Figure 6).

In the light of raising the coverage of NPs on CNTs to obtain the CNT/Au heterogeneous nanowires, other experimental factors such as the reaction time and the reaction temperature were also investigated. In the following experiments, the samples with a molar ratio of 40:1 were prepared similarly to other samples. First, we investigated the influence of reaction time on the morphology of the CNT/Au NP composites. The mixed solutions were heated at 60 °C for 120 and 210 min, respectively. Figure 7 shows the TEM images of the products obtained at 120 and 210 min. With increasing reaction time, the coverage of gold particles increases greatly (Figure 7A and B). When the reaction time is increased to 210 min, the resulting product appears to be composite CNT/Au heterogeneous nanowires with small pinholes on the shells (indicated by arrows).

Next, the influence of reaction temperature on the morphology of the CNT/Au NP composites was investigated. When the mixed solutions are heated at 120 °C for 20 min, a layer of gold NPs evenly coats the CNT surfaces with slight coalescence (Figure 8A). When the reaction time is increased to 90 min, the CNT/Au heterogeneous nanowires are obtained again (Figure 8B) and the tubular morphologies of the CNTs cannot be distinguished, which indicates that the MWNTs are almost enwrapped completely by a gold nanowire shell. It is assumed that a higher temperature and a longer reaction time afford a sufficient reacting condition and that the coating is complete.

Up to now, the CNT/Au NPs nanocomposites or even CNT/Au heterogeneous nanowires are obtained by using the in situ reduction method. The gold NPs tightly adhere to the surfaces of CNTs because they can resist extensive washing and sonicating. The method presented here opens up a new route for the fabrication of composite heterogeneous nanowires. Moreover, the controlled coating of gold NPs on CNTs favors

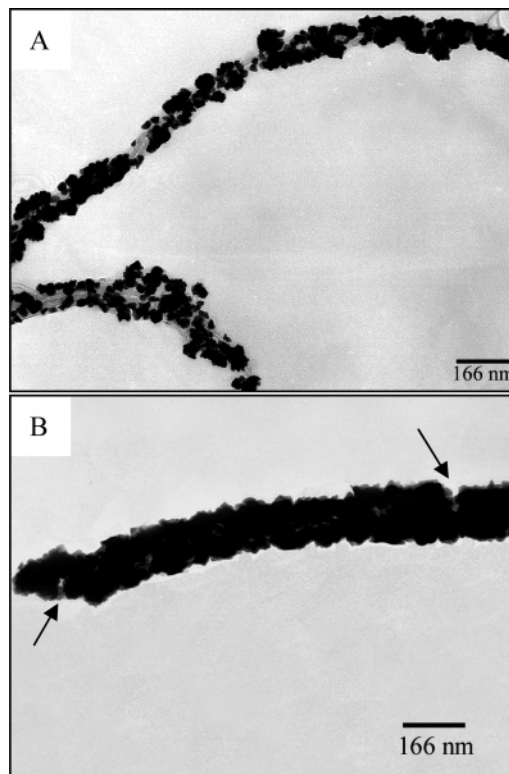


Figure 7. TEM images of the resulting composites obtained by heating the mixed solutions at 60 °C for 120 min (A) and 210 min (B).

the investigation of the electronic properties and the exploration of a new type of electronic devices.

The CNT/Au NP composites are thought to be useful in electrocatalytic applications. The electrocatalytic activity of the composite employed here for dioxygen reduction was investigated. Figure 9 shows the typical cyclic voltammograms (CVs) of dioxygen reduction at the CNT/Au NP composite (sample 2) modified glassy carbon electrode (GCE) in a 0.1 M H_2SO_4 solution in the presence and absence of dioxygen. Curve a corresponds to the CV of the modified electrode in N_2 -saturated 0.1 M H_2SO_4 . In the presence of dioxygen, a remarkable catalytic reduction peak current occurs at -0.14 V (lines b and c). As a comparison, a small reduction peak current occurs at a more negative potential on GCE modified with pure MWNTs. The results indicate that the CNT/Au NP composites have electrocatalytic activity for dioxygen reduction.

Conclusion

In conclusion, we have reported a novel and simple in situ synthetic route for the preparation and coverage control of CNT/

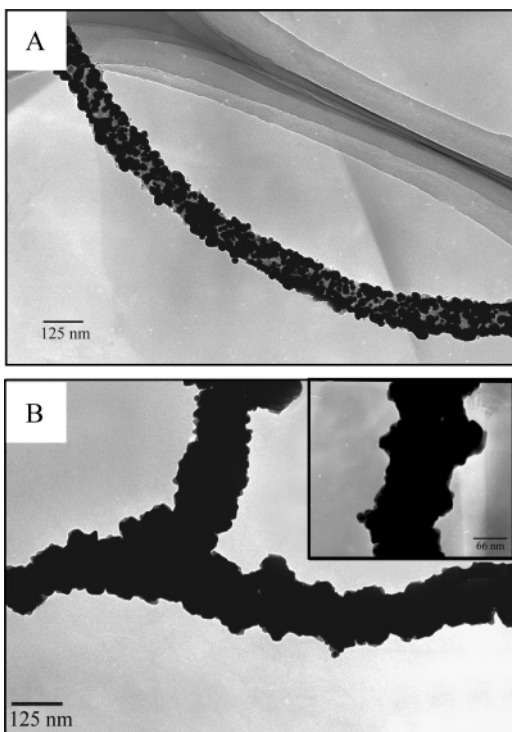


Figure 8. TEM images of the products obtained by heating the mixtures at 120 °C for 20 min (A) and 90 min (B). The inset shows that the gold NPs coalesce to form a continuous gold nanowire with a MWNT core.

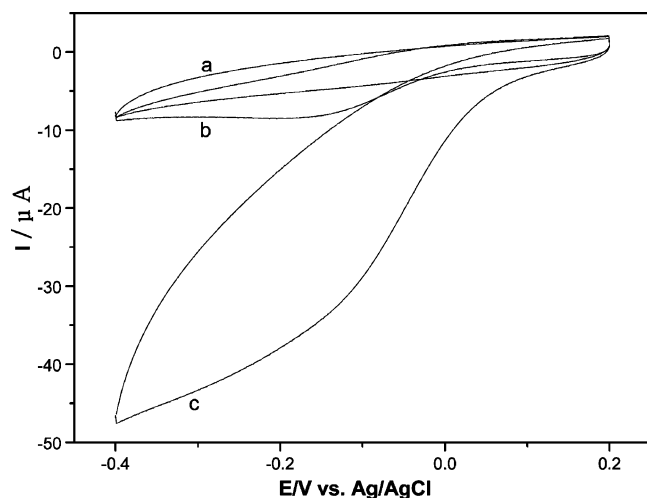


Figure 9. CVs of O_2 reduction at the CNT/Au NP composite-modified GC electrode in the presence and absence of O_2 . Supporting electrolyte: in N_2 saturated (line a), air saturated (line b), and O_2 saturated (line c) 0.1 M H_2SO_4 solution. Scan rate: 50 $mV s^{-1}$.

Au heterogeneous composite materials. This synthetic route involves a mild heat-treatment process, which induces the in-situ reduction of $HAuCl_4$ on MWNTs' sidewalls. The heterogeneous nanostructures have been confirmed by TEM images. This route is facile and simple, and it requires mild experimental conditions and does not need the additional steps of oxidizing the MWNTs with mixed acids and introducing other reducing agents. More importantly, the coverage and loading of gold NPs on MWNTs' surfaces can be tuned by control over the experimental parameters. In addition, this method is expected to be universal for preparing composites of CNTs and other noble metals.

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