

Preparation and Characterization of New Nanocomposites Synthesized of Au and Au–Ag Bimetallic Nanoparticles Encapsulated in Functionalized Multiwalled Carbon Nanotubes

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ABSTRACT

Highly dispersed Au and Au-Ag nanoparticles supported on carbon nanotubes are generated using an easy synthesis. MWCNT was opened and its derivative containing -COOH and -OH functional groups was obtained. Polycondensation of monohydrate citric acid in the presence of functionalized MWCNT in the melting state was lead to nanotube-graft-poly (citric acid) (CNT-g-PCA) nanocomposites. The CNT-g-PCA were soluble in water freely and stirring their water solution and metal at room temperature lead to the CNT-g-PCA containing encapsulated metallic nanoparticles in their polymeric shell. The structure and composition of the resulting MWCNT/Au and Au-Ag nanoparticle hybrids were characterized with TEM and spectroscopy methods. The results imply that the obtained CNT-g-PCA-Au and CNT-g-PCA-Au/Ag nanocomposites have a good application potential in catalysis, sensor, and fuel cells.

Keywords: nanocomposites, Au nanoparticles, Au-Ag nanoparticles, characterization methods, functionalized carbon nanotubes.

1 INTRODUCTION

Gold nanoparticles since a long time are motive of intense research because of their special optical properties and electrochemical activities which heretofore produced with difficult methods [1-4]. Also silver nanoparticles (Ag NP) are used in electronics, biosensing, clothing, food industry, paints, sunscreens, cosmetics and medical devices [5]. Combination of CNTs and metal nanoparticles has been exploited for applications in biomedical devices, biosensors, optical devices. Bimetallic nanoparticles are of considerable interest, since they possess interesting size-dependent electrical, chemical and optical properties. They are of special importance in the field of catalysis, since they often exhibit better catalytic properties than their

monometallic counterparts [6]. Ag–Au nanoparticle is introduced to the research of the glucose electrode, because silver is the best conductor among metals and gold has good biocompatibility [7]. There is an ever increasing interest in synthesizing CNT–metal NP composites in recent years, and various approaches and strategies, including spontaneous deposition [8], electrochemical deposition [9], substrate enhanced electroless deposition [10] and NP decoration on chemically oxidized CNT side walls [11] have been attempted to assemble metal NPs or nanoclusters on the functionalized CNTs. However, further development in the modification of carbon nanotubes is still required. However, to the best of our knowledge, most of the reported techniques for the synthesis of gold nanoparticles are still limited to the laboratory scale due to some unresolved problems, such as special conditions, tedious procedures, complex apparatus, need for expensive agents or special equipment, and high-cost. From a practical viewpoint, it is vital to develop a way to manufacture high-quality nanoparticles at a high throughput with low cost. Herein, we present a novel and simple wet-chemical method for the synthesis of CNT-metal NP assemblies with a wide range of NP coverage. The product was identified by Fourier transformed infrared spectroscopy (FTIR), UV–Vis spectroscopy and transmission electron microscopy (TEM).

2 EXPERIMENTAL

2.1 Apparatus and Reagents

A Shimadzu model UV-1650PC UV-Visible spectrophotometer with 1-cm glass cells was used for recording the absorption spectra and absorbance measurements. HNO₃ (Merck) and H₂SO₄ (Merck) was purchased. The multi-wall carbon nanotubes (MWCNT, <95%) from Ntrino and HAuCl₄.3H₂O and AgNO₃ from Sigma was purchased respectively.

2.2 Preparation of MWCNT-g-PCA nanocomposites

CNTs were opened and citric acid Polymerized onto functionalized carbon nanotubes according to the reported procedures in literatures [12]. Briefly, MWCNTs were activated in nitric acid solutions to give carboxyl group modified MWCNTs (MWCNT-COOH), followed by reaction with monohydrate citric acid, resulting in hyperbranched poly (citric acid) grafted onto MWCNT (CNT-g-PCA).

2.3 Preparation of MWCNT-g-PCA nanocomposites containing Au and Au-Ag nanoparticles

The prepared MWCNT-g-PCA composites were mixed with moderate concentration chloroauric acid (HAuCl_4) and placed in an ultrasonic bath for 20 min in order to well disperse metal ions in the polymeric shell of nanocomposite. The solution was then stirred at room temperature for 8 h. The effect of reaction parameters (such as pH, temperature, ultrasonic time) on the syntheses of metal nanoparticles with MWCNT-g-PCA was studied by UV-Vis experiments. Then prepared solution from previous process was mixed with moderate concentration of AgNO_3 and placed in an ultrasonic bath for 20 min. The solution was then stirred at room temperature for 7h.

2.4 Characterization techniques

UV-visible spectra of as prepared solutions were taken by UV-Vis spectrophotometer (Shimadzu 1650PC) in the wavelength range of 200–800 nm at room temperature. The formation of Au nanoparticles was monitored in the visible absorption range of ≈ 530 nm. The shape and size of gold nanoparticles were characterized by transmission electron microscopy (TEM). The effect of reaction parameters (such as pH, temperature, ultrasonic time) on the syntheses of metal nanoparticles with MWCNT-g-PCA was studied by UV-Vis experiments.

3 RESULTS AND DISCUSSION

Multiwalled carbon nanotubes were opened and functionalized using a sulfuric and nitric acid mixture (3/1) Both citric acid and functionalized MWCNTs are containing alcoholic and acidic hydroxylfunctional groups, hence citric acid can be polymerized onto functionalized MWCNT through polycondensation reaction. Figure 1 shows the color change during the progression of the complexation of gold with the PCA shell. The colorless color of the primary solution turned to the lavender after 25 min ultrasonic and increasing in the darkness of the solution

continued during the reaction to reach violet. Changes in the color of reaction are related to the complexation of gold and polymeric shell of the hybrid material and formation of the nanoparticles. Figure 2 shows the UV spectra of complexation of Au and MWCNT-poly (citric acid) in different time period. The weak absorption peak centered at 530 nm in the spectrum of MWCNT/gold NP composites was in good agreement with the reported values for gold NPs [13]. Enhancing the intensity of absorption bands during the time demonstrates gradual increases in the surface plasmon absorption by the colloidal gold particles in solution in which the concentration of the nanoparticles is increased due to the increasing of encapsulated Au nanoparticles in the polymer host. Figure 3 shows the TEM image of encapsulated gold nanoparticles in the PCA shell of the CNT-g-PCA. It is clear that nanoparticles are placed on the surface of CNTs which confirmed nanoparticles are fitted on the CNT wall by PCA shell. In the other part of this work, the encapsulation of the silver nanoparticles by CNT-g-PCA-Au was also investigated. Figure 4 shows the UV spectra of complexation of Ag and MWCNT-g-PCA-Au for different time.



Fig. 1. The color change during progression of the complexation between Au and MWCNT-g-PCA: (a) initiate, (b) 25 min after ultrasonic, and (c) 17.5h.

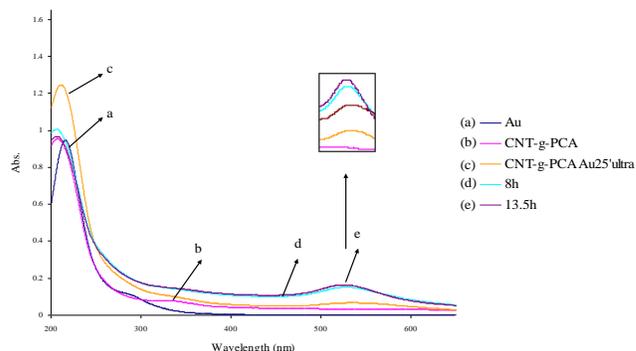


Fig.2. The absorption spectra change during progression of the complexation between Au and MWCNT-g-PCA.

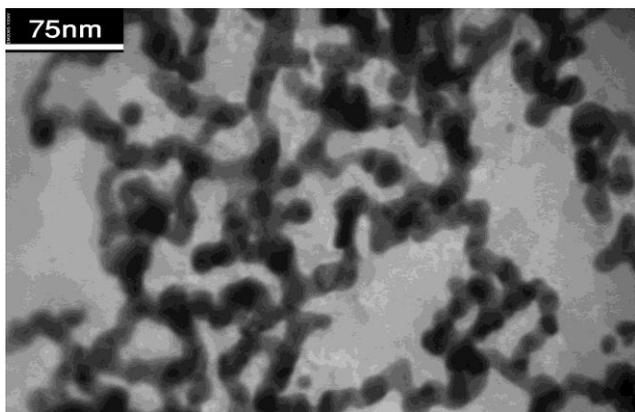


Fig.3. TEM images of CNT-g-PCA-Au.

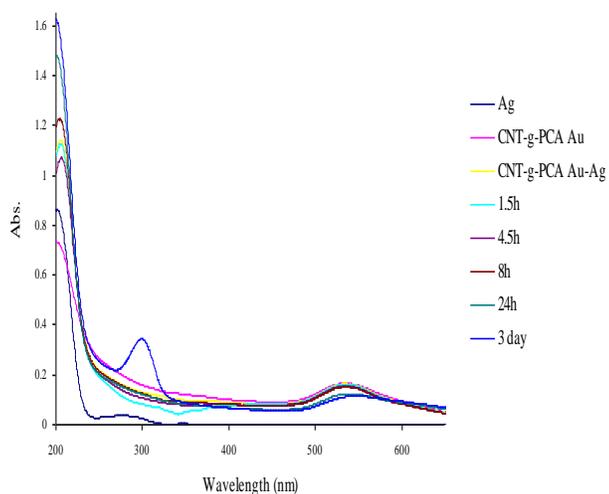


Fig.4. The absorption spectra change during progression of the complexation between Ag and MWCNT-g-PCA-Au.

In this figure, the absorption peak of the ligand to metal charge transfer (LMCT) can be clearly observed at 250 and 350 nm. The peak at 350 nm is related to the formation of silver nanoparticle and agreed well with the reported results in the literatures [14]. Enhancing the intensity of absorption bands during the time demonstrates gradual increases in the surface plasmon absorption by the colloidal of encapsulated Ag nanoparticles in the polymer host. Figure 5 shows the TEM silver nanoparticles in solution in which the concentration of the nanoparticles is increased due to the increasing amount of encapsulated gold and silver nanoparticles in the PCA shell of the CNT-g-PCA. It is clear that nanoparticles are placed on the surface of CNTs which confirmed nanoparticles are fitted on the CNT wall by PCA shell.

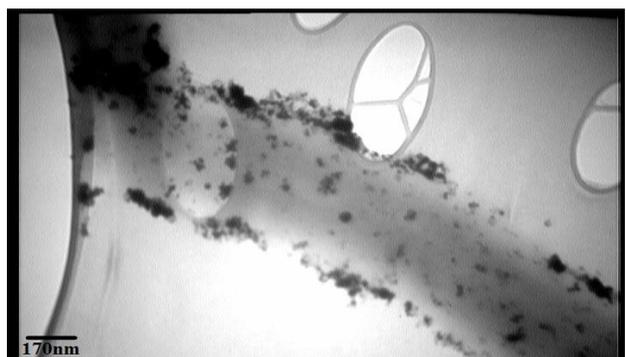
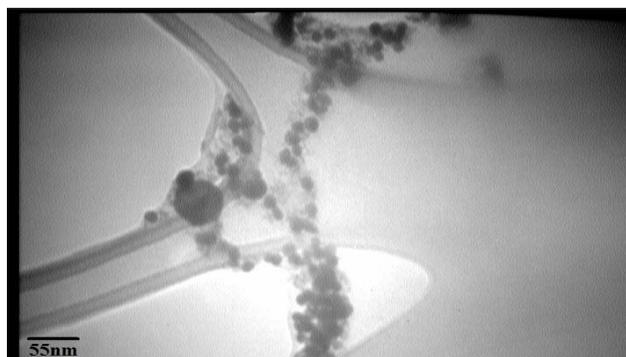
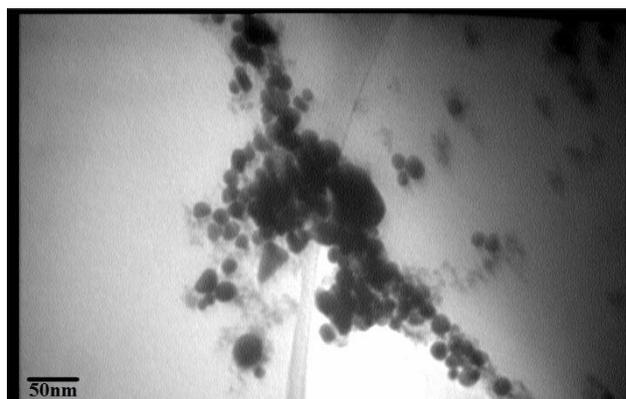


Fig.5. TEM images of CNT-g-PCA-Au-Ag.

4 CONCLUSION

In conclusion, we reported an easy and novel approach to loading of gold and silver NPs on the functionalized MWCNTs. TEM images clearly show the presence of metal nanoparticles on the surface of MWCNTs. This method is not limited to gold and silver, however, it may be used to assemble a variety of other metal NPs on the modified CNT surfaces. The prepared nanostructure hybrids have potential applications for the generation of electrical, optical, and sensor devices.

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