



Simple and efficient gold nanoparticles deposition on carbon nanotubes with controllable particle sizes

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ABSTRACT

There are important applications of multiwalled carbon nanotubes (MWCNT) with deposited nanoparticles and several methods exist for synthesizing these nanocomposites. However, a simpler and more efficient method is desired in many cases. Here, we introduce a method where MWCNT were pre-mixed with sodium citrate, and using ultrasonication, shells of sodium citrate were formed on the nanotubes. These functionalized MWCNTs served as substrates for gold nanoparticle growth. When HAuCl_4 was added to the reaction system, Au^{3+} was directly reduced at the surface of the MWCNT and gold nanoparticles were assembled along the MWCNT. Transmission electron microscopy (TEM) demonstrated that the density of the gold nanoparticle coating process depended on the amount of the carbon nanotubes when the sodium citrate concentration was kept unchanged. In addition, by controlling the concentration of sodium citrate and HAuCl_4 , the size of gold nanoparticles could be controlled. Scanning electron microscope (SEM), energy dispersive X-ray (EDX), and UV–vis were also used to characterize the MWCNT–Au nanocomposites. Compared with other methods, the procedure described here required only water solutions and there are no needs for high temperature steps, surfactants or organic solvents, resulting in a simple and fast method for efficient gold nanoparticle decoration of carbon nanotubes.

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1. Introduction

Nanocomposites of carbon nanotube and metal/metal oxide are of great interest due to either the combination of the unique properties of these two kinds of materials or the emergence of new properties, leading to novel applications [1–4], for a review see ref. [5]. Researchers have demonstrated that these kinds of hybrid nanocomposites can be used in nanoelectronics, biosensors, etc. [6–8]. Due to this diverse set of applications, different kinds of methods have been developed to synthesize these nanocomposites. Commonly used methods [5] include wet-chemical methods [9,10], self-assembly [11,12], electrodeposition [13] and physical vapor deposition [14]. Gold nanoparticles are the most investigated ones, since they are easily synthesized and functionalized and may be linked to many molecules or groups. Generally, there are two ways to decorate the carbon nanotubes with gold nanoparticles: indirect or direct deposition.

For the indirect deposition, a linkage is introduced between the carbon nanotube and the gold nanoparticle. Two types of bonds could be used, covalent and non-covalent. For covalent bonding, the gold nanoparticles or the carbon nanotubes are functionalized with some linkages, forming covalent bonds both at the carbon nan-

otube site and the gold nanoparticle site [15–17]. For non-covalent bonding, other types of binding are used such as π – π stack [18], electrostatic [19,20] or hydrophobic interaction [21]. These kinds of non-covalent method are commonly used and high densities of gold nanoparticles are deposited on the carbon nanotubes. However, two obstacles with these methods are the need for several process steps and the yield of carbon nanotube modification is sometimes not very high.

The other set of methods is direct deposition. This means that gold nanoparticles are coated on the sidewall of carbon nanotube without any link of other molecules or groups. Microwave assisted deposition is one of the reported methods, where carbon nanotubes are exposed to microwaves and carboxyl groups are generated on the sidewalls of the nanotubes, followed by a reduction of gold ions at the sidewall [22]. Xue and co-workers reported another method by mixing the carbon nanotube with gold salt solution and subsequently dried. Then the gold ions were reduced by H_2 at high temperature between 573 and 973 K [23]. Jiang and co-workers showed a process to attach gold nanoparticles on carbon nanotube by first treating carbon nanotube with polyethylenamine (PEI) or sodium citrate, then, gold nanoparticles were synthesized either on the outside or inside of the carbon nanotubes using a reaction at 80° during 8 h [24]. Solvated metal atom dispersion method (SMAD) is another way to fabricate gold/carbon nanotube hybrids. In the SMAD procedure, bulk gold and an organic solvent (Acetone) are co-evaporated, then, after condensation, gold clusters

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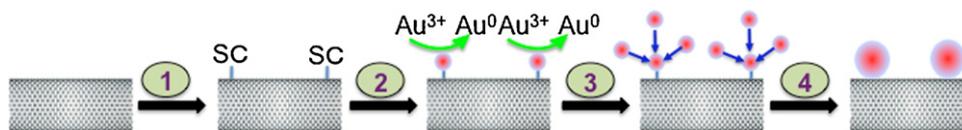


Fig. 1. Schematic drawing for synthesizing of MWCNT/Au nanocomposites. (1) Carbon nanotubes was first pre-mixed with sodium citrate (SC) using ultrasonication. (2) HAuCl_4 is added into the reaction system causing reduction of Au^{3+} ions to Au^0 . (3) The reduced gold atoms on the carbon nanotube act as seeds for self-assembling of other gold atoms. (4) Gold nanoparticles are deposited on the carbon nanotube.

are obtained which could hybrid with MWCNT [25]. Xiao and co-workers reported a simple method to deposit gold nanoparticles on carbon nanotube recently, which used sodium dodecyl sulfate to disperse the carbon nanotube [26,27]. Although these methods are very successful and useful, one important aspect is that even simpler methods are desired in some cases, without the need of high temperature [23], organic solvent [25] or a long reaction time [22,24]. Especially, bulk production of nanocomposites will benefit from simple methods. In addition, water solutions will make the collection of the synthesized nanocomposites easier.

Here, we report on a new simple method to deposit gold nanoparticles by directly reducing gold ions on the carbon nanotubes. A pre-mixing step was used to form sodium citrate shells on the carbon nanotubes, making the carbon nanotube a suitable substrate for gold deposition. By adjusting the amount of HAuCl_4 solution in the reaction system, the size of the gold nanoparticles on the carbon nanotube could be controlled. Compared to the reported methods, these experiments were done at low reaction temperature (100°), organic and surfactant free (in water solution) and with a shorter reaction time (less than 1 h).

2. Experimental details

2.1. Materials

Carbon nanotubes were purchased from SIGMA with diameters of 110–170 nm. The carbon nanotubes were used in the following experiment without further purification. HAuCl_4 and sodium citrate were also purchased from SIGMA and dissolved in doubly distilled water at a concentration of 1 wt%.

2.2. MWCNT/Au nanocomposite synthesis

In the pre-mixing step, different amounts of carbon nanotubes were added in 4 ml sodium citrate solution, and the mixture was then exposed to ultrasonic treatment for 5 min. After the pre-mixing step, the carbon nanotube suspension was transferred to 96 ml doubly distilled water. The diluted suspension was heated to the boiling point while stirring, and then different amount of HAuCl_4 was injected. The suspension was kept boiling for 5 min and then carbon nanotubes were separated and washed from the suspension by centrifugation at 6000 rpm for 5 min.

To study the influence of the amount of carbon nanotubes, nanotubes were added as 16, 8 and 3 mg, and 1 ml HAuCl_4 was injected to the reaction system after the boiling step mentioned above.

To investigate the influence of the concentrations of HAuCl_4 , the amount of carbon nanotubes was kept as 3 mg, and then different amount of HAuCl_4 were injected as 1.5, 1.0 and 0.5 ml.

2.3. Characterization

The synthesized nanocomposites were characterized by TEM at 160 kV working voltage (JEM2000-FX, JEOL), SEM (EVO50, ZEISS) and SEM–EDX. The samples were prepared by dropping the solu-

tions on Cu grids for TEM and on carbon specimen tape for SEM and dry in air at room temperature. Optical spectra were obtained by a UV–vis spectrometer (UV-160A, SHIMADUZE).

3. Results and discussions

3.1. The influence of the amount of carbon nanotubes

Using sodium citrate to reduce Au^{3+} ions to Au^0 is a commonly used wet chemical method to synthesize gold nanoparticles. In this process, one Au^{3+} is first reduced to a Au^0 atom, and then the other reduced Au^0 will aggregate to this atom and assemble a gold nanoparticle. In our experiment, carbon nanotubes was first pre-mixed with sodium citrate, forming a sodium citrate shell on the surface of the carbon nanotubes [24]. Subsequently, when HAuCl_4 solution was added to our reaction system, HAuCl_4 molecules were reduced when they met the sodium citrate at the carbon nanotube surface and were thus serving as growing points. The other reduced Au atoms in solution were then absorbed at these seed points and gold nanoparticles were grown (as shown in Fig. 1).

First, we kept the amount of sodium citrate in our experiment constant. Thus, by using different amounts of carbon nanotubes, the surface coverage of sodium citrate shells on the nanotubes were altered during the pre-mixing step. We selected three different amounts of carbon nanotube as 16, 8 and 3 mg in our experiments. TEM characterizations (Fig. 2A, 16 mg; Fig. 2B, 8 mg; Fig. 3B, 3 mg) showed the effect of different amounts of carbon nanotubes in the pre-mixing step; the densities of deposited gold nanoparticles on the carbon nanotube surfaces were clearly different. With 16 mg carbon nanotubes (Fig. 2A), only a few gold nanoparticles could be observed and the shapes of the gold nanoparticles were not always spherical. This effect was interpreted as a sodium citrate concentration that was not enough to form a complete shell at the carbon nanotube surface due to too high amount of carbon nanotubes. But, when we decreased the amount of carbon nanotubes to 8 mg (Fig. 2B), we observed that the number of gold nanoparticles at the carbon nanotube surface were increased and the shape of the gold nanoparticles were more spherical than with 16 mg carbon nanotubes. Subsequently, we decreased the amount of carbon nanotubes to 3 mg. As shown in Fig. 2B, at this amount level, the density of deposited gold nanoparticles on carbon nanotube surface was highly increased. Besides, the gold nanoparticles was deposited along the carbon nanotube and the size of gold nanoparticles were well controlled at 40 ± 2 nm. As indicated in the TEM image the gold nanoparticles were grown along the carbon nanotube, meaning the carbon nanotubes were homogeneously covered with sodium citrate. These results demonstrated that a decreased amount of carbon nanotubes leads to an increased surface coverage of sodium citrate.

3.2. The influence of the concentration of HAuCl_4

Even though we have obtained well-covered MWCNT/Au nanocomposites, the density of gold nanoparticles is not high

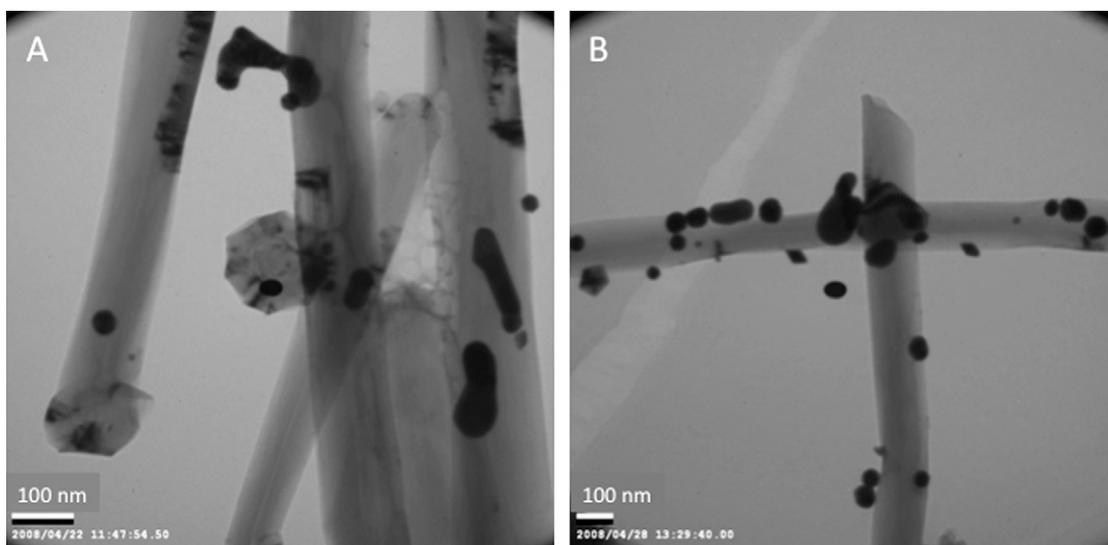


Fig. 2. TEM of synthesized MWCNT/Au nanocomposites at different carbon nanotube amount. (A) 16 mg MWCNT and (B) 8 mg MWCNT (the black dot in the center of the images is an imaging artifact).

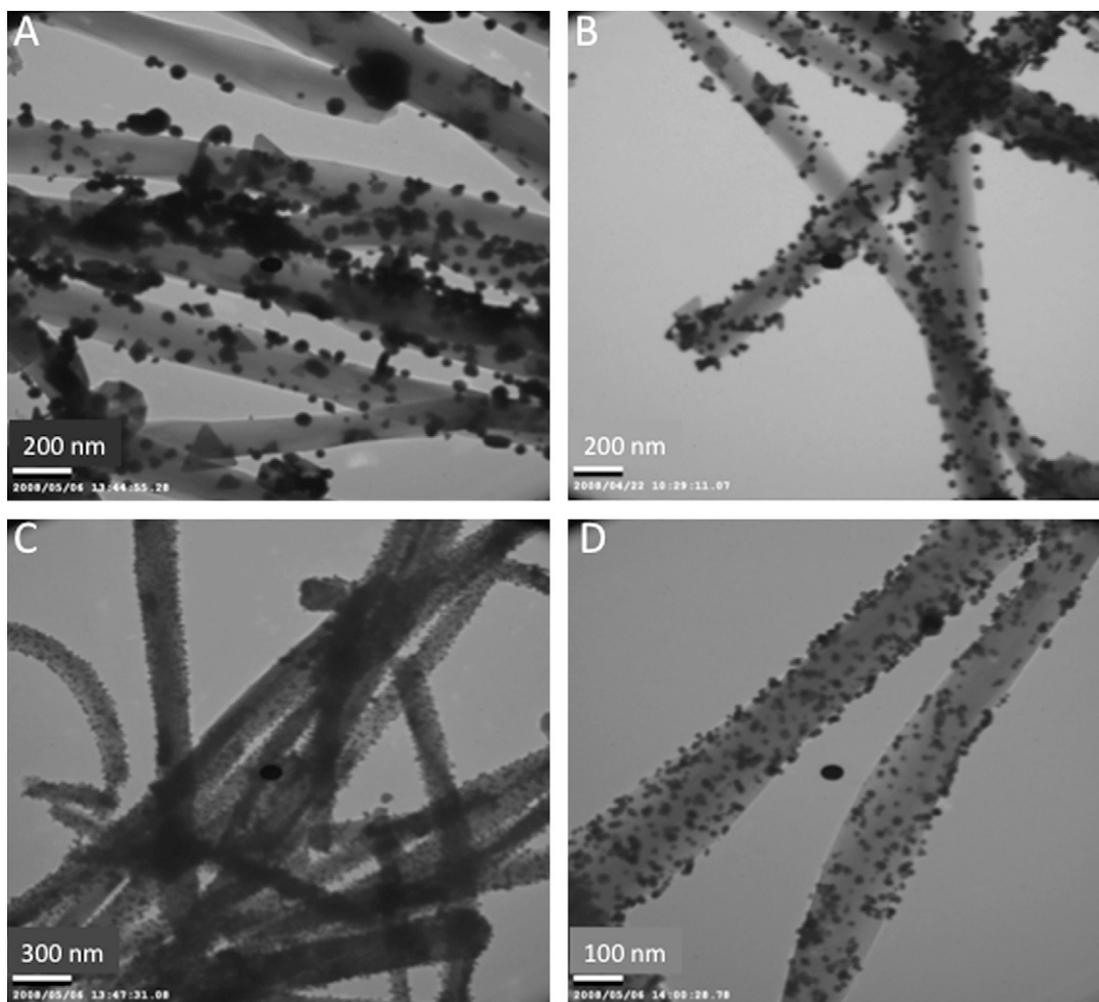


Fig. 3. TEM of synthesized MWCNT/Au nanocomposites at different HAuCl_4 amount. (A) 1.5 ml, (B) 1.0 ml and (C) 0.5 ml. The amount of carbon nanotubes in these three figures was 3 mg. (D) was from the sample (C) with higher magnification (the black dot in the center of the images is a imaging artifact).

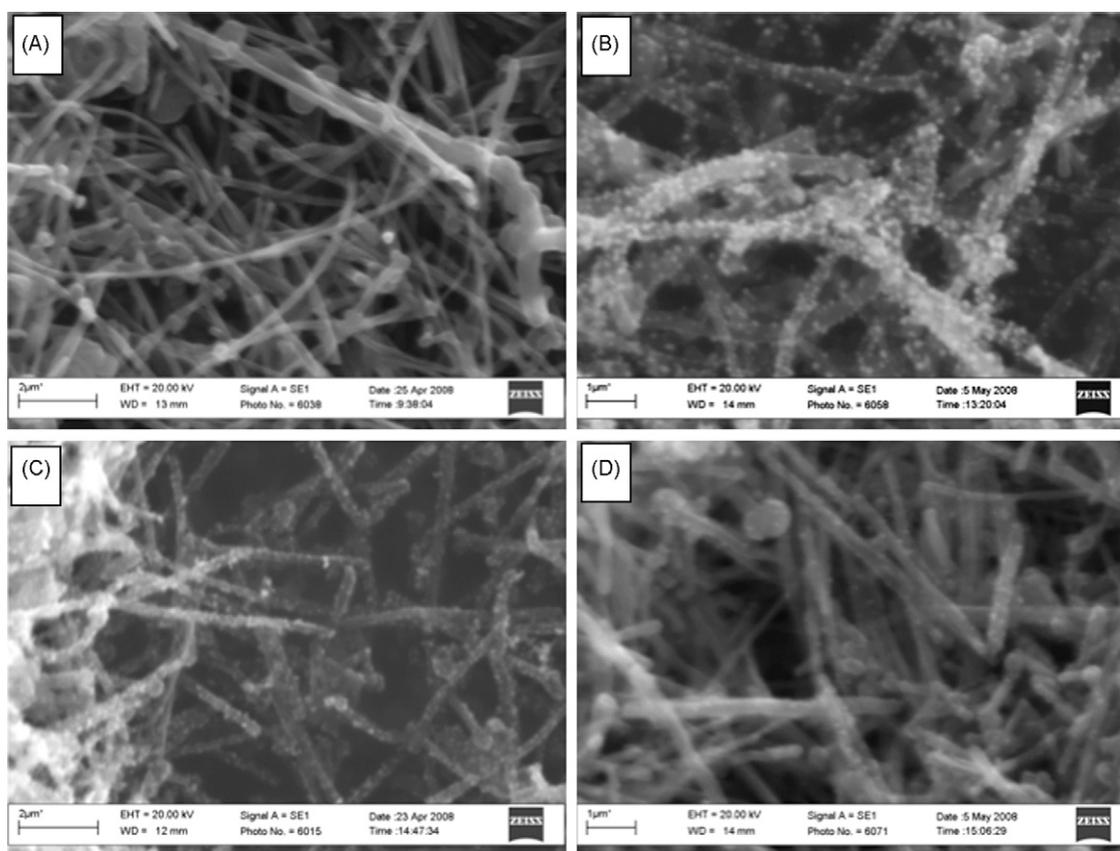


Fig. 4. SEM images of pure MWCNT (A), MWCNT/Au nanocomposites at different HAuCl₄ concentrations (B) 1.5 ml, (C) 1.0 ml and (D) 0.5 ml. The amount of carbon nanotubes used in these images were 3 mg.

enough for certain applications. If we keep the amount of carbon nanotubes and sodium citrate unchanged, while controlling the gold nanoparticle size, the surface density of gold nanoparticles will increase since more nanoparticles will be deposited per unit area if the size of the nanoparticles decreased.

In the synthesis of gold nanoparticles, using wet chemical method, the size of gold nanoparticles can be adjusted by changing the concentration ratio of sodium citrate and HAuCl₄. In our experiment, to obtain different sizes of deposited gold nanoparticles, we selected three different amounts of HAuCl₄. Fig. 3 shows TEM images of synthesized MWCNT/Au nanocomposites with different gold nanoparticle size. As shown in Fig. 3A, when 1.5 ml, 1 wt% HAuCl₄ was added into the reaction system, the size of gold nanoparticles at carbon nanotube was 60 ± 5 nm. The shape of gold nanoparticles was not uniform; there are several different shapes beside the spherical shape. The coverage of gold nanoparticles was not homogenous; in some places the gold nanoparticles were concentrated, while no coverage at other places. In contrast, when we decreased the nanoparticle size by injecting 1.0 ml HAuCl₄, the size of the obtained gold nanoparticles were 40 ± 2 nm. As described above, in this case, the size of the gold nanoparticles were well controlled and the coverage of gold nanoparticles was more homogenous.

In order to increase the coverage of gold nanoparticles, we further decreased the amount of HAuCl₄ to 0.5 ml. As shown in Fig. 2C, the coverage of gold nanoparticles was significantly increased, and the entire carbon nanotubes were covered by gold nanoparticles with a high density. Compared to the reported direct deposition methods [22,23], we obtained a higher gold nanoparticles coating ratio. With the aim to get more information about the size, we increased the magnification of TEM. Fig. 3D shows the gold

nanoparticles on single carbon nanotube at high magnification. Generally, there were two kinds of gold nanoparticle size, 8 ± 3 nm and 20 ± 2 nm. The most common gold nanoparticles had diameters of 20 ± 2 nm. The results indicated that the highest density of gold nanoparticles on carbon nanotube could be obtained by a concentration ratio of 8:1 (4 ml, 1 wt%:0.5 ml, 1 wt%) for sodium citrate and HAuCl₄.

3.3. SEM and SEM-EDX characterization

We further characterized the synthesized MWCNT/Au nanocomposites using SEM. Fig. 4 shows typical SEM images. The SEM images show nanocomposites resulting from different HAuCl₄ concentrations while the amount of carbon nanotubes was fixed at 3 mg. Firstly, the pure carbon nanotubes as received from SIGMA were imaged as shown in Fig. 4A, indicating clean surfaces of the carbon nanotubes. Fig. 4B shows the result of nanocomposites when 1.5 ml HAuCl₄ was used. The sizes of gold nanoparticles were large and the coverage was not uniformed. When we decreased the size of gold nanoparticles by decreasing the injected amount of HAuCl₄ to 1.0 ml, the coverage of gold nanoparticles was higher as shown in Fig. 4C. In agreement with the TEM results, the size of gold nanoparticles was decreased. Fig. 4D shows an image of the MWCNT/Au nanocomposites when the amount of HAuCl₄ was 0.5 ml. However, we could not see details of the gold nanoparticles, because the resolving power of the SEM is too low.

Fig. 5 shows the energy dispersive X-ray (EDX) spectra of synthesized MWCNT/Au nanocomposites. It shows that gold nanoparticles was supported on the multiwalled carbon nanotubes. The peak of O and Na elements is probably from the sodium citrate.

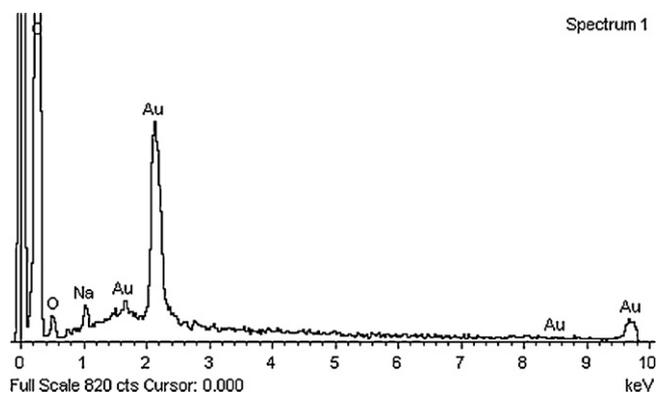


Fig. 5. EDX spectra of gold nanoparticles deposited MWCNT on carbon.

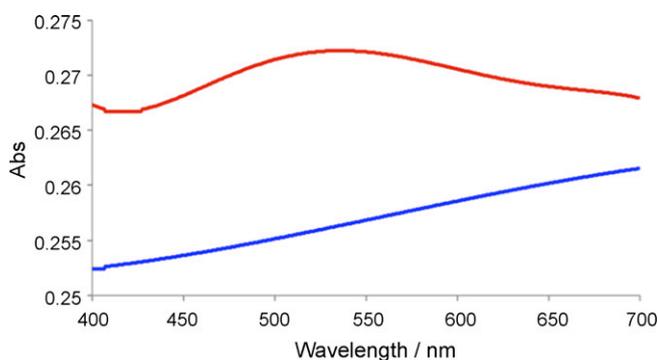


Fig. 6. UV-vis absorption spectra of MWCNT (bottom), MWCNT/Au (top) nanocomposites synthesized with a HAuCl_4 concentration of 0.5 ml. A typical absorption peak of gold nanoparticle around 520 nm was observed on the MWCNT/Au nanocomposites, while it was not existed on pure MWCNT.

3.4. UV-vis characterization

Fig. 6 shows the UV-vis absorption spectra of MWCNT and the synthesized MWCNT–Au nanocomposites when 0.5 ml HAuCl_4 was added. As indicated above, in this MWCNT/Au nanocomposites, the size of gold nanoparticles was about 20 nm, and the UV-vis absorption peak should be around 520 nm. In the UV-vis curve, the peak was also around 520 nm, which means there was no interparticle plasmon coupling causing red shift of the surface plasmon resonance (SPR) band [18,28,29]. For the MWCNT/Au nanocomposites that were synthesized by adding 1.0 and 1.5 ml HAuCl_4 , the absorption peak was around 542 and 560 nm (see supplementary data), which is close to the absorption peak of gold nanoparticles of that size [30].

4. Conclusions

In summary, we have here described on a new method to deposit gold nanoparticles on multiwalled carbon nanotubes. Using a pre-mixing step, where carbon nanotubes were mixed with sodium citrate using ultrasonication, a sodium citrate shell was formed on the carbon nanotubes, and then the gold nanoparticles were deposited on the carbon nanotube directly without any linkage. The deposition efficiency of gold nanoparticles was influenced by the ratio of carbon nanotubes and HAuCl_4 amounts if the concentration

of sodium citrate was fixed. A high density of gold nanoparticles coverage was obtained when the amount of carbon nanotubes, sodium citrate and HAuCl_4 were 3 mg, 4.0 ml (1 wt%) and 0.5 ml (1.0 wt%), respectively, for a total reaction volume of 100 ml. Generally, using this method, one could control the coverage and the size of gold nanoparticles simply and quickly without any other reagent assistance. Compared to earlier methods, the procedure described in this paper allows for faster processing (within 1 h), usage of only water solutions for all steps, and without surfactants or high temperature steps.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.mseb.2008.12.038.

References

- [1] G. Yamamoto, M. Omori, K. Yokomizo, T. Hashida, K. Adachi, *Mater. Sci. Eng. B* 148 (2008) 265–269.
- [2] P. Santhosh, A. Gopalan, K.P. Lee, *J. Catal.* 238 (2006) 177–185.
- [3] Y.J. Chen, C.L. Zhu, T.H. Wang, *Nanotechnology* 17 (2006) 3012–3017.
- [4] J.T. Abrahamson, N. Nair, M.S. Strano, *Nanotechnology* 19 (2008) 195701.
- [5] G.G. Wildgoose, C.E. Banks, R.G. Compton, *Small* 2 (2006) 182–193.
- [6] Y. Wang, X. Xu, Z.Q. Tian, Y. Zong, H.M. Cheng, C.J. Lin, *Chem. Eur. J.* 12 (2006) 2542–2549.
- [7] S. Hrapovic, Y. Liu, K.B. Male, J.H.T. Luong, *Anal. Chem.* 76 (2004) 1083–1088.
- [8] K.J.C. Van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem.* 115 (2003) 1010–1030.
- [9] R.Y. Zhang, X.M. Wang, *Chem. Mater.* 19 (2007) 976–978.
- [10] Z.Y. Sun, Z.M. Liu, B.X. Han, Y. Wang, J.M. Du, Z.L. Xie, G.J. Han, *Adv. Mater.* 17 (2005) 928–932.
- [11] G.N.A. Rahman, D.M. Guldi, E. Zamboni, L. Pasquato, V. Tzitzios, D. Gournis, D. Petridis, *Small* 1 (2005) 527–530.
- [12] B.J. Taft, A.D. Lazareck, G.D. Withey, A. Yin, J.M. Xu, S.O. Kelley, *J. Am. Chem. Soc.* 126 (2004) 12750–12751.
- [13] B.M. Quinn, C. Dekker, S.G. Lemay, *J. Am. Chem. Soc.* 127 (2005) 6146–6147.
- [14] Y. Zhang, H.J. Dai, *Appl. Phys. Lett.* 77 (2000) 3015–3017.
- [15] D.H. Marsh, G.A. Rance, R.J. Whitby, F. Giustiano, A.N. Khlobystov, *J. Mater. Chem.* 18 (2008) 2249–2256.
- [16] T. Sainsbury, D. Fitzmaurice, *Chem. Mater.* 16 (2004) 2174–2179.
- [17] R. Zanella, E.V. Basiuk, P. Santiago, V.A. Basiuk, E. Mireles, I. Puente-Lee, J.M. Saniger, *J. Phys. Chem. B* 109 (2005) 1629016295.
- [18] Y.Y. Ou, M.H. Huang, *J. Phys. Chem. B* 110 (2006) 2031–2036.
- [19] B. Kim, W.M. Sigmund, *Langmuir* 20 (2004) 8239–8242.
- [20] K.Y. Jiang, A.E. Linda, L.S. Schadler, P.M. Ajayan, R.W. Siegel, *Nano Lett.* 3 (2003) 275–277.
- [21] T. Wang, X.G. Hu, X.H. Qu, S.J. Dong, *J. Phys. Chem. B* 110 (2006) 6631–6636.
- [22] M. Raghuvver, S. Agrawal, N. Bishop, G. Ramanath, *Chem. Mater.* 18 (2006) 1390–1393.
- [23] B. Xue, P. Chen, Q. Hong, J.Y. Lin, K.L. Tan, *J. Mater. Chem.* 11 (2001) 2378–2381.
- [24] L.Q. Jiang, L. Gao, *Carbon* 41 (2003) 2923–2929.
- [25] A. Tello, G. Cárdenas, P. Häberle, R.A. Segura, *Carbon* 46 (2008) 884–889.
- [26] I. Streeter, L. Xiao, G.G. Wildgoose, R.G. Compton, *J. Phys. Chem. C* 112 (2008) 1933–1937.
- [27] L. Xiao, G.G. Wildgoose, R.G. Compton, *Carbon* 620 (2008) 44–49.
- [28] C. Guarise, L. Pasquato, P. Scrimin, *Langmuir* 21 (2005) 5537–5541.
- [29] K.G. Thomas, S. Barazzouk, B.I. Ipe, S.T.S. Joseph, P.V. Kamat, *J. Phys. Chem. B* 108 (2004) 130766–130768.
- [30] T.L. Chang, Y.W. Lee, C.C. Chen, F.H. Ko, *J. Colloid Interface Sci.* 84 (2007) 1698–1701.