

Coating MWNTs with Cu₂O of different morphology by a polyol process

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Abstract

Homogeneous cuprous oxide (Cu₂O) nanoparticles with size of 8–10 nm are deposited on multiwall carbon nanotubes (MWNTs) by a polyol process using Cu(CH₃COO)₂·H₂O as a precursor and diethylene glycol as both solvent and reducing agent. The composition of the resulting Cu₂O/MWNTs composites is confirmed by XRD pattern, XPS spectrum and HRTEM images. With the change of the reaction conditions, it is found that Cu₂O nanoparticles on the surface of MWNTs can be leafage-like or big spherical particle coated on the surface of MWNTs. HRTEM images indicate that all the leafage-like and big spherical particles are assembled by small Cu₂O particles with size of about 2–5 nm. With the assistance of FTIR spectrum, a tentative mechanism is proposed for the formation of Cu₂O nanoparticles with different morphologies on the surface of MWNTs.

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1. Introduction

Carbon nanotubes (CNTs), due to their special structure, extraordinary mechanical and unique electronic properties and potential applications, have attracted considerable attention since they were discovered [1]. CNTs can be used to form different composites, which have applications such as reinforcement fibers, novel catalysts or potential electronic nanodevices [2]. For example, because of the cylindrically layered and hollow tubule nanostructures, CNTs can be used as supports for preparing nanosized particle catalysts. Metals such as Pt [3] and Ru [4] have been deposited on CNTs to enhance their catalytic activity.

Cuprous oxide (Cu₂O) is a *p*-type semiconductor with a direct band gap of 2.0 eV [5], which offers it important

applications in hydrogen production, and superconductor, solar cell and negative electrode materials [6–9]. It also has a potential application in photocatalytic degradation of organic pollutants under visible light [10]. Cu⁺ deposited on zeolite has been used for the photocatalytic decomposition of NO_x into N₂ and O₂ [11]; CuO-activated carbon catalyst can decompose methanol to H₂ and CO directly [12]. Nevertheless, when the narrow gap semiconductor (i.e., Cu₂O) is used as a photocatalyst, there is a limitation that the carriers excited by light cannot be transferred efficiently and are easy to recombine [13]. Theoretical calculation shows that CNTs have metallic or semiconducting properties depending upon the fiber geometry and the curvature of the graphitic planed [14,15]. If CNTs act as the support of Cu₂O, it is expected that the recombination of the carriers may be inhibited and the photocatalytic activity of Cu₂O under visible light would then be improved because of the properties of enhanced electron transfer and high surface area for CNTs [16].

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The polyol process is a synthetic technique for material preparation with the properties of simplicity, and convenience, and being less energy-demanding and less material-consuming. Meanwhile, this method enables an accurate control of the size distribution and the shape of the particles from the micrometric to the colloidal scale [17]. Over the past two decades, this method has been widely used to synthesize inorganic materials, such as metals and alloys, metal oxides, binary sulfides [18,19], in which the reducing and dissolving properties of a high-boiling alcohol with regard to a suitable precursor are utilized. In the previous study [20], through a polyol process with the assistance of sonication, Cu₂O nanoparticle can be homogeneously dotted on the surface of multiwall carbon nanotubes (MWNTs). In this study, we investigate the deposition of Cu₂O on the surface of MWNTs under different conditions in the polyol process. Polyol, diethylene glycol (DEG), functions as both solvent and reduction agent. By changing the conditions in the preparation process, it is found that the assembled morphology of Cu₂O nanoparticles on the surface of MWNTs can be easily controlled.

2. Experimental

2.1. Materials

MWNTs used in the current work were grown by chemical vapor deposition with a C₂H₂ gas on the Fe, Co catalytic layer at 973 K. The details of the preparation are shown in Refs. [20,21]. For purification, plain MWNTs were dispersed in concentrated nitric acid and refluxed for 4 h at 413 K. Subsequently, the MWNTs were filtered and washed with distilled water to remove acid and dried at 393 K overnight. The feeding materials Cu(CH₃COO)₂·H₂O, absolute ethanol and DEG were all analytical grade and used without further purification. Here, DEG is used instead of glycerol since it is a more moderate reductant and the valence of the product is more easily controlled.

2.2. Preparation of Cu₂O/MWNTs composites

The preparation process of Cu₂O/MWNTs composite includes two steps [22]. In the first step, 460 mg of Cu(CH₃COO)₂·H₂O was dissolved into 50 mL of absolute ethanol. Then, 50 mg of purified MWNTs was dispersed into the above solution with sonication for 30 min. After that, the mixture was magnetically stirred for 6 h and then placed in the air for 2 h. Finally, it was dried at 348 K for 10 h and Cu(CH₃COO)₂/MWNTs composites were obtained.

In the second step, the Cu(CH₃COO)₂/MWNTs composites were mixed with 50 mL of DEG under

sonication in a 250 mL round-bottomed flask for 15 min. Then the solution was heated to 140 °C under vigorous magnetical stirring. Subsequently, distilled water (2.5 mL) was added and the mixture was heated at 453 K for 2 h. Finally, a yellow–black suspension was obtained. After the system was cooled to room temperature in the air, the suspension was centrifuged, washed by absolute ethanol thrice to remove the remaining DEG and soluble by-product, and dried in a vacuum oven at 333 K for 6 h. The obtained Cu₂O/MWNTs composites were yellow–black.

2.3. Characterization of Cu₂O/MWNTs composites

X-ray powder diffraction (XRD) pattern of the prepared Cu₂O/MWNTs composites was carried out on a Rigaku D_{max} X_o-ray diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). A scan rate of $0.03^\circ \text{ s}^{-1}$ was applied to record the powder patterns for 2θ between $20^\circ \leq 2\theta \leq 65^\circ$. X-ray Photoelectron Spectrum (XPS) of the composites are detected at a PHI Quantum 2000 XPS system with a monochromatic AlK α source and a charge neutralizer. The morphology of Cu₂O/MWNTs composites was characterized by transmission electron microscopy (TEM) by a JEM-100CXV TEM using an accelerating voltage of 80 kV. High resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM 2010FEF electron microscope using an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) spectrum was detected by a Nicolet 560 E.S.P. FTIR spectrometer (USA) as KBr disks.

3. Results and discussion

3.1. Results

Fig. 1 shows the XRD pattern of the as-prepared Cu₂O/MWNTs composites. All the peaks are clearly distinguished. There are four peaks with 2θ values of 29.60, 36.52, 42.44 and 61.54, corresponding to $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 200 \rangle$ and $\langle 220 \rangle$ crystal planes of pure Cu₂O with cubic phase (JCDs 5-669), respectively. The peak at $2\theta = 26.02^\circ$ corresponds to the plane of (002) of graphite of MWNTs [23]. From the XRD pattern, it can be concluded that the obtained Cu₂O-MWNTs composites are composed of cubic Cu₂O and MWNTs. Meanwhile, the $\langle 111 \rangle$ reflection of the samples obtained is relatively strong. The result is different from the sample prepared by the polyol method with the assistance of long time sonication. In that case, the $\langle 200 \rangle$ reflection is the strongest [20]. The reason may be that long time sonication is beneficial for the formation of the stronger interaction between the precursor and MWNTs since more holes and defects

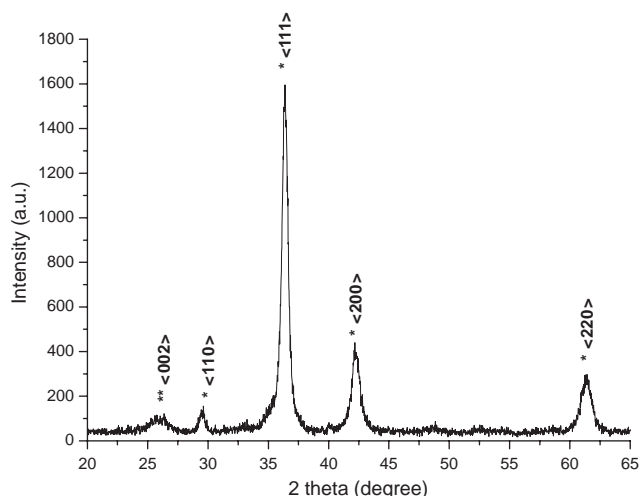


Fig. 1. XRD spectrum of the $\text{Cu}_2\text{O}/\text{MWNTs}$ composite. The symbol “**” stands for the peak corresponding to Cu_2O crystal and “*” stands for the peak ascribed to MWNT.

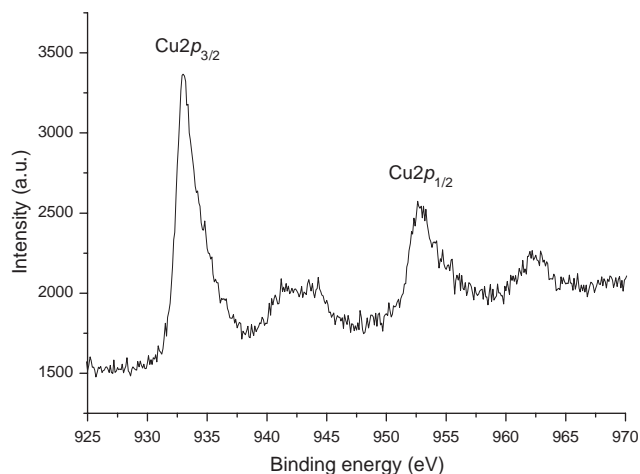


Fig. 2. XPS $\text{Cu } 2p$ level for $\text{Cu}_2\text{O}/\text{MWNTs}$ composites.

can be formed under similar condition in the presence of a polymer [24]. Moreover, the local high energy produced by sonication may be much higher than that generated by magnetical stirring [25] so that the interaction between the precursor and MWNTs may be enhanced greatly. The enhanced interaction between MWNTs and precursor can affect the growth direction of Cu_2O .

Fig. 2 shows the high resolution XPS spectrum for the $\text{Cu } 2p$ core level for the $\text{Cu}_2\text{O}/\text{MWNTs}$ composite. The peak at 932.6 eV, which is corrected with reference to $\text{C } 1s$ (284.6 eV), corresponding to the binding energy of $\text{Cu } 2p_{3/2}$, is in good agreement with data observed for copper (I) oxide [26]. Meanwhile, the occurrence of a weak satellite feature on the higher binding energy side of the $\text{Cu } 2p$ main peak indicates the presence of CuO on the surface of the composites [27]. The fact that no CuO

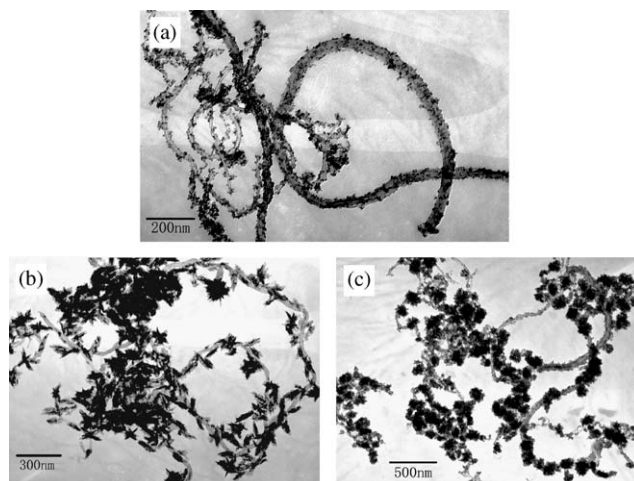


Fig. 3. TEM images of Cu_2O nanoparticles with different assembled morphology on MWNTs: (a) nanoparticle; (b) leafage; and (c) big spherical particle.

phase is found on the XRD pattern of the composites implies that the amount of CuO is tiny. This CuO may result from the oxidation of Cu_2O on the surface.

Fig. 3 shows a set of TEM images of $\text{Cu}_2\text{O}/\text{MWNTs}$ composite prepared under different conditions. In the polyol process, after water is added (the second step of the preparation process), when the system is directly heated from 413 to 453 K, Cu_2O nanoparticles deposited on the surface of MWNTs are separated and the particle size is uniform (Fig. 3a). When the temperature of the system keeps at 413 K for 10 min, then increases to 453 K and holds for 2 h, the finally obtained composites are shown (Fig. 3b), where no Cu_2O nanoparticles are found on the surface of MWNTs, but leafage-like Cu_2O particles are found. These Cu_2O leafages are likely to grow directly on the surface of MWNTs. When the temperature of the system keeps at 413 K for more than 20 min, both nanoparticles and big spherical particles of Cu_2O are found on the surface of MWNTs. Therefore, the morphology of the Cu_2O crystal deposited on the MWNTs can be easily controlled by the change of the experimental parameters.

In order to clearly observe the morphology and composition of different Cu_2O particles on the surface of MWNTs, HRTEM measurements of these samples are conducted (Fig. 4). It can be seen from Fig. 4a that Cu_2O nanoparticles are separately dotted on the surface of MWNTs. The “A” area is the graphite structure of MWNTs, of which the interplanar spacing is bigger than that of Cu_2O . The value is about 0.34 nm, which is similar to the distance between the adjacent straight lines of MWNTs, corresponding to the $\langle 002 \rangle$ spacing of graphite sheet [28]. The interplanar spacing of Cu_2O is about 0.25 nm shown in the “B” area of Fig. 4a, which corresponds to the $\langle 111 \rangle$ plane of the cubic Cu_2O . It is a good match with the result of XRD. Meanwhile, the

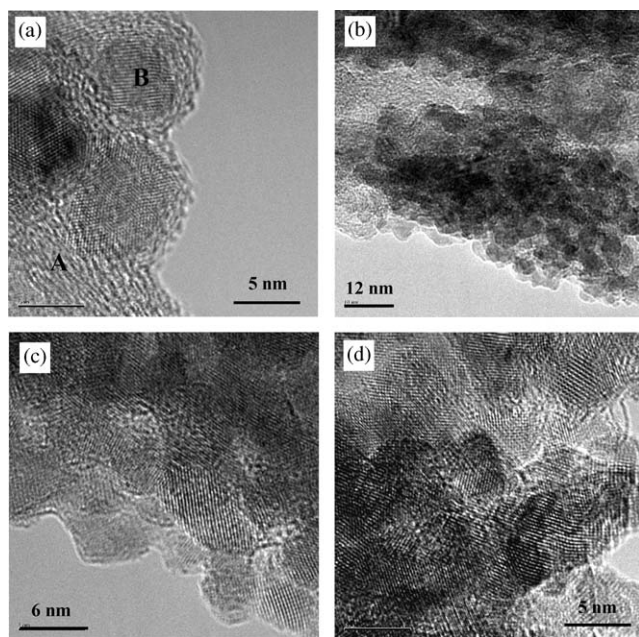


Fig. 4. HRTEM images of the morphology of Cu_2O on the surface of MWNTs. (a) HRTEM image corresponding to Fig. 3a; (b) and (c), HRTEM image corresponding to Fig. 3b; and (d) HRTEM image corresponding to Fig. 3c.

particle size of Cu_2O dotted on the surface of MWNTs is estimated to be about 8–10 nm. Figs. 4b and c are a set of HRTEM images corresponding to the sample shown in Fig. 3b. It can be seen that the leafage-like particles on the surface of MWNTs are assembled by small particles with the size 2–5 nm (Fig. 4c). The phenomenon is like the coating of MWNTs with thick layers of SnO_2 [29]. First, inner Cu_2O nanoparticles are immobilized on MWNTs through strong interaction. The agglomeration is then formed because of surface potential energy of individual nanocrystals. Moreover, the interplanar distance of the crystal is also 0.25 nm, identical to that shown in Fig. 4a. The HRTEM image corresponding to the sample shown in Fig. 3c is presented in Fig. 4d, which indicates that the big spherical Cu_2O particle on the surface of MWNTs is also assembled by small Cu_2O crystallite, similar to the coating shown in Ref. [29].

Fig. 5 shows the FTIR spectrum of $\text{Cu}_2\text{O}/\text{MWNTs}$ composites. The peak at 1557 cm^{-1} can be assigned to the carbon skeleton and the peaks near 1634 and 3447 cm^{-1} correspond to the bending vibration of adsorbed molecular water and stretching vibrations of OH group [29]. The peaks at 2361 and 2341 cm^{-1} are assigned to the adsorbed CO_2 . The peak at 1772 cm^{-1} corresponds to carboxyl groups. Meanwhile, the peak at low wavenumber 630 cm^{-1} should be assigned to bulk Cu_2O [27]. Compared with the spectra of pure Cu_2O and the treated MWNTs (supplementary data), it can be found that when Cu_2O is dotted, deposited or coated on

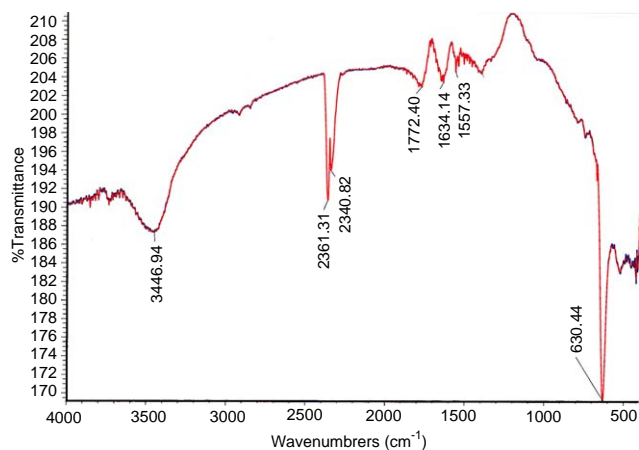


Fig. 5. FTIR spectrum of $\text{Cu}_2\text{O}/\text{MWNTs}$ composites.

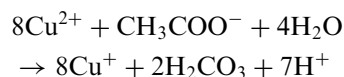
the surface of MWNTs, the characteristic peak of carbon skeleton shift from 1588 to 1557 cm^{-1} . The peaks assigned to carboxyl group shifts from 1712 to 1772 cm^{-1} and its relative intensity increases. Meanwhile, the characteristic peak of Cu_2O also has five wavenumbers change, from 625 to 630 cm^{-1} . This significant shift of the characteristic peaks and increase of the intensity results from the strong interaction between MWNTs and Cu_2O [29]. That is, the interaction leads to the homogeneous Cu_2O -dotted, leafage-like Cu_2O deposited and big spherical Cu_2O particles coated or deposited on the surface of MWNTs.

3.2. Discussions

The general scheme for the formation of the metal oxide particles by a polyol process involves three procedures as follows: (1) dissolution of the metal salts in solution; (2) precipitation of an intermediate solid phase that acts as a reservoir phase and controls the supersaturation concentration of the metal ions in solution; and (3) nucleation and growth of the metal oxide particles from the solution at a temperature close to the boiling point of the polyol [30]. Heterogeneous nucleation can be achieved by introducing into the solution a small amount of other substance, which can act as nuclei for further growth of metal oxide particles. In this study, MWNTs are refluxed with concentrated HNO_3 at 413 K for 4 h . Thus, the outer surface of MWNTs can certainly be modified with functional groups [20,29]. During the first step of the preparation process, the precursor diffuses to the surface of MWNTs; interacts with the surface carboxyl groups by electrostatic attraction; and then serves as nucleation precursor [29]. This process can be confirmed directly by FTIR spectra shown in Fig. 5 and supplementary data. Therefore, for the preparation of $\text{Cu}_2\text{O}/\text{MWNTs}$ composites by our polyol process, the procedure for the deposition of copper acetate on the surface of

MWNTs should be added as the first one so that the modified scheme has four procedures. Herein, MWNTs can provide nuclei or function as nucleation centers for Cu_2O to directly grow on the surface because many Cu_2O nanoparticles are observed to be coated on their surface (Fig. 3).

In the second step of the preparation process, on the one hand, DEG can produce some products with reduction property [31]. On the other hand, after the precursor $\text{Cu}(\text{OOCCH}_3)_2/\text{MWNTs}$ is mixed with DEG under vigorous stirring, $\text{Cu}(\text{OOCCH}_3)_2$ is dissolved in this solvent. Before reducing reaction, water must be added since no Cu_2O but metal copper nanoparticles were formed without water at 413 K for the same reaction time. It is proposed that the added water makes the concentration of these products derived from DEG decrease so that their reduction ability is detrimental. Meanwhile, with the assistance of water, Cu^+ is more easily to be formed according to the following equation [32]:



Thus, the Cu (I) oxide is finally obtained. Moreover, water can improve the hydrolysis of copper (II) metal ion [33]. Thus, the formation of CuO (an intermediate solid phase), one of the four important procedures, is easier, and the supersaturation concentration of Cu^{2+} in solution may be easily controlled through the control of the amount of the formed CuO. Therefore, at 453 K, the last procedure, nucleation and growth of copper(I) oxide on the surface of MWNTs from the solution is achieved.

The control of the assembled morphology of Cu_2O on the surface of MWNTs can be attributed to the second step in DEG system after a suitable amount of water is added into the system at 413 K. Polyol is an excellent capping reagent as well as a good dispersive medium, which plays a critical role in the nucleation and growth of the crystalline Cu_2O [34]. It is reported that monodisperse colloids can be obtained when the nucleation step is fast enough and the growth step does not interfere with the nucleation step [35]. Here, no matter what kind of assembled morphology of Cu_2O is on the surface of MWNTs, the particle size dispersion of Cu_2O is almost uniform. It may result from the solvent DEG, which can enhance and shorten the nucleation step, because without MWNTs, the uniform Cu_2O nanoparticles are also obtained (Fig. 6) in the presence of DEG. The particle size of pure Cu_2O is more than 10 nm.

Solubility of solutes can change the results of chemical reactions in solutions [36]. When the solution undergoes supersaturation, solid particles are formed through nucleation and crystal growth. At lower degrees of supersaturation, the occurrence of heterogeneous nu-

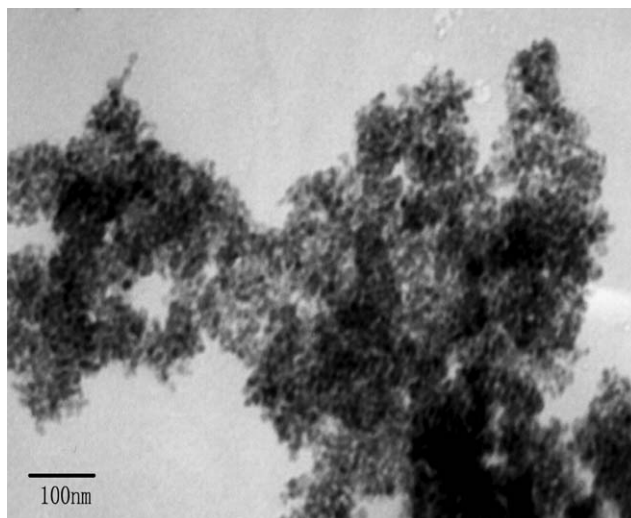


Fig. 6. TEM image of cubic Cu_2O prepared with polyol process without the presence of MWNTs.

cleation on foreign surfaces is more preferential in the solution [37]. In the present study, the concentration of copper acetate in DEG is low, which results in a low degree of supersaturation and preferential heterogeneous nucleation. With the presence of MWNTs, Cu_2O can grow into nuclei on the surface of MWNTs or grow directly from the surface of MWNTs by heterogeneous nucleation. Without MWNTs, Cu_2O may grow into nuclei directly from solution. Crystal growth in solution is characterized by two fundamental processes. In a mass transport process in crystal growth, the solute is transported from the bulk of the solution to the solution/crystal interface. Then the solute is incorporated into the crystal by a surface kinetics process. The driving force of the growth is a steep gradient of the solute concentration generated around the growing crystal [36]. When temperature directly reaches to 453 K, the diameter of the particles on the surface of MWNTs is larger because there are so many solutes around the growing crystal at a higher temperature, which can supply Cu_2O immediately. Thus, after 2 h, the particle size can reach 8–10 nm. Meanwhile, when the temperature is maintained at 413 K for a period of time, the solute cannot transport as quickly as it does at 453 K to the solution/crystal interface. It is not easy for Cu_2O to grow large since the solute is not enough around the crystal on the surface of MWNTs and Cu_2O cannot be supplied in time. The crystal size may remain unchanged after the heating temperature increases to 453 K. Thus, the finally obtained Cu_2O on the surface of MWNTs is smaller.

According to the data of XRD pattern for pure Cu_2O , the mean particle size of Cu_2O calculated by Scherrer equation for the main diffraction peak is about 6.5 nm, which is close to the size shown in TEM (Fig. 6). However, that of Cu_2O in the composites is about

15.6 nm, which is greater than the size observed in TEM (Fig. 4). Therefore, the presence of MWNTs has a great effect on the crystallite size of Cu_2O .

Besides the particles on the surface of MWNTs, there are particles in solution although the mole ratio of copper and carbon is about 1:1.8. These particles have the tendency to be assembled, which can be confirmed by the fact that the mean particle size of Cu_2O in the composites is much larger than that shown in TEM (Fig. 4). If the particle size is larger, particles cannot be easily assembled together because the surface potential energy for larger particles is not great. Therefore, individual Cu_2O nanoparticles with the size 8–10 nm can be dotted on the surface of MWNTs (Fig. 3a). However, when the temperature is maintained at 413 K for a period of time and then increased to 453 K, the small particles (2–5 nm) present in the solution are apt to be assembled onto the Cu_2O nanoparticles, which have attached on the surface of MWNTs, to overcome the surface potential energy of the individual nanocrystals under some limitation. Thus, the morphology of leafage and big spherical particles on the surface of MWNTs is formed. The reason that the two different morphologies are formed on the surface of MWNTs is not clear at present. It may be that when the temperature is maintained at 413 K for a longer time, many more particles with small size are assembled into a spherical ball since the spherical state is more stable and there is enough time to complete the process. We have tried to prepare the assembled Cu_2O of leafage-like morphology and big spherical Cu_2O particles without MWNTs but failed. The obtained materials are shown in Fig. 6. Therefore, the presence of MWNTs favors the formation of the assembled morphology of Cu_2O as shown in Figs. 3b and c. It is speculated that the role of MWNTs is to disperse assembled Cu_2O particles, confine Cu_2O particles on their surface not to grow very large, and affect the tiny particles around them. As for the big particles, which are present in the system due to the assemblage of small particles, it is also related to MWNTs since there are no big particles of pure Cu_2O in the system without MWNTs. Details are needed to explore further.

4. Conclusions

Cu_2O /MWNTs composites can be synthesized through a polyol process by using DEG as the solvent and reducing agent. Under different experimental conditions, Cu_2O on the surface of MWNTs changes from monodisperse nanoparticles, leafage-like particles to larger spheres. The formation of Cu_2O with different morphologies is related to the Cu_2O nucleation and growth process under different conditions. Furthermore, the presence of MWNTs is also responsible for the formation.

Based on this study and other reports [38], we expect that this polyol process can be used to prepare the other metal oxide or metal/MWNTs composites.

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Appendix A. Supplementary data

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2005.02.016](https://doi.org/10.1016/j.jssc.2005.02.016).

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