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Synthesis of Cu(CuO)/Single Walled Carbon Nanotubes Composite by Electro-Deposition and Its Sensitive Gas Discrimination to NO

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In this paper, the Cu(CuO)/single walled carbon nanotubes composite was synthesized by direct current electrochemical deposition. The morphology of Cu(CuO)/single walled carbon nanotubes composite was investigated by SEM, TEM, Raman and UV-VIS-NIR. The electrical performance of the composite (especially the resistance) was greatly improved, which could be applied into the facture of NO-gas sensor in the near future.

Key Words: Electro-deposition, Single walled carbon nanotubes, Composite, NO.

INTRODUCTION

In 20th century, carbon nanotubes has been considered to be one of the most promising materials. Because of its unique structure and its nanosize, apparatus based on multi-walled carbon nanotubes have been applied in electrochemical sensors and transducers for a wide range of biologically active ananlytes[1-3]. Single-walled carbon nanotubes have more unique properties than multi-walled carbon nanotubes, they may exhibit much better if modified by other materials. For example, there are many measures to realize the admixture of single-walled carbon nanotubes and metal particles or metallic oxides, which includes electrochemical methods[4], thermal decomposition[5], *etc.*

The sorption of metal particles onto functionalized carbon nanotubes has been investigated[6]. While the morphology of the composite differs a lot through different synthetic methods, a convenient, inexpensive method is of great importance and electro-deposition can be taken as a good choice. Carbon nanotubes decorated by noble metals such as Pb, Ag, Au and Pt[7] have already been studied through electro-deposition and Ni[8], Cu[5] have been also investigated these years. The morphology of metal particles on the surface of carbon nanotubes depends on the predisposal of carbon nanotubes[6], preparation method of single-walled carbon nanotubes, also its type and density, the distance of electrodes and other electro-parameters[8] involved.

The mechanical properties of Cu reinforced by carbon nanotubes composite can be improved. For example, if synthesized by powder metallurgy method, the coefficient of friction of the Cu/CNTs composite decreases with increasing the mass fraction of the carbon nanotubes and the achieved friction coefficient of the carbon nanotubes component is 0.15[9]. The grain size of Cu/CNTs composite *via* ball milling and high-pressure torson is less than 25 nm[10]. In our experiment, the grain size of Cu is ranging from 5 nm to 30 nm. Of course, the homogeneous distribution of carbon nanotubes in Cu matrix is the most critical issue to enhance the physical and mechanical properties of the composite. By using electroless copper deposition process on the carbon nanotubes surface, the homogeneity could be futher increased and the agglomerations of carbon nanotubes at the copper grain boundaries are decreased[11].

Being a common pollution in the air, NOx could seriously harm to property and organic organisms. Every year, millions tons of NOx is drained into air from two sources, one origins from natural circulation, the other is from the consumption of fossil fuel and industrial production. Sensors based on Cu is sensitive to NO[12].

In this paper, the morphology of Cu(CuO)/SWCNTs composite is studied. While placed in a NO atmosphere, the resistance of the above composite is changing evidently. And the composite can be manufactured into NOx sensor with higher sensitivity.

EXPERIMENTAL

The single-walled carbon nanotubes in this experiment was achieved through arc discharge method and was functionalized by base-disposal, acid-disposal after purified. The salt origin was from $CuCl_2$ and a certain amount of surfactant was added to improve the dispersion state of single-walled carbon nanotubes. The volume of electrolytic cell was 60 mL. Al plate were employed as anode with the effect electrode area of 2 × 1.5 cm, pure Cu sheet employed as cathode with the effect electrode area of 2 × 1.5 cm. In the electro-deposition, the potentiostat (ZF-9, made in Shanghai, China) was controlled at 0.3 V. The deposition time was from 50s to 3000s.

An interdigitated electrode was fabricated for the following gas-sensing. The dimension of the electrode was 7 mm × 5 mm × 0.38 mm, with the interelectrode distance of 50 μm. The Cu/SWCNTs composite with different $CuCl_2$ concentration were dispersed in acetone to form a homogeneous, stabilized solution. The aforesaid solution was spin-coated onto this interdigitated electrode to observe the gas-sensing behaviour of the composite[13]. The volume of the gas chamber was 250 mL.

SEM was carried out on a XL-30-ESEM-FEG scanning electron microscope with an operating voltage varying from 5 to 20 kV. The optimum resolution of the SEM was 1.5 nm. TEM was employed for the study of the structure of Cu based single-walled carbon nanotubes by JEOL-2100 electron microscope. Raman spectra were collected at ambient temperature on a Jobin Yvon HR 800 micro-Raman spectrometer.

RESULTS AND DISCUSSION

During the electrodeposition, the morphology of the composite deposited on cathode is shown in Fig. 1. Of course, under the action of current, the detailed morphology is various as presented in Fig. 1. In the above process, as the deposition time increasing, the diameter of Cu particles grow with the diameter ranging from several nanometers to hundreds of nanometers and the content of C, Cu, O element in the Cu(CuO)/SWCNTs is changing. In consideration of carbon nanotubes content, optimal morphology, etc, the corresponding parameters are optimized and the optimal composite is marked as the composite-final.

The Raman spectra in Fig. 2b is rougher than that of Fig. 2c and Fig. 2a, that is to say the metal particles in the composite deposited on cathode in Fig. 2b has effect on the Raman spectra and after electrodeposition the vibration frequency of G-band is also changed in Fig. 2b and Fig. 2c compared with Fig. 2a[14]. Also, the diameter of the single walled nanotubes calculated is about 1.23 nm.

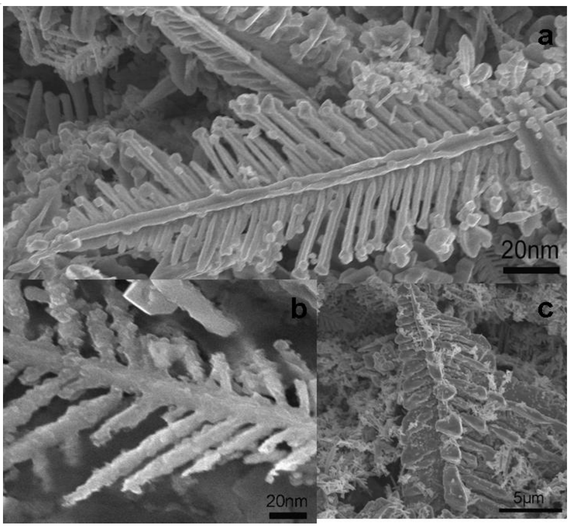


Fig. 1. SEM images of Cu(CuO)/SWCNTs composite of different morphology

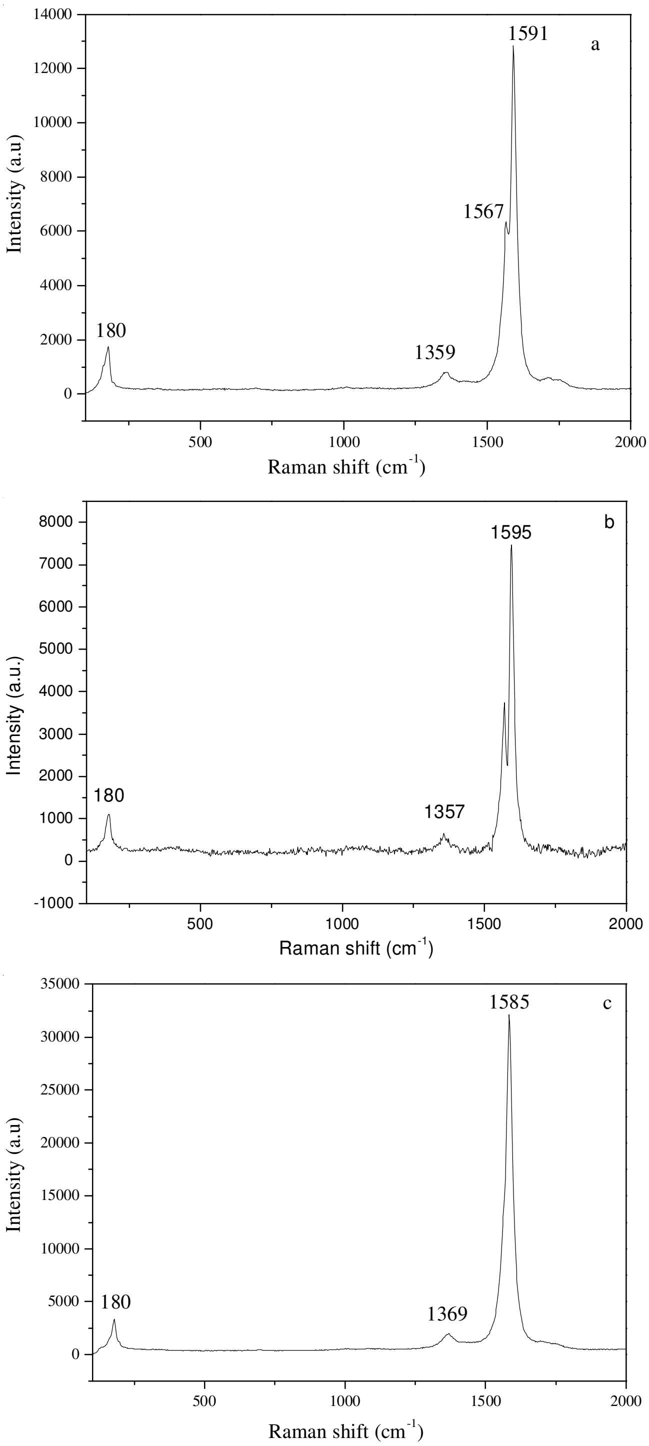
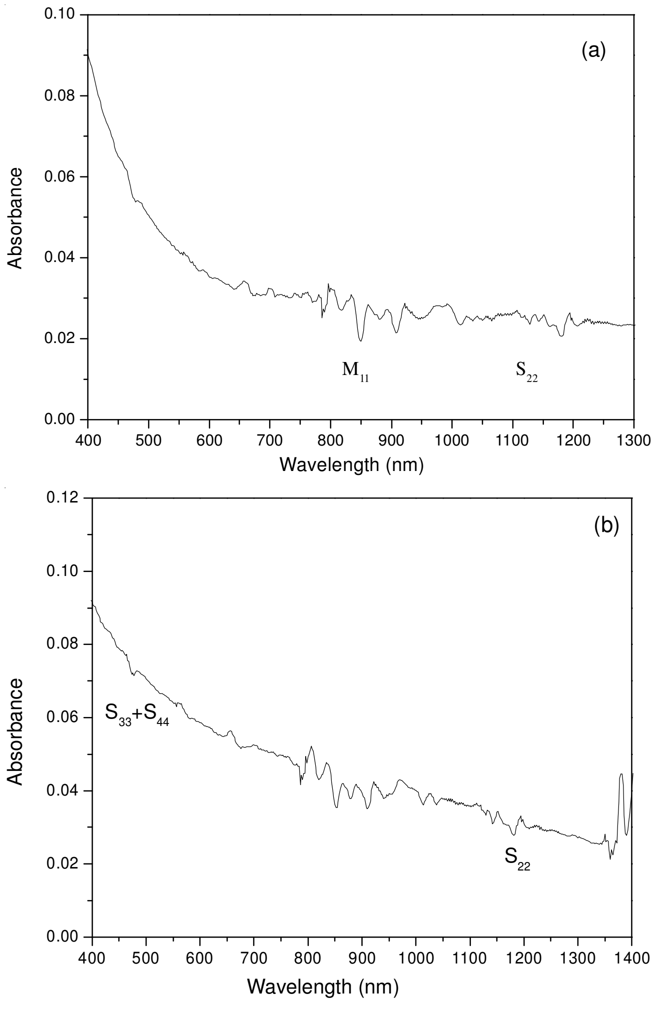


Fig. 2. Raman spectra of: a) purified single walled nanotubes ; b) composite deposited on cathode; c) electrolyte after electrodeposition

The optical absorption of metallic and semiconducting single walled nanotubes could be largely affected by their surrounding compositions, such as the interactions with other tubes, the surfactant used for dispersion, even the energy gaps of the single walled nanotubes *etc*.[15].

Lian *et al.*[16] found that the radial breathing modes (RBM) in Raman spectra has relationship with the characteristic absorption bands in UV-VIS absorption spectra: the Raman spectra of single walled nanotubes used in this paper is shown in Fig. 2., the radial breathing modes is about 180 cm^{-1} and the relative three characteristic absorption bands observed at approximately 941, 374-466 and 310 nm according to Ref.[16] (because of the difference of single walled nanotubes, the absorption bands observed in my experiment is 1200 nm, 800 nm and 500 nm respectively): 1200 nm is attributed to electronic transitions between the second pair of VHSs in semconducting-SWNTs (S_{22}), 500 nm to the third and fourth pair of VHSs in semconducting-SWNTs ($S_{33} + S_{44}$) and 800 nm to the first pair of singularity in metallic-SWNTs (M_{11}).

The ordinate-absorption intensity of Fig. 3b is a little bit stronger than that in Fig. 3a and Fig. 3c and it is to say that the proportion of semconducting-SWNTs (s-SWNTs) and metallic-SWNTs (m-SWNTs) is altered after electrodeposition. The UV-VIS-NIR result of composite-final shows that after the electrodeposition process the composite deposited on cathode has more s-single-walled carbon nanotubes (Fig. 3b) than that of electrolyte (Fig. 3c). That is to say that most of s-single-walled carbon nanotubes is deposited on cathode electrode. It is known that it is difficult and time-consuming to separate s-single-walled carbon nanotubes from m-single-walled carbon nanotubes, while in this experiment s-single-walled carbon nanotubes can be enriched to a certain extent.



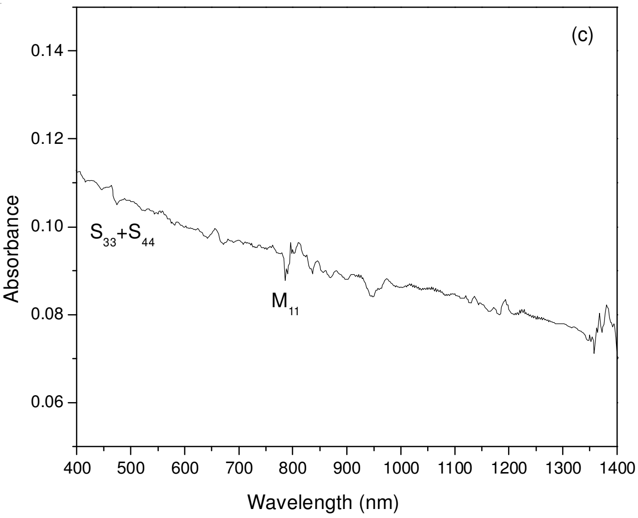


Fig. 3. The UV-VIS-NIR absorption spectra: a) purified single-walled carbon nanotubes; b) the Cu(CuO)/SWCNTs composite deposited on cathode; c) the electrolyte collected after electro-deposition

Fig. 4 shows the surfacial morphology of the composite-final, which reflects the combination of metal particles and carbon nanotubes. Also from Fig. 4a, it can be obseved that the Cu/CuO particles are enwrapped by the single-walled carbon nanotubes bundles and the average diameter of Cu particles is about 20 nm, while on the edge of the composite the diameter of Cu particles can be as large as several hundred nanometers as in Fig. 4b. According to the data of EDAX, most of the composite is Cu with small amount of C and O. Because of the small diameter of Cu, some of Cu particles may be oxidated into CuO. Here, carbon nanotubes are taken as the joint of Cu particles (or CuO particles), which could strengthen the mechanical property of the composite.

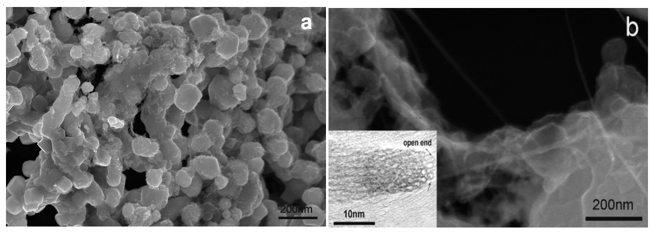


Fig. 4. SEM images of Cu(CuO)/SWCMTs composite Cu^{2+} = 0.42 mol/L

Fig. 4b showed that the diameter of the single walled carbon nanotube bundle is about 10 nm and the diameter of single walled carbon nanotube is about 1.5 nm which is in conformity with the information of the Raman spectroscopy, it can be also seen that on the fringe of the composite, the shape of Cu is irregular, which may be due to the oxidation of Cu.

In the composite, metal particles connect carbon nanotube in two ways: the Cu/CuO particles are not only enwrapped by the single-walled carbon nanotubes bundles, but surround single walled carbon nanotube bundle as presented in Fig. 5. Relatively speaking, metal particles and carbon nanotube of the second way (as in Fig. 5) connect firmmer than in the first way (as in Fig. 4). Different sizes of Cu(CuO) particles are chained by carbon nanotubes, the mechanical property of the composite is greatly improved[11]. Comparatively speaking, the

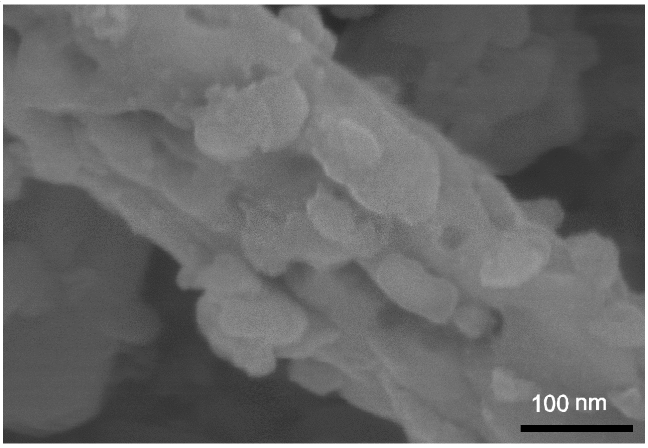


Fig. 5. SEM image of Cu(CuO)/SWCNTs composite Cu^{2+} = 0.1 mol/L

interface of metal and carbon nanotubes could stand more load and transmit stress effectively.

After the electrodeposition, the powder of as-fabricated composite is exfoliated from cathode electrode and then ultrasonicated carefully in acetone. The middle layer of the suspension is then dropped onto an interdigitated electrode for further resistance tests and placed into a NO atmosphere afterwards. The resistance of the material changes evidently as in Fig. 6.

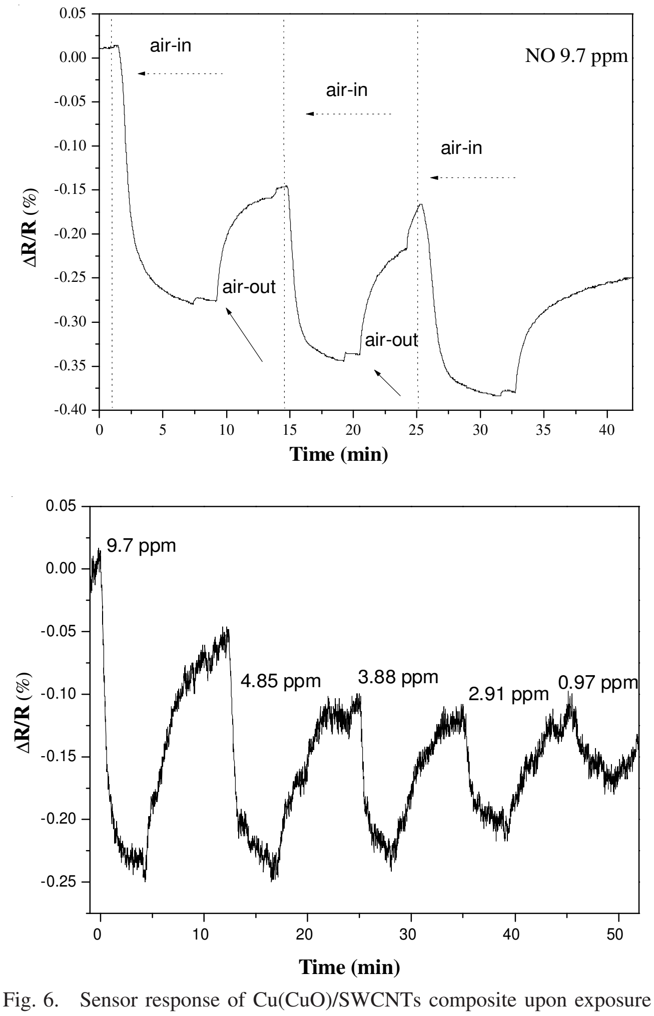


Fig. 6. Sensor response of Cu(CuO)/SWCNTs composite upon exposure to NOx molecules; temperature: 18 ºC; humidity =30 %

Ramgir *et al.*[17] found that CuO thim films have response in the NO atmosphere. While the joint among CuO particles is weak, the material made of CuO does not have fine mechanical strength which hinders its further application. In this paper, the composite of Cu(CuO)/SWCNTs is synthesized, not only the mechanical property of the composite is improved, the performance of gas sensor would also be improved as in Fig. 6. During the resistance tests, the composite is placed under different concentration of NO ranging from 9.7 ppm to 0.97 ppm. The response time is about two minutes and the lowest detection limit is below 1 ppm with the sensitivity of higher than 10 %. Relative electrical properties are being studying.

Conclusion

Cu(CuO)/SWCNTs composite is synthesized by electrodeposition and is studied by SEM and TEM. The electrical performance of the composite is improved owing to the cohesion of the carbon nanotubes. During the gas sensitivity tests, the composite is sensitive to NO with an obvious alteration of resistance and the lower detection limit can be lower than 1 ppm.

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