

Coating of ZnO nanorods with nanosized silver particles by electroless plating process

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Abstract

Metallodielectric composites of silver-coated ZnO nanorods were prepared comprising the formation of ZnO nanorod substrate by aqueous solution reaction and the deposition of silver nanoparticles by electroless plating technique. Silver-coated ZnO nanorod composites were characterized with electron microscopy and X-ray diffraction. The results showed that metallic Ag of high crystallinity covered on the surfaces of hexagonal ZnO nanorods. The addition of silver nanoparticles had an effect on the infrared emissivity properties of the composites. The infrared emissivity value of ZnO nanorods was obviously decreased by the introduction of silver nanoparticles onto the ZnO surface. By controlling the silver deposition, the infrared emissivity properties could be tailored.

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1. Introduction

Metallodielectric composite particles are of extensive scientific and technological interest due to their unique and tailored properties for various applications in materials science [1–3]. Semiconductor materials are usually modified by nanometer-sized metal clusters (e.g., Ag and Au) and have potential applications in optics, catalysis, and so forth. Several investigators have reported on the coating of silica sphere with a thin layer of silver [4–7] and gold [8,9].

In the present work, we describe a simple electroless plating method to deposit silver nanoparticles on ZnO nanorods, which has been used for decoration of carbon nanotubes [10] and spherical colloids [5,6,11] such as silica, but has not been employed on ZnO nanorods modification until now. The two steps of the formation of the composites are presented in Fig. 1. First, the surface of ZnO nanorod is modified with Sn^{2+} ions via electrostatic attraction. Subsequently, a redox reaction is carried out on the ZnO surface after the addition of Ag^+ ions, on which Sn^{2+} ions are oxidized to Sn^{4+} and at the same time Ag^+ ions are reduced into metallic Ag. The Ag nanoparticles finally anchor on

the surface of ZnO nanorod. The structure and infrared emissivity of obtained silver-coated ZnO nanorod composites were investigated.

2. Experimental

2.1. Materials

Methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99%), zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%], silver nitrate (AgNO_3 , 99.5%), stannous (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), trifluoroacetic acid (CF_3COOH , 99.5%) and ammonia water (NH_3 , 28%) were all obtained from Shanghai Chemical reagent Company and used as received without further purification. In all preparations absolute ethanol and deionized water were used.

2.2. Methods

Various two-dimensional ZnO of microrods, nanorods, as well as nanowires can be obtained by varying the concentration of the precursor [12,13]. In detail, by decreasing the precursor concentration by an order of magnitude from 0.1 M to 0.001 M, the width of two-dimensional ZnO varied trending to nanometer-size. Herein, 0.01 M of zinc salt was chosen to form ZnO

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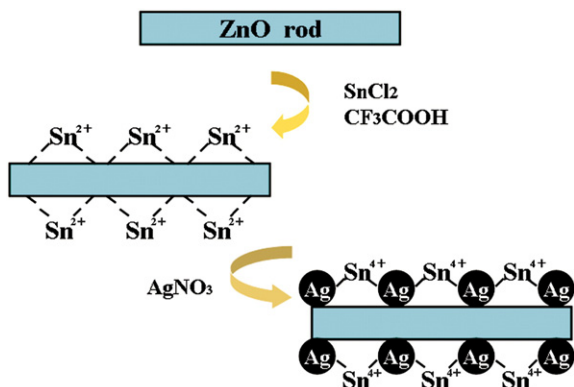


Fig. 1. Schematic illustration for the deposition procedure of silver nanoparticles on ZnO nanorod.

nanorods, which were directly synthesized by the thermal decomposition of methenamine and zinc nitrate in aqueous solution. Typically, 40 mL of an equimolar aqueous solution of zinc nitrate and methenamine (10 mM) was added to a flask and heated at a constant temperature of 95 °C for 1.5 h with vigorous stirring. As expected, ZnO nanorods with the diameter of about several hundred nanometers were obtained with the observation of morphology of samples.

The deposition and growth of Ag nanoparticles on the surfaces of ZnO nanorods were carried out as follows. The ZnO nanorods (40 mg) were added to 20 mL of mixture of methanol and water (1:2, w/w) containing SnCl_2 (0.029 M) and CF_3COOH (0.072 M). After the agitation for 30 min, the suspension was centrifuged, removing supernatant, and adding 10 mL of water, followed by 10 mL of ammonical AgNO_3 solution. When the reaction was finished, a dark brown precipitation was observed. The resulting silver-coated ZnO nanorod composites were centrifugally separated from the suspension and ultrasonically washed with water. By varying the number of deposition cycles, the Ag nanoparticles of desired dimension and density could be attached on the ZnO surface.

2.3. Characterization

Transmission electron microscopy (TEM) was performed with a Hitachi H-600 microscope operating at 120 kV. Samples were prepared by placing drops of the colloids dispersion on a Cu grid and letting the solvent evaporate at room temperature. Scanning electron microscopy (SEM) was performed with a microscope of LEO-1530VP. X-ray diffraction (XRD) pattern was performed with an X-ray diffractometer (XD-3A) operating at 40 kV and 30 mA with $\text{CuK}\alpha$ radiation. IR reflectance spectra

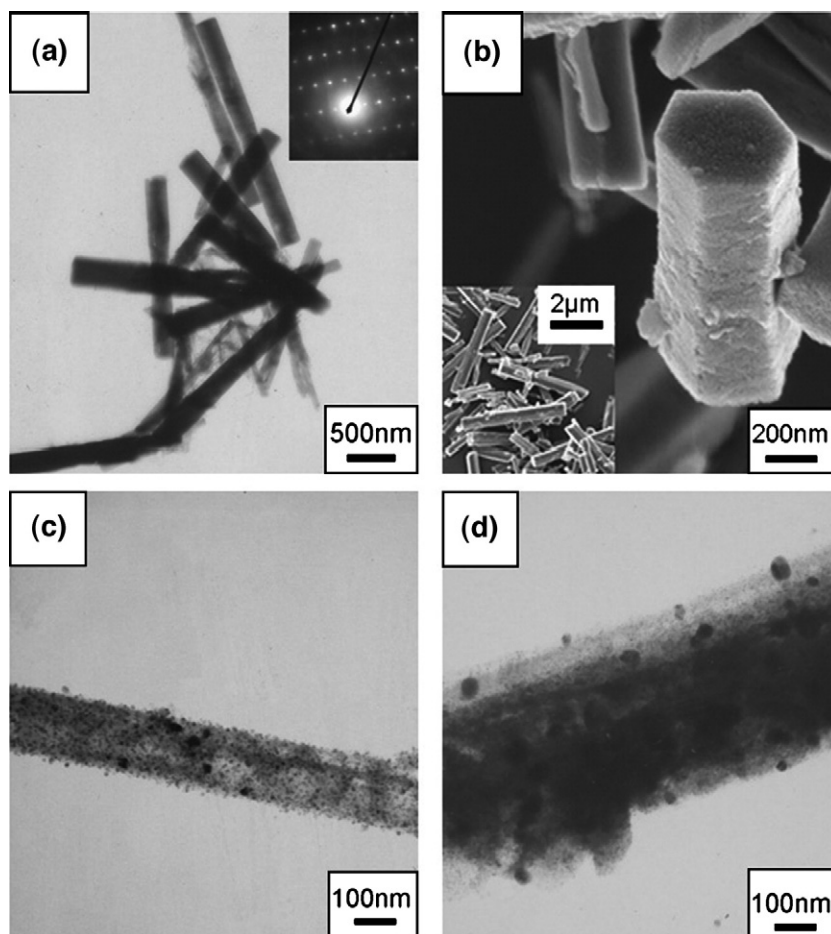


Fig. 2. SEM and TEM images: (a and b) TEM and SEM images of the ZnO nanorods (insets: corresponding selected-area electron diffraction (SAED) pattern in a; the low-resolution image in b), (c and d) TEM images of ZnO nanorod after the first and the second deposition of silver nanoparticles, respectively.

were measured with a Nicolet Magna-IR 750 spectrometer. Infrared emissivity values of the samples were carried out on IRE-I Infrared emissivity measurement instrument of Shanghai Institute of Technology and Physics, China.

3. Results and discussion

Fig. 2 shows the TEM and SEM micrographs of the ZnO nanorods and Ag-coated ZnO nanorod composites. As expected, hexagonal nanorods with the diameter ranged from 300 to 600 nm are obtained. Furthermore, each nanorod shows a uniform diameter throughout its entire length. The nanorods are single-crystalline and grow along the *c* axis of [001] direction [13,14] as indicated by the corresponding SAED pattern (Fig. 2a, inset). The XRD pattern of ZnO nanorods is shown in Fig. 3a. Sharp diffraction peaks corresponding to the hexagonal wurtzite structure of ZnO with the diffraction peaks of the (100), (002), (101), (102), (110) and (103) planes are observed, indicating the formation of pure ZnO of high crystallinity (JCPDS file, No. 36-1451). In addition, this result is in agreement with the TEM measurements. No obvious XRD peaks arising from impurities are found, suggesting wurtzite zinc oxide was produced by aqueous solution reaction.

Before the deposition of Ag nanoparticles on the ZnO surface, pre-modification of ZnO with Sn^{2+} ions was necessary to generate suitable surface properties, which could secure the reduction of Ag proceeded on the surface of ZnO, which is similar to the work by Liz-Marzan et al. [5,6] and Wang et al. [11] concerning silver modification on the surfaces of silica spheres.

TEM micrographs (Fig. 2c and d) represent the ZnO nanorod after the first and second silver deposition. After the first deposition, an incalculability of remarkably monodisperse silver nanoparticles with a diameter of approximately 10 nm is uniformly distributed on the surface of ZnO nanorod in agreement with the phenomenon referring to Ag deposition on the surfaces of silica spheres in Ref. [6]. The growth of silver nanoparticles was carried out by repeating the coating step the same as the first coating. It is obvious that the surface coverage of Ag nanoparticles is increased (Fig. 2d), resulting from not only the fresh formation of Ag nanoparticles but also the growth of previously existing Ag nanoparticles. After the second deposition, the size of Ag nanoparticles reaches around 60 nm. XRD pattern of silver-coated ZnO nanorod composites after the first deposition in Fig. 3b exhibits other diffraction peaks compared to that of pure ZnO nanorods, which corresponded to the face-centered cubic (*fcc*) structure of metallic Ag (JCPDS file, No. 4-783). The result further demonstrates that the electronation occurs on the surfaces of ZnO nanorods with the formation of Ag nanoparticles. In this case, the characteristic diffraction peaks of hexagonal wurtzite ZnO disappear due to the addition of large amount of Ag nanoparticles. The Ag nanoparticles size calculated by Scherrer

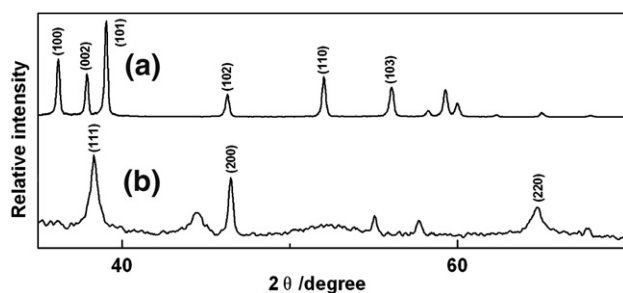


Fig. 3. XRD spectra of (a) pure ZnO nanorods and (b) Ag-coated ZnO nanorods corresponding to Fig. 2c.

Table 1
Infrared emissivity values of samples

Samples	Infrared emissivity (ϵ_{TIR} at 8–14 μm)
ZnO nanorods	0.964
Ag-coated ZnO nanorods ^a	0.763
Ag-coated ZnO nanorods ^b	0.655

ZnO nanorods after the first^a and the second^b silver deposition.

formula is about 12.5 nm in accord with that obtained from TEM (Fig. 2c).

Several kinds of materials with low infrared emissivity, such as sol-gel indium tin oxide films of various composition, grafted collagen/ In_2O_3 nanocomposites, and polyimide/mesoporous silica composite films et al. have been investigated [15–17]. But little research is related to the infrared emissivity properties of metal/inorganic composites. The infrared emissivity values (ϵ_{TIR}) of the samples at wavelength of 8–14 μm are summarized in Table 1. It is clear that pure ZnO nanorods exhibit high infrared emissivity value of 0.964. With the deposition of Ag nanoparticles, an abrupt decrease of the ϵ_{TIR} appeared. On the basis of the law of Kirchhoff [18]

$$\epsilon = 1 - R$$

(where R =reflectance), when a solid is opaque in a frequency region, the spectral emissivity is directly related to the bulk reflectance of the materials. The ϵ_{TIR} value decreases as the reflectance increases. IR reflectance spectra of the ZnO and Ag-coated ZnO after the second silver deposition are shown in Fig. 4. Compared to Fig. 4a, the increase of the reflectance in the wavelength from 1250 cm^{-1} to 700 cm^{-1} (about 8–14 μm) is obviously observed in Fig. 4b after the silver deposition, which is in correspondence to the variation of the infrared

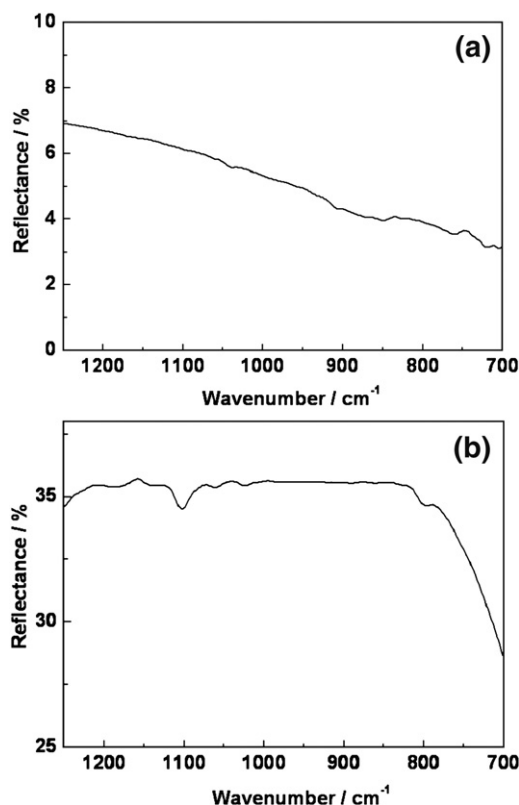


Fig. 4. Reflectance spectra of (a) ZnO nanorods and (b) Ag-coated ZnO nanorod composites after the second silver deposition.

emissivity value. In addition, with the increase of the quantity and the dimension of the Ag nanoparticles deposited, the ϵ_{TIR} value further decreased. It can be proved that metal materials with the advantage of high reflectance decrease the infrared emissivity value effectively.

4. Conclusions

Silver nanoparticles were successfully deposited on the surfaces of ZnO nanorods by the electroless plating method. The density and the size of Ag nanoparticles are tailored by repeating the cycles of Ag deposition process with further controlling the corresponding infrared emissivity values. The infrared emissivity values decreased remarkably after the introduction of Ag of high reflectance. This work opens up new possibilities for the production of low infrared emissivity materials by doping metal to semiconductor materials. The detailed research will be reported elsewhere.

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