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Tribulus terrestris leaf extract assisted green synthesis and gas sensing properties of Ag-coated ZnO nanoparticles

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ABSTRACT

Ag-coated ZnO nanoparticles are synthesized by a biological process using *Tribulus terrestris* leaf extract. The characterization results confirmed that Ag nanoparticles have been coated on the surface of ZnO nanoparticles. Ag nanoparticles on the surface of ZnO are spherical in shape, ranging between 6 and 10 nm in diameter. Gas-sensing tests reveal that all the resistance values of the sensors decrease with increasing of eathanol concentration. Moreover, the resistance of Ag-coated ZnO sensor was generally much lower than that of pure ZnO sensor. Thus, Ag nanoparticles coating paly an important role for the sensitivity of the gas sensor working at room temperature.

1. Introduction

Zinc oxide (ZnO) is a thermally stable n-type wurtzite structure semiconductor with a wide direct band gap of 3.37 eV at room temperature and a large exciton binding wide direct band gap of 3.37 eV at room temperature and a large exciton binding energy of bout 60 meV [1]. ZnO as one of the important semiconductor materials has attracted considerable attention in recent years for its potential applications in ultraviolet laser, high power light emitting diode, gas sensor and spintronics devices [2–4]. Nanostructured ZnO, due to its high surface-to-volume ratio, also has potential advantages in detecting volatile gas [5]. Similar to other semiconducting oxides, it also suffers from the inherent drawback of poor selectivity or cross sensor response. Accordingly, it is often modified with different additives/sensitizers like gold [6,7], platinum [8] and silver [9] to achieve selective sensors towards different gases with enhanced sensor response. Typically, the noble metal acts as a catalyst to modify surface reactions of metal oxide semiconductors to enhance gas sensing and results in higher sensor response than that of pure ZnO.

Use of plants in synthesis of nanoparticles is quite novel leading to truly green chemistry as it is cost effective and environment friendly easily scaled up for large scale synthesis and in this method there is no need to use high pressure, energy, temperature, and toxic chemicals. In addition, plant extract can hinder aggregation of the synthesized metal nanoparticles and control their particle sizes. A recent advance in plant extract based bioreduction processes is their utilization for the functionalization of material surfaces with metal nanoparticles such as silver. Currently, there are few works that utilize green processes for the functionalization of materials with silver nanoparticles. Our group has also recently functionalized ZnO with Ag nanoparticles using *Tribulus terrestris* leaf extract. In this study, a green approach of synthesis of Ag-coated ZnO nanoparticles has been described by reducing of aqueous Ag ions using the leaf extract of T. terrestris. The structure, morphology and sensing properties of as-synthesized products were investigated.

2. Experimental

T. terrestris leaf extract was prepared by putting 30 g of *T. terrestris* leaf dry powder into 115 ml deionised water and boiling the mixture for 15 min. After cooling, the solution was filtered and filtrate was stored at 4 °C for further experiment.

ZnO nanoparticles were prepared by sol–gel method according to the reference [13]. 2 g of ZnO powder were dispersed in 60 ml of 0.1 M silver nitrate solution at room temperature under ultrasonic treatment for over 10 min. Afterwards, 30 ml of *T. terrestris* leaf extract was added under continuous stirring at 60 °C. A change in the color of the reaction mixture from yellow into reddish dark brown after 1 h, indicating the formation of silver nanoparticles.

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The stirring was continued for another 2 h in order to complete the reduction reaction. Finally, Ag-coated ZnO nanoparticles were obtained through centrifugation. The obtained products were washed several times with ethanol and dried at 80 °C.

The Ag and Ag-coated ZnO nanoparticles were determined by X-ray diffraction (XRD; Rigaku D/MAX-YA) using Cu Kα, λ=0.154 nm, scans were performed from (2θ) 10° to 80° by rate 5°/min. The microstructures of powders were observed using a transmission electron microscopy (TEM; JEM-2100, Japan) operated at 200 kV accelerating voltage. The gas sensing properties of sensor was measured at room temperature and performed by calculating the resistance of sensor upon controlled concentration of ethanol in a sealed chamber [11].

3. Results and discussion

The XRD patterns of Ag nanoparticles are shown in Fig. 1(b). The diffraction peaks at 2θ=38.1°, 44.3°, 64.4° and 77.4° assigned to the (111), (200), (220) and (311) planes of a faced center cubic lattice of silver were obtained [12] and no diffraction peaks corresponding to the precursor ($AgNO_3$) and bi-products (such as silver oxide) were observed. The intensity of peaks reflect the high degree of crystallinity of the Ag nanoparticles. The morphology of Ag nanoparticles are shown in Fig. 1(a). The TEM image shows individual silver nanoparticles as well as a number of aggregates with spherical shape. The histogram of the size distribution in Fig. 1(c) indicated that the nanoparticles measured between 15 and 65 nm and possessed a average size of 55 nm. Under careful inspection of TEM images, it is clearly indicated that a faint thin layer of other material was visualized on the surface of Ag nanoparticles which might be due to the capping organic materials of leaf extract. The alkaloids, flavanoids, tannias, ascorbic acid and phenolic compounds are present in *T. terrestris* leaf extract. In this scheme, Ag ions can form intermediate complexes with phenolic OH groups present in hydrolysable tannins which consequently undergo oxidation to ascorbic acid forms with ensuing reduction of Ag ions to Ag nanoparticle [13]. Thus, we may safely suggestted that such flavonoid and phenolic of leaf extract may act as reducing, stabilizing, and capping agents [14].

Fig. 2(a and b) shows the TEM image of pure ZnO and Ag-coated ZnO samples. As shown in Fig. 2(a), it can been seen that ZnO particles have a homogeneous spheroid-like shape with clean surface and the diameters are around 59 nm. In contrary to smooth of pure ZnO, Fig. 2(b) shows that there are many Ag nanoparticles coating on the ZnO nanoparticles, making the nanoparticle surface very rough. In addition, the size of Ag nanoparticles on the surface of ZnO are much smaller than that of the Ag nanoparticles shown in Fig. 1(a). This is due to the availability of more nucleating sites offered by the dispersed ZnO particles [15]. Fig. 3(c) displays the XRD pattern of Ag-coated ZnO nanoparticles. The major peaks which are observed at 31.7°, 34.4° and 36.2° 2θ values are assigned to the (100), (002) and (101) planes respectively which are the characteristic peaks of ZnO phase. By close observation three diffraction peaks can be seen at 38.1°, 44.3° and 64.4°, which can be attributed to metallic Ag. Thus, this also confirms the formation of Ag nanoparticle onto ZnO particles. In addition, no other peaks related to impurities were found in the

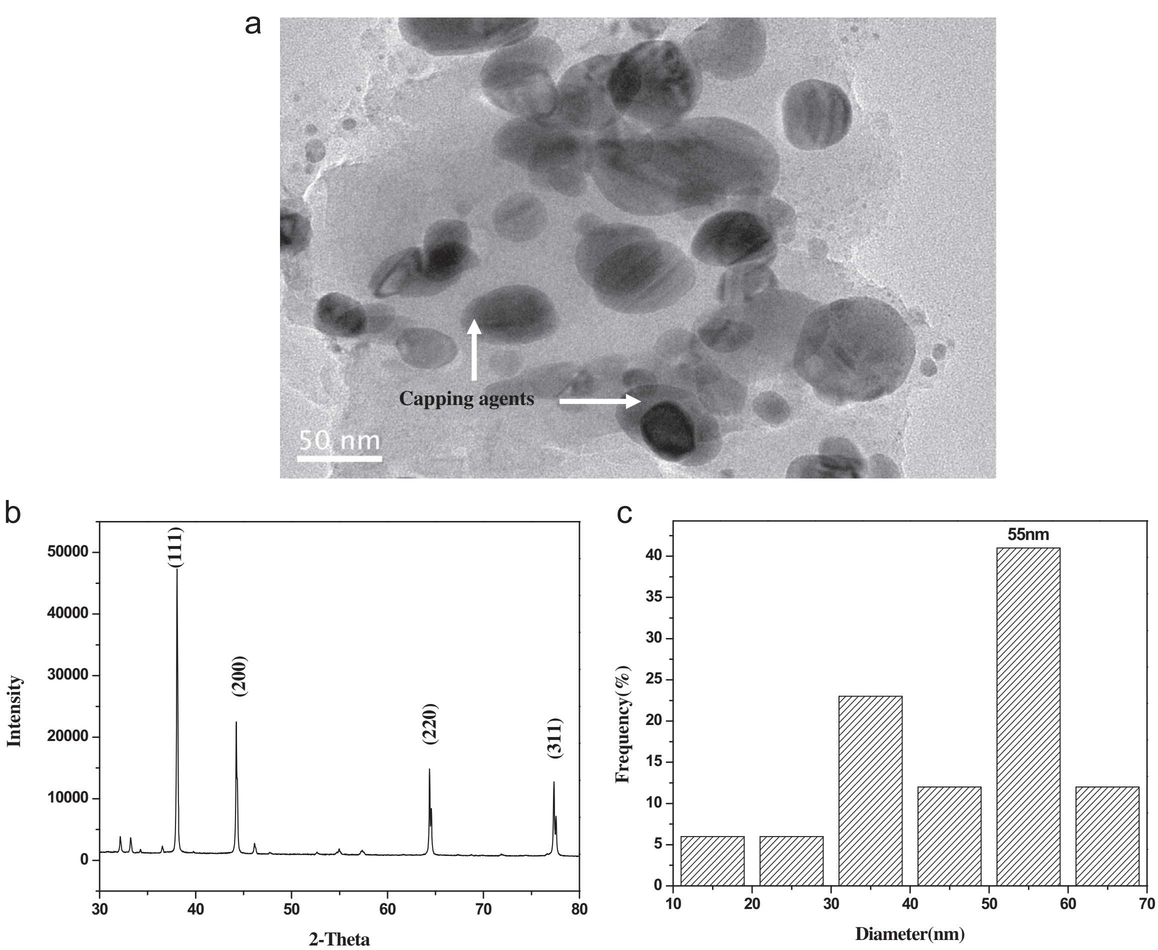

Fig. 1. (a) the TEM image, (b) XRD patterns and (c) the size distribution of Ag nanoparticles.

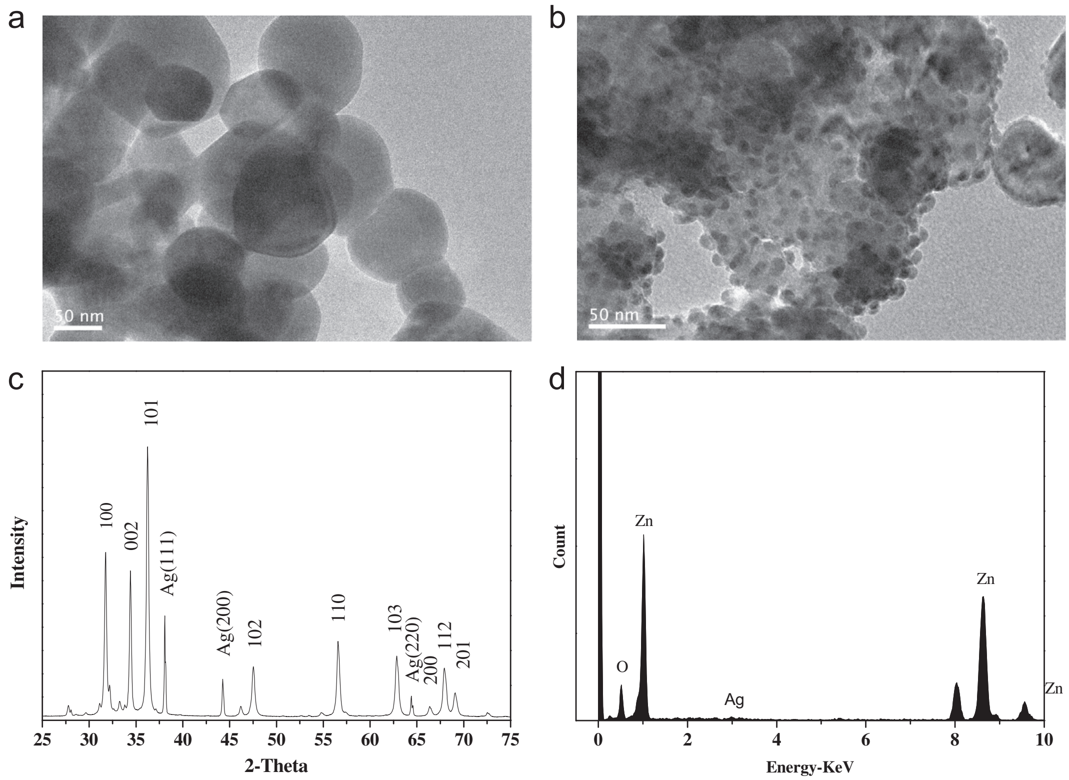

Fig. 2. (a) the TEM image of ZnO nanoparticles; (b) the TEM image of Ag-coated ZnO nanoparticles; (c) XRD patterns and (d) EDS spectra of Ag-coated ZnO nanoparticles.

pattern. The composition of Ag-coated ZnO nanoparticles are detected by EDS in Fig. 2(d). From spectra, it can been seen that Zn and O appeared as the main components with low levels of Ag. It is further indicated that Ag nanoparticles are coated on the surface of ZnO nanoparticles.

I–V characteristrcs of ZnO sensor and Ag-coated ZnO sensor in various ethanol concentration at room temperature are shown in Fig. 3(a). The slopes increase rapidly with the increase of ethanol concentration and the current vs. voltage relationship is a linear curve indicating that the property of sensors is good and stable. Fig. 3(b) shows the resisitance–concentration behavior of ZnO and Ag-coated ZnO sensor. The resistance values of pure ZnO sensor decrease from 2.5×10^6 to 1.25×10^6, while the resistance values of Ag-coated ZnO sensor decrease from 5×10^5 to 2.4×10^5 in range of 0–20 ppm. Furthermore, it can been seen that the resistance of Ag-coated ZnO sensor was generally much lower than that of pure ZnO sensor. This means that Ag nanoparticles could enhance the sensitivity of ZnO nanoparticles remarkably. In this situation, Ag nanoparticles can promote the chemiadsorption and ionization; simultaneously, Ag nanoclusters enhance the chemical reaction activity of the surface [16]. Accordingly, the gas response of Ag-coated ZnO sensor is remarkably higher than that of pure ZnO sensor.

4. Conclusion

In summary, Ag-coated ZnO nanoparticles were successfully prepared by a biological process using *T. terrestris* leaf extract. Ag nanoparticles on the surface of ZnO nanoparticles have an average size of 6–10 nm. Gas-sensing property measurements had shown that, compared with pure ZnO sensor, the synthesized Ag-coated ZnO nanoparticles had an enhanced ethanol-sensing property at room temperature. This research opens a way that simply

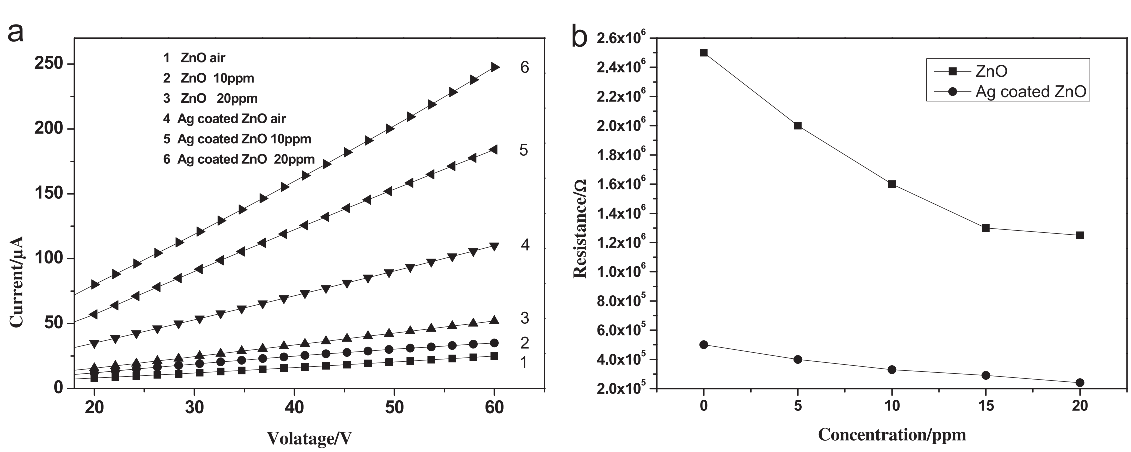

Fig. 3. (a) *I–V* characteristrcs and (b) electrical resistance of ZnO sensor and Ag-coated ZnO sensor.

synthesized Ag-coated ZnO nanomaterials could be used as efficient electron mediators for the fabrication of various effective chemical sensors.

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