One-step synthesis of Al-doped ZnO nanocrystalline aggregates with polydisperse and high specific surface area

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Introduction

ZnO, one of the most attention II-VI semiconductors, can be easily fabricated into various nanostructures such as nanowires, nanotubes, nanoflowers as well as nanocrystalline aggregates (NCAs). In recent years, nanostructured ZnO powders display a great power in many applications such as gas sensors [1], solar cells [2], varistors [3] and photocatalyst with high chemical activity. Especially, the polydisperse Li-doped ZnO NCAs have been successfully used to enhance the photoelectric conversion efficiency of the dye sensitized solar cells due to its high specific surface area and scattering property [4]. In this paper, the Al-doped ZnO (AZO) NCAs were prepared by a low cost colloid chemistry method, and effects of the Al-doped concentration on the morphological and structural properties of the AZO NCAs were studied.

Experimental

Materials

$Zn(CH_3COO)_2 \cdot 2H_2O$ (0.01 mol) was first added to diethylene glycol (DEG, 100 mL) with vigorous stirring. Then appropriate amounts of $AlCl_3 \cdot 6H_2O$ were added to the precursor solution. Five solutions doped with different concentrations of Al/Zn = 0, 1, 2, 3 and 4 at.% were prepared, respectively. The mixture was heated in an oil bath and kept it at 130°C for 30 min, followed the solution was rapidly heated to 180°C and kept 15 min to yield milk-white colloidal solution. The obtained colloidal solution was then sequentially cleaned and concentrated by the centrifugal process, thus the crystallized AZO NCAs powders were obtained after the as-prepared powders being annealed at 450°C for 1 hour. In order to simplify, the AZO NCAs samples doped with concentrations of 1, 2, 3 and 4 at.% were labeled as AZO1, AZO2, AZO3 and AZO4, respectively.

Characterization

The structural properties of the NCAs were characterized by using a D/max-2400 X-ray diffraction (XRD) analysis (Rigaku). Field emission scanning electron microscopy (FESEM, JSM-7000F, JEOL Inc., Japan) was further used to characterize the morphological and structural properties of the fabricated NCAs. The particle size distribution of the NCAs samples were measured by the BT-9300H laser particle analyzer.

Results and Discussion

The XRD patterns of the ZnO and AZO1~4 NCAs are showed in Fig. 1. It can be observed that the diffraction patterns of all samples are assigned to the wurtzite hexagonal-shaped ZnO. It is evident that no other impurity peaks related to the Al-doped component are detected, which indicates that the doping Al ions do not change its wurtzite structure similar to the case of our previous report [5]. The crystal grain sizes of the ZnO and AZO1~4 samples are 20.4, 15.1, 13.7, 13.5 and 13.8 nm, respectively. Obviously, the crystallite grain size of these samples decreases with increasing the Al concentration in the precursor solution. It is probably ascribed to that the Zn^{2+} is substituted by the Al^{3+} at the lattice point of ZnO crystal and the radius of Al^{3+} (~0.05 nm) is smaller than that of Zn^{2+} (0.074 nm), thus leading to a decrease of the crystallite grain size.

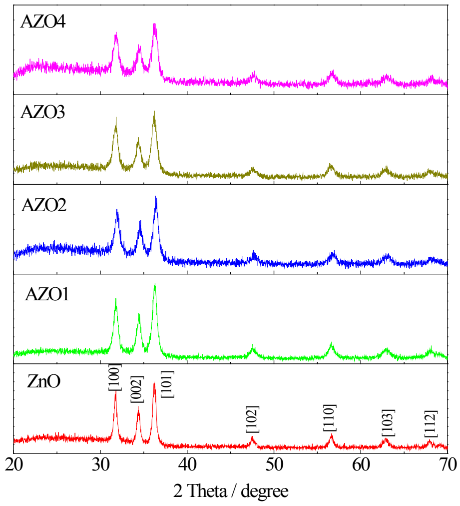

Fig. 1 XRD patterns of the ZnO and AZO1~4 NCAs.

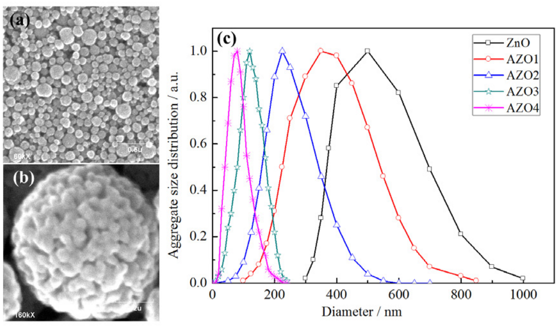

Fig. 2 SEM images of the AZO4 NCAs (a) low-magnification image, (b) high-magnification image and (c) particle size distribution curves of the ZnO and AZO1~4 NCAs.

Figure 2(a) and (b) shows the SEM images of the AZO4 NCAs. It can be observed that the NCAs are spherical in shape and the AZO sphere is composed of the AZO nanocrystallites, which indicates that the AZO sphere has a high surface area and surface roughness. It should be mentioned here that the AZO NCAs with other Al-doped concentrations have similar results. Furthermore, it can be seen from Fig. 2(c) that the particle size distribution of the NCAs also decreases with an increasing of the Al-doped concentration in the precursor solution, that is to say, the specific surface area of the AZO NCAs increases with the increasing of the Al-doped concentration and the AZO4 NCAs have the largest specific surface area in all five samples.

Conclusions

The ZnO and AZO NCAs have been successfully prepared by the colloid chemistry method. Effects of the Al-doped concentration on the morphological and structural properties of the AZO NCAs have been also studied. Results indicate that the doping of the Al ions not only does not change the wurtzite structure of the AZO crystal but also reduces the crystallite grain size and the particle size distribution of the AZO NCAs, which makes them have higher specific surface area than that of the ZnO NCAs.

References

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