Controlled synthesis of ZnO nanocrystals with various morphologies by capping molecules assisted hydrothermal process and their application in the dye sensitized solar cells

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Introduction

The fabrication of nanomaterials with a controllable size and shape is of great scientific and technological interest, mainly due to the significant influences of size and shape on their properties. Past decades, oxide semiconductors are receiving much attention in photo electrochemistry because of their exceptional stability against photo-corrosion optical excitation in the band gap[1]. Nano porous titanium dioxide (TiO_2) films were found to be useful as photoanodes for dye-sensitized solar cells (DSSCs)[2]. Among all oxide semiconductors for photoanode materials, zinc oxide (ZnO) has been expected to be comparable to TiO_2 because of its higher electronic mobility, similar band gap energy (3.37eV) and similar energy level of the conduction band. However, overall all conversion efficiencies (η) of ZnO based DSSCs have been presented lower to TiO_2-based DSSCs. Recently, several techniques such as electrodeposition[3,4], sol–gel[5], and powder technique[6] have been used to prepared photoanode materials for DSSCs. Including these, various nanostructures of ZnO including nanobelts, nanorods, nano-flowers and nanoribbons have been fabricated by thermal evaporation methods, solution phase synthesis[8.9]. Out of all, the simple solution synthesis followed by hydrothermal treatment of the reaction may be the most simple and effective way to prepare sufficiently crystallized, well-defined shape and size materials at relatively low temperatures.

In this paper, various morphologies of high quality nanoflowers, nanoplates and spheres ZnO were synthesized in a hydrothermal method with the constant concentration of alkali solutions by changing capping agent such as ammonia, oxalic acid and citric acid in the same reaction conditions. Much improved performance (overall conversion efficiency of 2.61 %) as an electrode material of dye-sensitized solar cell was observed with the ZnO spheres owing to its high surface area and uniform film morphology. Finally, synthesized ZnO materials were characterized and applied as the electrode materials of dye-sensitized solar cell (DSSCs)

Experimental

In typical synthetic procedure, 1.5gm of Zn $(CH_3COO)_2$ was put into the 100 ml of water and stirred for 30 minutes, with continuous stirring 20% ammonia, oxalic acid and citric acid solution was added and further stirring for 10 minute. Then alkali solution of 5M was prepared. And above prepared solution, 20 ml of 5M NaOH solutions was introduced and whole reaction mixture transferred to Teflon lined stainless steel autoclave, which was sealed and temperature was maintained at 160^0C for 12 hrs. After cooling, the product was taken out and centrifuged at 5000 rpm, and filtered, washed with distilled water and ethanol well to remove if some existing ions, then the final product was dried at 80^0C in oven in presence of air. The synthesized product was characterized by FESEM (FE-SEM, Hitachi 4700) TEM (JEOL JEM-2010), XRD (Rigaku, with Cu $K\alpha$ radiation), Raman spectra and Photoluminescence. DSSC was fabricated with the ZnO thin film as a working electrode as described in elsewhere [7]. The photocurrent density of ZnO thin film and the current–voltage (I-V) characteristics of the DSSCs were recorded under an illumination of 1 Sun (100 mW/cm^2) as described in above reference. The active area of the ZnO electrode was ca. 0.25 cm^2.

Result and discussion

Morphologies of synthesized materials

Figure 1, Illustrates the FESEM images of ZnO nanostructures prepared by hydrothermal process using different capping agents and same concentration of alkali. The different types of capping molecules are influencing the morphology of ZnO nanocrystals and obtained flowers, nanoplates and spheres bundles by hydrothermal treatment with 5 M NaOH aqueous solutions at 160^0C respectively. Thus, nanostructured ZnO morphologies could be controlled by adjusting the pH of reaction mixture and molecules of capping. Among them, spheres ZnO shows high surface area (13.11m^2/g) due to uniform growth of materials during the reaction.

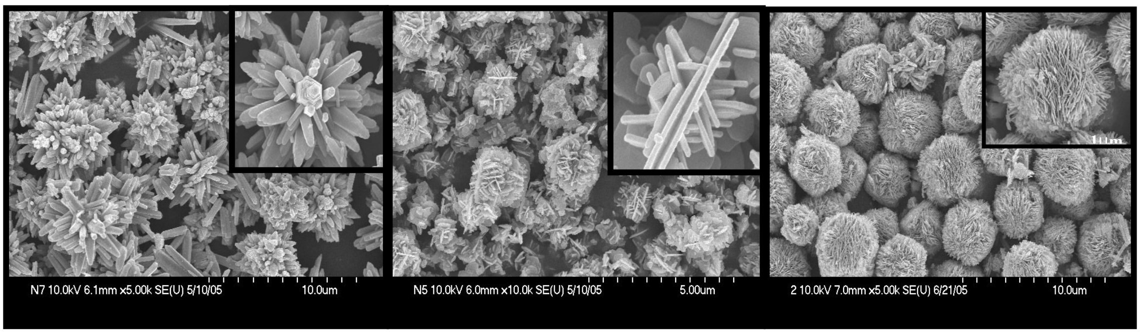

Fig. 1. Typical FESEM images of ZnO structures grown by hydrothermal process: (a) hexagons; (b) microspheres, and (c) nanorods flowers.

UV-Vis absorption spectra

Fig.2 represents the UV-Vis absorption spectra of synthesized ZnO electrodes with Ru-dye. It is possible to notice that the major part of dye absorbed ZnO substrates has a prominent peak for the absorption 502 nm. Spheres ZnO substrate is shown the maximum absorption about 3.832 x 10^{-7} mol/cm^2 of Ru-dye due to uniform distribution of particles on the TCO glass and high surface area of materials. Comparatively, ZnO flowers substrate has very low ability to absorb Ru-dye because distribution of particles is not uniform on TCO glass and maximum impurities are found in this sample, these are caused many oxygen vacancies. Therefore, uniform distribution of ZnO particles on the TCO glass and high surface area leads the maximum absorption of Ru-dye to surface.

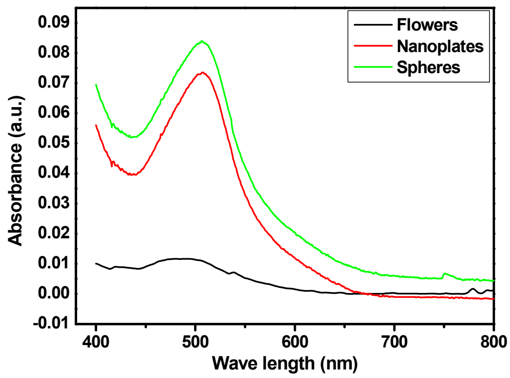

Fig. 2 UV-Vis absorption spectra of ZnO electrode with dye: Flowers (black line), spheres (green line), and nanoplates (red line)

Photovoltaic properties

The high surface area of materials provides much surface for the absorption of dye molecules which increases the current density of device. Fig. 2 and Table 1 represent the I-V curves of and photovoltaic performance summary of various ZnO based DSSCs respectively. Most improved photocurrent density and highest overall conversion efficiency of 2.61% was observed in the spheres ZnO nanomaterials, which is believed owing to the most uniform surface morphology and high surface area of the materials as shown in Table. The consistency in short-circuit current (I_{SC}) and open circuit voltage (V_{OC}) was observed maximum of 12.28 mA/cm^2 and 0.557volt. Hence, the high uniform morphologies and substrate along with the low charge transfer resistance may gives rise to superior photo-activities. These results acknowledge that morphologies of zinc oxide and surface morphology of film are essential factors, which determines photocurrent densities and performance of DSSCs.

To finely modulate the morphology of ZnO, the relationship between the morphologies and reaction conditions were investigated. It is found that by changing the capping agents have shown the significant effects on ZnO morphology. The fabrication of DSSCs with ZnO substrates was found that the different morphologies of ZnO substrates are play a crucial role to enhance the performance and photocurrent densities of ZnO based DSSCs.

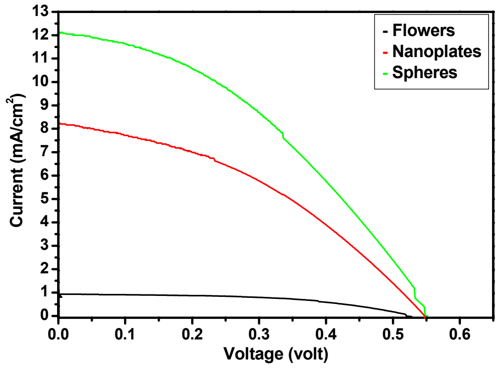

Fig. 3 I-V curves of ZnO based DSSCs: Flowers (black line), spheres (green line), and nanoplates (red line)

Table 1. Summary of photovoltaic performances of DSSCs.

Shape	V_{OC} (Volt)	I_{SC} (mA/cm^2)	FF (%)	η (%)
Flower	0.535	1.042	53.7	0.30
Nanoplates	0.554	8.38	40.8	1.9
Spheres	0.557	12.28	38.3	2.61

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