Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 151 (2015) 56–63

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization, low temperature solid state PL and photocatalytic activities of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ nanocomposite

Md Abdus Subhan [a,c,*], Nizam Uddin [a], Prosenjit Sarker [b], Hiroyasu Nakata [c], Ryuzi Makioka [c]

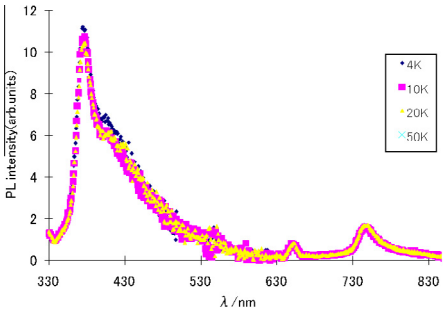
[a] Department of Chemistry, Shah Jalal University of Science and Technology, Sylhet 3114, Bangladesh
[b] Square Pharmaceuticals Ltd., Bangladesh
[c] Deparment of Arts and Science, Osaka Kyoiku University, Kashiwara, Osaka, Japan

HIGHLIGHTS

- Nanocomposite oxide $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been prepared.
- Characterized by XRD, SEM, EDS and PL spectra.
- Low temperature solid state PL spectra observed.
- NBE, blue, green, orange and red emissions are observed.
- Excellent photocatalytic and anti-bacterial activities observed.

GRAPHICAL ABSTRACT

Nanocomposite oxide $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been prepared and characterized by XRD, SEM, SEM–EDS and PL spectra. Low temperature solid state PL spectra of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ have been studied exciting at 325 nm by a line of He–Cd laser. NBE, blue, green, orange and red emissions are observed.



ARTICLE INFO

Article history:
Received 6 February 2015
Received in revised form 10 June 2015
Accepted 17 June 2015
Available online 24 June 2015

Keywords:
Photoluminescence
Photocatalyst
Nanocomposite oxide
NBE emission
Anti-bacteria

ABSTRACT

A novel multi-metal nanocomposite oxide $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been prepared by co-precipitation of their carbonates from aqueous solutions of the metal nitrates following calcinations and annealing 5 h at 450 °C and 4 h at 600 °C. $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been characterized by XRD, SEM, EDS and PL spectra. According to XRD results the crystallite size of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ varies in the range of 19–111 nm with an average size of 50 nm, which is in good agreement with SEM results. Elemental analysis was performed by SEM–EDS. Emissions of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been observed in UV (NBE emission), visible and NIR regions at 325 nm excitation by a line of He–Cd laser. Photocatalytic as well as anti-bacterial activities have been studied. The nano composite $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ shows an excellent photocatalytic dye degradation activity.

1. Introduction

In recent years, nano-sized metal oxide particles have got much attention due to its unique optical, electrical and magnetic properties, which depends on the size and shape of the particle. Oxide semiconductors containing metal atoms have wide band gap resulting in transmission of visible light [1]. Mixed metal oxides comprise high carrier concentrations and high mobilities, and various devices have been designed by using these semiconductors [2–3]. There have been studies on multi-metal-oxide (MMO) nano particles to test their suitability as luminescent [4], catalyst [5], adsorbent [6] and wide-band-gap semiconducting oxide [7].

* Corresponding author at: Department of Chemistry, Shah Jalal University of Science and Technology, Sylhet 3114, Bangladesh.
E-mail address: subhan-che@sust.edu (M.A. Subhan).

http://dx.doi.org/10.1016/j.saa.2015.06.094
1386-1425/

Silver oxide (Ag_2O) nanoparticle is a well-known material having vast applications in the field of oxidation catalysis [8,9], sensors [10], fuel cells [11], photovoltaic cells [12], all-optical switching devices, optical data storage systems [13] and as diagnostic biological probes [14].

The band gap energy of pure CeO_2 is 3.2 eV [15]. Addition of a second metal to the lattice of ceria can increase strain within the lattice and induce formation of crystal defects which can convert the material to a good semiconductor [16]. CeO_2 is considered as a candidate for replacing silicon dioxide in electronic appliances [17].

Zinc oxide (ZnO) particles with various morphologies and sizes can be prepared in different forms such as doped or undoped dry powders. Due to different sizes and morphologies research related to the applications of ZnO is rising rapidly [18–23]. It is a potential luminescent material because the binding energy of exciton is 60 meV, which is extremely larger than that in the other semiconductors. Zinc oxide, a wide-band-gap semiconducting material is potentially very important because it can be used as transparent conductive films, high-efficiency vacuum fluorescent displays, field-emission displays, solar-cell windows, acoustic wave devices, light emitting devices and piezo-electric devices [24–25]. In order to realize all these applications, it is important to devise simple and efficient methods for preparing ZnO on a large scale at low cost. Typically, various ZnO structures have the same crystalline structure. The morphology of ZnO is a key factor in differences in their properties. Many applications of ZnO nanostructures have been identified due to their morphological dependence. For example, the luminescence property of ZnO is morphology-dependent. The relative intensity of luminescence is greatest for nanowire and least for nano-particle (nanowire > powder > nano-needle > nanoparticle) [26].

The properties arise from the assemblage of metal oxides on formation of multi-metal composite oxides; make the materials potentially important in the fields of microelectronic devices, ceramics, catalysis, and nonlinear optical and semiconductor devices [7,27–31]. Here we reported on synthesis, characterization, photoluminescence (PL) spectra, photocatalytic and anti-bacterial activities of nano $Ag_2O{\cdot}CeO_2{\cdot}ZnO$.

2. Materials and methods

2.1. Preparation of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ mixed metal oxide nanocomposite

The $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ composite metal oxide was prepared by co-precipitation method. This nanocomposite was prepared by co-precipitation of their carbonates from the aqueous solution of the metal nitrates. The metal carbonate was made because carbonate can be easily converted to metal oxide by heat treatment. Solutions of 0.25 M $AgNO_3$, $Ce(NO_3)_3{\cdot}6H_2O$, $Zn(NO_3)_2$ and a solution of 1.0 M Na_2CO_3 in distilled water were prepared. The two nitrate solutions, $Zn(NO_3)_2$ and $Ce(NO_3)_3{\cdot}6H_2O$ were mixed together in a beaker in 1:1 ratio and stirred vigorously at room temperature for few minutes. Then other two solutions of $AgNO_3$ and Na_2CO_3 were added in the above mixture at the same time at 1:1 ratio and kept on stirring vigorously for 3 h at room temperature. The precipitate formed was separated by suction pump and was washed thoroughly with distilled water for several times. The washed sample was transferred to Petri dish and taken in an oven. The sample was then dried at 120 °C for 2 h. The dried sample was then calcined in a Muffle Furnace for 5 h at 450 °C and 4 h at 600 °C. The calcinations converted the carbonates of the sample into their oxides as the following reaction:

$$M_2(CO_3)_n \rightarrow M_2(O)_n + nCO_2 (M = Ag,\ Ce,\ Zn)$$

2.2. Characterization

In order to obtain compositional and structural information about the multi metal oxide $Ag_2O{\cdot}CeO_2{\cdot}ZnO$, XRD measurements were performed with a Bruker-AXD advance laboratory diffractometer, using a Cu-Kα X-ray radiation. The diffraction patterns were recorded in the step scan mode at 0.05 steps and at a measurement rate of 10 s/step. The diffraction patterns were registered within the 2θ angle range from 20° to 90°. The morphology of the multi metal oxide particle, $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ was investigated with a scanning electron microscope, Hitachi S-4800 scanning electron microscope (SEM). Samples for the SEM were prepared by dispersing the multi metal oxide on a carbon tape. The SEM images of the sample with different magnification were taken with 5 and 15.3 mm working distances by applying an accelerating voltage of 20 kV and current of 20 μA. Thermo Electron Corporation – NORAN System SIX microanalysis system was used to perform the qualitative chemical analysis of the sample. Point-and-shoot analyses were employed to determine the presence and distribution of elements in the sample. Solid state PL spectra of the nanocomposite prepared at 450 °C were measured at low temperatures using a line of He–Cd laser as an excitation source (at 325 nm). The change in concentration of dye solutions were measured spectrophotometrically using Shimadzu-1800 double beam spectrophotometer for photodegradation study.

3. Results and discussion

3.1. X-ray diffraction analysis of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ mixed metal oxide

Fig. 1 shows the XRD pattern of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$. The diffraction peaks for crystalline ZnO appeared at 2θ diffraction angle of 34.06°, 36.267°, 47.12°, 56.16° and 67.66° (ICDD 00-036-1451). The diffraction angles, 2θ of 28.10°, 32.66°, 47.12°, 56.16°and 77.03° are due to the diffraction of crystalline CeO_2 (ICDD 00-43-1002). The diffractions of Ag_2O appeared at 2θ diffraction angle of 37.72°, 38.85°, 43.94°and 64.09° (ICDD 00-04-0783). Using Scherrer's formula [32], the particle size of the $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ was found to be in the range of 19.43–110.98 nm with an average size of 51.298 nm. As seen in Fig. 1, annealing at a high temperature increased the sharpness of the XRD peaks indicating a higher order crystalline nature of the annealed sample. Crystallinity of multi-metal-oxide nanoparticles increased on calcinations due to removal of impurities and formation of pure oxides.

3.2. SEM and SEM–EDS of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$

The SEM images of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ at different magnificent has been recorded. The SEM images of multi metal oxide nanocomposites were obtained to observe the particle size and morphology. A characteristic textures and morphology of $Ag_2O{\cdot}CeO_2{\cdot}ZnO$ has been revealed by the SEM study as shown in the Fig. 2. SEM image showed that the sample contains three kinds of particles. The SEM image indicated that the annealed sample contains nanosized particles with roughly spherical, cubic as well as hexagonal morphology (Fig. 2).

According to the EDS spectra different parts of the sample (measurements points in Fig. 3) have an identical elemental composition of silver (Ag), cerium (Ce), zinc (Zn) and oxygen (O). Presence of elemental oxygen indicates the formation of metal oxides. Fig. 3 shows an EDS spectrum measured from one point. On the basis of EDS result, metal oxides are dispersed at microscopic level in the nanocomposite.