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Photocatalytic activity of binary metal oxide nanocomposites of CeO_2/CdO nanospheres: Investigation of optical and antimicrobial activity

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ABSTRACT

We report the synthesis of high quality CeO_2-CdO binary metal oxide nanocomposites were synthesized by a simple chemical precipitation and hydrothermal method. Cerium nitrate and cadmium nitrate were used as precursors. Composition, structure and morphology of the nanocomposites were analyzed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). XRD pattern proves that the final product has cubic phase and the particle size diameter of the nanocomposites are 27 nm, XRD results also indicated that the crystalline properties of the nanocomposite were improved without affecting the parent lattice, FESEM analysis indicates that the product is composed of spherical particles in clusters. The morphological and optical properties of CeO_2-CdO nanosamples were characterized by HRTEM and DRS spectroscopy. The IR results showed high purity of products and indicated that the nanocomposites are made up of CeO_2 and CdO bonds. Absorption spectra exhibited an upward shift in characteristic peaks caused by the addition of transition metal oxide, suggesting that crystallinity of both the metal oxide is improved due to specific doping level. TGA plots further confirmed the purity and stability of nanomaterials prepared. Hence the nanocomposite has cubic crystal lattice and form a homogeneous solid structure. From the result, Cd^{2+} ions are embedded in the cubic crystal lattice of ceria. The growth rate increases which are ascribed to the cationic doping with a lower valence cation. Ce-Cd binary metal oxide nanocomposites showed antibacterial activity, it showed the better growth inhibition towards *p.aeruginosa*. Exploit of photodegradation and photocatalytic activity of large scale synthesis of CeO_2-CdO binary metal oxide nanocomposites was reported.

1. Introduction

Ceria based ceramic nanomaterials attracted great interest recently, due to its properties like high refractive index, wide band gap, high dielectric constant and high melting point [1,2]. These excellent properties emerge from the fact that the ionic and charge ratio between Ce^{4+} and O^{2-} ions allow for the changes in the CeO_{2-x} structure which is a most available inner transition metal oxide (ITMO). Cadmium oxide (CdO) is a well-known transition metal oxide (TMO) of II-VI semiconductor with a direct band gap of 2.2 eV (520 nm) and these metal oxides has developed various applications, such as its use in automobile exhaust catalyst [3], UV absorbers [4–6], gas sensors [7,8], catalysis [9,10], solar cells [11], fuel cells [12], photodiodes [13], phototransistors [14] and oxygen storage materials [15]. Metal oxides of cadmium and cerium are basically n-type semiconductors with cubic crystal structure. Literature often attributes the catalytic activity of cerium oxide, due to its high oxygen storage capacity [16–21] which is largely due to the multivalence nature of cerium. Also doping can greatly affect the growth process and becomes an effective way to prepare the nanoparticles with the monodisperse size and shape. Cadmium oxide and cerium oxide can be prepared using several methods, such as chemical precipitation [22], wet-chemical method [23], micro-emulsion [24], hydrothermal [25], solvothermal [26] and microwave method [27]. In the present study, we have chosen precipitation method and hydrothermal method. In the precipitation method it seems to be advantages like simple and cost effective, surfactant free and usage of precursor are cheap. Hydrothermal method has the advantages like high reactivity of the precursors; easy control of solution, formation of metastable phase, reduced air pollution and low energy consumption. Carlos et al. reported the antimicrobial activity of nano cerium oxide against *Streptococcus*

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mutans [28], Masoud et al., investigated the antibacterial effect of cerium oxide nanoparticles on *Staphylococcus aureus* bacteria [29], Bahareh et al., also investigated the antibacterial effect of cadmium oxide nanoparticles on *Staphylococcus aureus* bacteria [30]. Lian Wang et al., prepared and investigated the morphology-dependent bactericidal activities of Ag/CeO_2 catalysts against *Escherichia coli* [31]. Gopinathan et al., reported the optical, surface analysis and Antibacterial Activity of ZnO-CuO doped cerium oxide nanoparticles [32], Although, the doped CeO_2 particles have been extensively studied, preparation of CeO_2-CdO binary metal oxide nanocomposites, characteristics and its applications have not been reported yet. Herein we synthesize the CeO_2-CdO nanocomposites with almost uniform size and spherical shape of clusters by simple precipitation and hydrothermal method. We report on the influence of the preparation method on the structural, optical and biological properties of CeO_2-CdO nanomaterials. It shows that there is a reduction in size of the CeO_2-CdO nanomaterial using these methods. To the best of our knowledge, there are no reports on the antibacterial activity of the CeO_2-CdO binary metal oxide nanospheres used in the present study.

2. Experimental Section

2.1. Precipitation Method

All the chemical reagents used in the experiment were of analytical grade (E-Merck, 99.99%) and used without further purification. Mixed binary oxides were synthesized by using uni-molar concentration of cerium nitrate [$Ce(NO_3)_3 \cdot 6H_2O$] and cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$]. Typically 0.1 M concentration of cerium nitrate and cadmium nitrate were dissolved in deionized water and stirred continuously with magnetic stirrer at room temperature (RT). Then these uni-molar solutions were mixed and stirred for 1 h to obtain homogeneous solution. 0.5 M NaOH solution was added drop-wise into the vigorously stirred cerium nitrate and cadmium nitrate solutions mixture till the pH is ~10.5. The pale yellow precipitate was collected and thoroughly washed with double distilled water followed by ethanol. The dried pale-yellow precipitate was kept in the muffle furnace, calcinated at 800 °C for 3 h and used for different characterization. This product is denoted as PC. The mechanism involved in this method is similar to hydrothermal method which is discussed under Section 2.2.

2.2. Hydrothermal Method

Cerium nitrate and cadmium nitrate salts of (0.1 M) were dissolved in distilled water with vigorous stirring, then they mixed together with constant stirring for 1 h and 0.5 M NaOH was added drop wise to form a precipitate until the pH reached about ~10.5. The pH value of the reaction solution was recorded using a digital pH meter. The mixture was transferred into stainless steel autoclave sealed tightly; it was kept in an air oven heated at 150 °C for 24 h. The formed pale-yellow precipitate was filtered, washed with double distilled water followed by ethanol, and dried in an oven at 80 °C under air atmosphere. This precipitate is named as HT. The growth mechanism of CeO_2-CdO nanomaterials is explained on the basis of simple chemical reactions and nucleation given below.

$$Ce(NO_3)_3(aq) + NaOH\ (aq) \rightarrow Ce(OH)_3(cp) + NaNO_3\ (l) + H_2O \quad (1)$$

$$Cd(NO_3)_2\ (aq) + NaOH\ (aq) \rightarrow Cd(OH)_2\ (cp) + NaNO_3\ (l) + H_2O \quad (2)$$

$$Ce(OH)_3(cp) + Cd(OH)_2\ (cp) + NaOH \rightarrow CeO_2{-}CdO(p) + Na^+ + OH^- + H_2O \quad (3)$$

In this process, the precursors [$Ce(NO_3)_3$] and [$Cd(NO_3)_2$] are hydrolyzed in the presence of a reducing agent (NaOH), and results in the formation of coagulated precipitates of cerium and cadmium hydroxides, which are unstable intermediates. When it attains super-saturation, the precipitation of CeO_2-CdO begins. The nucleation of CeO_2 crystals becomes easier than CdO, due to its lower activation energy and smaller size and hence starts growing on the surface of CdO, which in turn leads to the heterogeneous nucleation. The formation of higher concentration of CeO2 is confirmed by the presence of highest intensity peak at $2\theta = 28.7$ °C, which is observed in precipitation and hydrothermal method.

2.3. Characterization Studies

Phase identification of the fabricated CeO_2-CdO metal oxides was carried out by an X-ray diffraction CuK_α ($\lambda = 1.5417$ Å) in the radiation range of 20°–80°. A Field emission scanning electron micrograph (FESEM/EDX) was used to observe the morphology and elemental analysis of the CeO_2-CdO binary metal oxides. The microstructure and particle sizes of the samples were characterized by JEM-200CX transmission electron microscopy (TEM/SAED) working at 200 kV. The optical absorption spectra of the CeO_2-CdO were recorded on a JASCO V650 UV–vis-NIR spectrophotometer in the wavelength range of 200 nm–800 nm. The FTIR spectra were recorded on Bruker Tensor 27 FTIR spectrophotometer. TGA/DTA was analyzed by using thermogravimetric analysis instruments (NETZSCH STA 44950). The experiment was carried out by heating the samples up to 850 °C with a heating rate of 5 °C min^{-1} under high purity nitrogen atmosphere.

2.4. Antimicrobial Activity

Agar-well diffusion method was employed for the evaluation of antimicrobial activity of the CeO_2-CdO binary metal oxide nanocomposites against gram positive bacteria (*S. aureus* MTCC-96 and *S. pyogenes* MTCC-*1926*) gram negative bacteria (*P. aeruginosa* MTCC-4673 and *K. pneumoniae* MTCC-109) and fungi (*C. albicans* MTCC-183, *F. oxysporum* NAIMCC-F-00886, *A. niger* MTCC-282 and *A. candidus* MTCC-2202). Streptomycin (200 μg/ml) and Clotrimazole (200 μg/ml) were used as positive control. The antimicrobial activities were evaluated by measuring the zone of inhibition (mm), which appear as a clear area around the wells [33]. Bacterial cell suspensions of 10^8 CFU/mL and fungal suspension containing 10^5 spore/mL were prepared and evenly spread on the surface of Mueller-Hinton agar and Sabouraud dextrose agar medium using sterile swabs. Wells of 8 mm diameter were made using a sterile cork borer and the nanocomposites (200 μg) were suspended into the wells. The plates were incubated at 37 °C for 24 h to evaluate the zone of inhibition (ZOI).

2.5. Photocatalytic Performance Test

The photocatalytic activity of each sample was studied by degradation of Rhodamine-B under UV ($\lambda < 400$ nm), visible ($\lambda > 400$ nm), and UV + visible light. The UV and visible irradiance at the reactor surface was 0.15 W/m^2 (Philips 15W/G15 T8, Holland) and 14.5 W/m^2 (Philips 18W/54 1M7 India). The catalytic material loading of the experiment was kept at 0.5 g/L, and the average reactor temperature was maintained at 35 °C. The solution was kept in the dark for 2 h to achieve adsorption–desorption equilibrium in each case. The experiments were carried out by simultaneous exposure of the catalysts, each having 30 mL of Rhodamine-B of 1 mM concentration under stirred conditions. The catalyst-loaded RhB solution was illuminated under UV, visible, and UV + visible light for 60 min, respectively, and sampling was done at 15 min intervals. At given time intervals, the photo-reacted solution of the centrifuged sample was analyzed by recording variations of the absorption band maximum (664 nm), using a UV–visible spectrophotometer (Shimadzu 1700, Japan).