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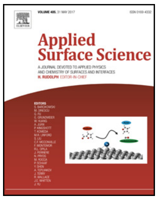

Full length article

Influence of Ce doping on CuO nanoparticles synthesized by microwave irradiation method

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ABSTRACT

This article focuses the effect of Ce doping on the crystal structure, optical, electrochemical and magnetic properties of CuO nanostructures synthesized by microwave irradiation method. Synthesized samples were characterized by x-ray diffraction, ultraviolet-visible spectrometer, photoluminescence spectrometer, fourier transform infrared spectrometer, transmission electron microscope, cyclic voltmeter and vibrating sample magnetometer. X-ray diffraction pattern discloses that the synthesized samples have monoclinic structure without impurity. Transmission electron micrograph shows that Ce substitution induces microstructural change from spherical to rod shape. The optical bandgap calculated from UV–vis absorption spectrum is found to vary between 3.63 and 3.13 eV for undoped and 7(wt%) Ce doped samples, respectively. The photoluminescence spectrum suggests that Ce doped CuO nanoparticles may be used in optoelectronic devices. The functional group analysis carried out by fourier transform infrared spectroscopy confirmed the substitution of Ce in the samples. The specific capacitance analysis confirmed that the Ce doped CuO can be used as electrode material for supercapacitor application. Magnetic properties of the synthesized samples show that ferromagnetic property of CuO increases with Ce content.

1. Introduction

During the past few years, research on transition metal (TM) oxide nanostructures has gained a great interest in the midst of material scientists and engineers due to its diverse properties compared with the bulk counterparts, which in turn gives hopeful applications in various fields of technology [1,2]. The particle size distribution in nanometre range is the basic requirement in nanotechnology. TM oxide nanoparticles show unique physical and chemical properties due to their narrow size and high density of corner or edge surface sites. Different TM oxides like ZnO, TiO_2, CuO, MgO, CeO_2, SnO_2, In_2O_3, WO_3, V_2O_5 and SiO_2 are being investigated by various research groups [3]. Among these metal oxides, copper oxide (CuO) is an interesting multifunctional *p*-type semiconductor material which plays a major role in many areas of science and technology because of its unique properties. It has a narrow bandgap of 1.2 eV in bulk form [4] and it belongs to the monoclinic crystal system. Crystal structure of CuO reveals that Cu atom is coordinated by 4 oxygen atoms in an approximately square planar configuration. Lattice parameters of CuO are $a = 4.6837$ Å, $b = 3.4226$ Å, $c = 5.1288$ Å and $\alpha = \gamma = 90^\circ$, but $\beta = 99.54^\circ$ [5]. It is interesting to note that CuO exhibits antiferromagnetic nature and it has a Neel temperature below 225 K. CuO nanoparticles have been of considerable interest due to its wide application in solar energy conversion [6], lithium-ion batteries [7], nanofluid [8], anodes in battery [9], solar cell [10], superconducting materials [11], gas sensor [12], field effect transistors and field emitters [13], magnetic storage devices [14], photovoltaic devices [15], etc. CuO nanoparticles perform as a better catalyst for the ammonium perchlorate composite propellant (APCP) which is a modern solid-fuel used in rocket vehicles. It acts as a catalyst, thermoelectric materials, glass, ceramic resistors, near-infrared filters, and photothermal applications. All of these applications are enhanced by precise control of particle size in the nanoscale. CuO can be more readily mixed with polymers as compared to other metal oxides. Selective metal substitution into CuO nanoparticles can show the way to the creation of a large number of structural defects such as oxygen vacancies and interstitial defects. These wide applications motivated us to work in CuO nanomaterials.

Many researchers studied the effect of electrical, optical and structural properties of CuO nanoparticles by TM doping like Ni, Mn, Fe, Pb and Ag and rare-earth (RE) doping like Ce, Eu, Pr, Sm, and Tb. For example, Mohamed Basith et al., [16,17] have reported the structural, morphology, optical and magnetic prop-

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erties of Ni-doped CuO and Fe doped CuO nanostructures. They give an account that optical bandgap of CuO increases from 2.8 to 4.3 eV with increasing Ni and Fe dopants. They achieved room temperature ferromagnetism with an optimum value of saturation magnetization of 1.3140×10^{-3} emu/g for 2% Ni. Bayansal et al. [15] have shown that Pb-doping in CuO nanostructure influences the structural, optical and microstructural properties. Jichun Huang et al. [18] have investigated the electrochemical behavior of Ag-doped CuO nanosheet arrays for supercapacitors. They observed an improvement in electrical conductivity of Ag-coated CuO nanosheet arrays. Optoelectronic and photovoltaic application of Co-doped CuO nanomaterial has been discussed by Ponnarasan et al. [19]. In similar fashion, Mariammal et al. [20] have examined the effect of Mn doping in CuO nanoflakes for ethanol sensor.

With an intention to improve the optical, magnetic and photocatalytic properties, rare earth ions are being doped with TM oxides. Doping of rare-earth ions increases the photocurrent response and the separation of electron-hole pairs under ultraviolet (UV) illumination [21,22]. These previous findings demonstrate that rare-earth metal ion substitution has some remarkable effects on the optical and electronic properties of TM oxides. Relating to rare-earth, Abu-Zied et al., [23] have analyzed the Pr^{3+}, Sm^{3+} and Tb^{3+} substitution in CuO nanoparticles and they found that rare-earth substitution promotes the catalytic activity of CuO. Similarly, Ye et al. [24] have predicted that the rare earth–doped CuO nanopowder could be applied in the area of the catalysis and optics. In the same way, Majumder et al. [25] have analyzed the impact of Eu_2O_3 in CuO. They have proved that the incorporation of rare earth Eu_2O_3 up to 30 (wt%) is very effective in increasing the specific capacitive performances of the polypyrrole/CuO composite.

Cerium (Ce^{3+}) is one of the rare earth metal belongs to lanthanide group. Compared with TM doping, research on rare-earth metal doping, especially Ce doping, in CuO is still underprivileged. Only limited articles are available on Ce doping. In this context, Lang et al. [26] have observed that the Ce dopant has a strong effect on crystal structure and PL characteristics of TM oxide nanorod. Murugadoss et al. [27] have shown that Ce has a strong absorption and emission in the visible region and it decreases the size of nanorods, lowered the band gap and increased the intensity of green emission of TM oxide (ZnO) [28]. Another study demonstrated that the Ce doping decreases the crystallinity of the CuO nanoparticles. Moreover, Ce^{3+} is a good photodegradation material which geared 98% degradation within 180 mins under sunlight irradiation [29]. The cytotoxicity and energy gap analysis has shown that the Ce doped CuO nanostructures are biocompatible and non-toxic towards the human cells and lowers the energy gap of CuO from 2.48 to 2.20 eV with an increase in Ce content. This optical bandgap tuning is attributed to the merging of the impurity band with the conduction band of CuO [30]. Further, it is reported that Ce induces room temperature ferromagnetism in CuO nanoparticles and the saturation magnetization reaches 0.04 emu/g [31]. Likewise, Xing et al. [32] have studied the Cu ion distribution on the surface of Ce doped CuO composite oxides for selective catalytic reduction of NO.

Moreover, various metal oxide nanoparticles such as RuO_2, Fe_2O_3, CO_3O_4, NiO, SnO_2, MnO_2, and CuO are being investigated by different research groups for high-power electrochemical pseudocapacitor application. Out of these oxides, CuO is an attractive candidate for supercapacitor electrode materials because it is eco-friendly, cost-effective, and exhibits favorable pseudocapacitive characteristics. It is worth noting that Sheikh et al. [33] have observed the highest specific capacitance of 136 Fg^{-1} in a CuO–PAA hybrid films and Guohua Sun et al. [34] have observed that CuO nanoparticle enhances the specific capacitance of activated carbon to more than 20%.

It is clear from the above literature survey, even though CuO has this much industrial importance, a countable work has been carried out on CuO nanomaterial, most of them focusing on TM doped CuO and the detailed study of structural and optical properties of Ce doped CuO nanoparticles is still inadequate. Therefore, the main goal of this work is to evaluate the consequence of Ce doping on the structural, optical, morphological, electrochemical, and magnetic properties of CuO nanoparticles. In Ce doping, Ce^{3+} ions exhibit a $5d \rightarrow 4f$ emission with a large absorption in the ultraviolet region. Also, Ce doped CuO is good candidates for photonic devices. Therefore, the Ce has been chosen here as a dopant and our work may give new information about the effect of Ce doping on structural, optical, electrochemical and magnetic properties of CuO.

The synthesis method is one of the key factors which control the particle size, morphology, electrochemical and optical properties of metal oxide nanoparticles. The various chemical methods have been developed for the synthesis of CuO nanostructures such as electrode deposition method [35], hydrothermal method [36] co-precipitation method [37], reflux condensation method [38] spin coating method [39], microwave irradiation method [40], magnetron sputtering method [41] etc. But we have chosen the microwave irradiation method for the present work because it is a simple and novel method and it requires a less time for the synthesis of nanoparticles. It has several advantages like short reaction time, small particle size and narrow distribution with good purity of the crystal at the lower energy usage. Due to these advantages, we have chosen the microwave irradiation method and the CuO nanoparticles with diverse concentrations of Ce dopant and their structural, optical, morphological, magnetic and electrochemical properties have been reported in this article.

2. Materials and methods

2.1. Materials

The copper (II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$, 99.9% Merck], Cerium acetate tetrahydrate [$Ce(CH_3COO)_3 \cdot 4H_2O$, 99.9% Merck], Sodium hydroxide [NaOH, 99.5% Merck], Polyethylene glycol [PEG MW: 400] and ethanol [C_2H_2OH, 99.9% Merck] were used for the synthesis of Ce doped CuO nanoparticles discussed in this article. The double distilled water and ethanol were used as solvents. Weight percentage has been followed for the sample synthesis. Here $x = 0$, 0.02, 0.03, 0.05 and 0.07 refers 0, 2, 3, 5, and 7 wt% of Ce dopant.

2.2. Synthesis of CuO and Ce doped CuO nanoparticles

The pure and Ce doped CuO nanoparticles were synthesized by a microwave irradiation method. In a typical synthesis of CuO nanoparticles 5 g of copper acetate monohydrate and 4 g of sodium hydroxide were dissolved separately in 50 ml deionized water and magnetically stirred for 30 min, to obtain a clear transparent solution. It was then poured into a silica crucible, and placed in a domestic microwave oven and exposed to the microwave energy in a 2.45 GHz, multimode cavity 750W for 10 min. A great amount of dark brown precipitation formed. After cooling to room temperature, obtained samples were thoroughly washed using double distilled water and ethanol for several times to remove the unwanted impurities. The same procedure was adopted for Ce doped $Cu_{1-x}Ce_xO$ (with $x = 0$, 0.02, 0.03, 0.05 and 0.07) samples. Doping was achieved by adding the appropriate amount of cerium acetate tetrahydrate (in wt%). Finally, the samples were dried in a hot air oven at 80 °C overnight and then annealed at 400 °C for 3 h in a muffle furnace to get the good crystallites.

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