Rapid Communication

Structural and magnetic properties of self assembled Fe-doped Cu₂O nanorods

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ABSTRACT

Cuprous oxide (Cu₂O) nanorods doped with iron impurities have been synthesized by the polyol method using sodium dodecyl sulfate as the surfactant. The X-ray diffraction measurement reveals the pure phase of simple cubic Cu₂O and the electron microscopy displays its one dimensional morphology. Ferromagnetism was observed at room temperature in the magnetic measurements of the doped samples while undoped sample exhibits only diamagnetism. Room temperature Mössbauer spectra for the samples exhibited only doublets but no sextet, which corresponds to the presence of paramagnetic iron sites. As magnetic moment contribution of the doped ions was insignificant for the observed magnetism, ferromagnetic property in the doped samples could have been originated from the defects as cation vacancies. Existence of the defects was supported by the room temperature photoluminescence spectra of the doped samples in reference to the undoped sample.

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1. Introduction

The mass, charge and spin of electrons in the solid state materials lay the foundation of the current information technology (IT). The semiconductor devices generally take advantage of the charge of electrons, e.g. integrated circuits and high frequency devices. The ferromagnetic materials on the other hand use spin of electrons for mass storage of information, indispensable for IT by magnetic recording (hard disks, magnetic tapes, magneto-optical disks). It is therefore highly desirous to use both charge and spin of electrons to further enhance the performance of devices by using the capability of mass storage and processing of information at the same time. This may be made possible by introducing high concentration of magnetic moments in the semiconductors. Alternatively, we may be able to inject spin-polarized current into semiconductors to control the spin state of carriers, which may allow us to carry out quantum bit operations required for quantum computing [1]. Nanostructured semiconductors doped with transition metal ions are of great interest in this field as both physical properties like ferromagnetism and semiconducting properties co-exist in these materials. The doping of various semiconductors with transition metal ions has been investigated extensively in the recent times and while ferromagnetic behavior at low temperatures has been obtained for such systems frequently, there are fewer reports in the literature

observing ferromagnetism at room temperature and above in the literature.

Sato et al. in 2002 predicted the possibility of having materials with ferromagnetism with high Curie temperature (T_c) using first principle calculations [2], therefore it was quite natural to explore the possibility of observing ferromagnetism at room temperature and above in a wide variety of semiconductor materials like zinc oxide (ZnO), titanium oxide (TiO₂), gallium nitride (GaN) [3–5], etc. Following this theoretical prediction, there has been extensive research to achieve ferromagnetism at room temperature and above in a wide variety of electronic oxide materials for potential applications in the field of spintronic devices, in which the spin of the carriers can be exploited, in addition to their existing attractive applications in transport electronics, ultra-violet light emission, gas sensing, varistors and surface acoustics wave devices and low threshold spin-lasers [6]. In addition, if these nanomaterials are anisotropic, i.e. one dimensional (1D), they may have some additional advantages like extraordinary lengths, flexibility and unique electronic properties due to the quantum effect, therefore find applications in nano-optoelectronics, nanodevices and systems, nanocomposite materials, alternating energy resources, catalysis and sensors. Yuhas et al. have reported a novel all oxide nanowires [7–9] based solar cell design based on 1D nanowires.

Sieberer et al. in 2007 investigated the effect of transition metal substitution in Cu₂O on the basis of ab initio calculations using density functional theory [10]. There are reports of doping Cu₂O with various magnetic and non-magnetic impurities like Co, Mn, Ni, etc. in the literature [11–15] as Cu₂O, diamagnetic by nature, may yield interesting results like ferromagnetism when doped with magnetic ions, yet reports of observation of

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ferromagnetism at room temperature due to the doping of Fe ions are very few in the literature because of limited solubility of iron ions, stabilization of the single phase and the difficult synthesis. Here we report the solution phase synthesis of Cu_2O nanorods doped with dilute Fe impurities and the study of magnetic properties at room temperature.

2. Experimental

2.1. Materials

Diethylene glycol, sodium dodecyl sulfate (SDS), $Cu(CH_3COO)_2 \cdot H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ all of A.R. grade, ethanol (absolute 99.9%) and acetone of H.P.L.C. grade were purchased from S.D. Fine Chemicals, India. All these chemicals were used without further purifications.

2.2. Methods

A new method for synthesis of nanorods of Cu_2O was developed by modifying the well-known polyol method. In a typical procedure, requisite amount of diethylene glycol was taken in the three naked round bottom flask fitted with magnetic stirrer and water condenser. Inert gas atmosphere was created inside the flask by bubbling argon gas through the solution. Surfactant SDS was then added in the appropriate quantity into the flask solution. After sometime, the required amounts of cupric acetate monohydrate and $Fe(NO_3)_3 \cdot 9H_2O$ were added to it. The atomic percentage of iron was calculated with respect to Cu atomic composition for the experiments. Stirred the solution continuously and heated it at 140 °C temperature for the stipulated time of 30 min. After cooling the solution to room temperature, it was centrifuged and the product obtained was then washed twice each with ethanol and acetone, collected subsequentially each time by centrifugation. It was dried in vacuum overnight. The undoped sample was prepared following the same procedure without addition of the iron precursor $Fe(NO_3)_3 \cdot 9H_2O$.

2.3. Measurements

The samples were characterized by powder X-ray diffraction (XRD) by Cu $K\alpha$ radiation and Ni-filter in the 2θ range $32-78°$ using a Rich Seifert Isodebyflex X-ray unit model 2002. Morphology of the samples was characterized by Ziess, Supra-40 VP Field Emission Scanning Electron Microscope (FE-SEM) instrument. Magnetization measurements were done at room temperature by vibrating sample magnetometer (VSM). Mössbauer studies have been done at room temperature using a ^{57}Co source incorporated in Rh matrix and the spectra were analyzed by win-normos software supplied by Wissel, Germany. The room temperature photoluminescence spectra were recorded by Fluorolog (R)-3 Spectrofluorometer.

3. Results and discussion

The powder XRD pattern of the prepared samples shows that they are crystalline in nature and can be indexed to cubic Cu_2O lattice (JCPDS, Joint Committee on Powder Diffraction Standards, file 34–1354) as shown in Fig. 1. The average crystallite size (t) calculated from the line broadening using Scherrer's equation was found to be 6 nm. Fig. 2 shows the FE-SEM image of the Cu_2O anisotropic nanocrystals, i.e. nanorods with diameter 50–55 nm and length 350–400 nm. Therefore we can say that the sample is polycrystalline in nature as the particle size is much larger than
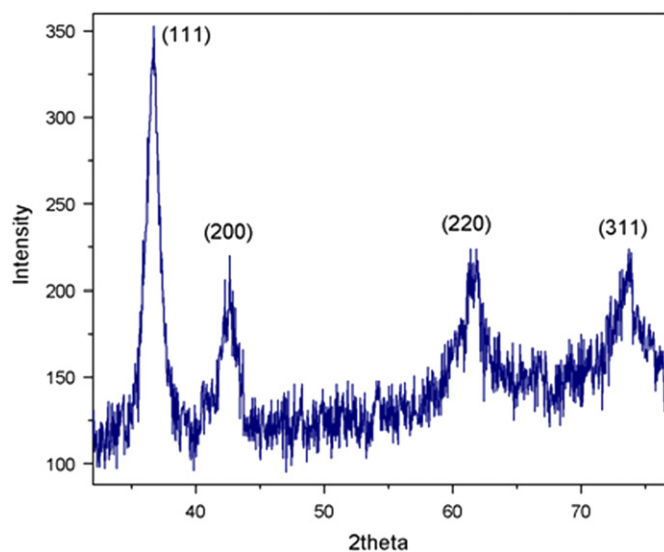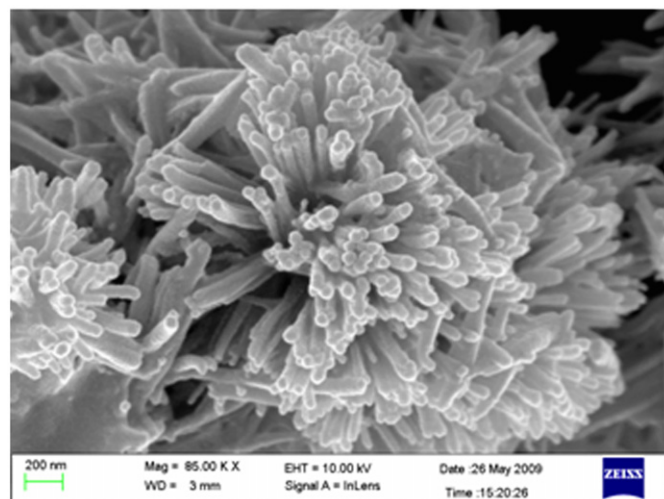

Fig. 1. Powder XRD pattern.

Fig. 2. FE-SEM image.

the crystallite size calculated from Scherrer's equation. As the powder XRD patterns as well the morphology of the nanomaterials were almost identical for the various Fe doped samples and the undoped sample, only representative powder X-ray diffraction pattern and electron microscopy image are given here.

The field dependent magnetization measurements at room temperature for the Fe doped samples and the undoped sample were carried out to study their magnetic property. As shown in Fig. 3, the curve A for 0.5% Fe doping exhibits substantial ferromagnetism at room temperature with a saturation magnetization of 0.884 emu/g and coercivity of 183.7 Oe. While the curve B for 0.2% Fe doping in the same figure displays saturation magnetization and coercivity of values only 0.344 emu/g and 64.5 Oe, respectively, a very weak ferromagnetic behavior was seen in the curve C for 0.1% doping. To confirm that the ferromagnetic behavior originates from the cuprous oxide nanorods rather than the unintentionally introduced magnetic impurities, this measurement was also conducted on the undoped sample. As we can clearly see in Fig. 4 that the curve D exhibits a diamagnetic curve as expected for the diamagnetic cuprous oxide. Therefore it was concluded that the impurities which may be
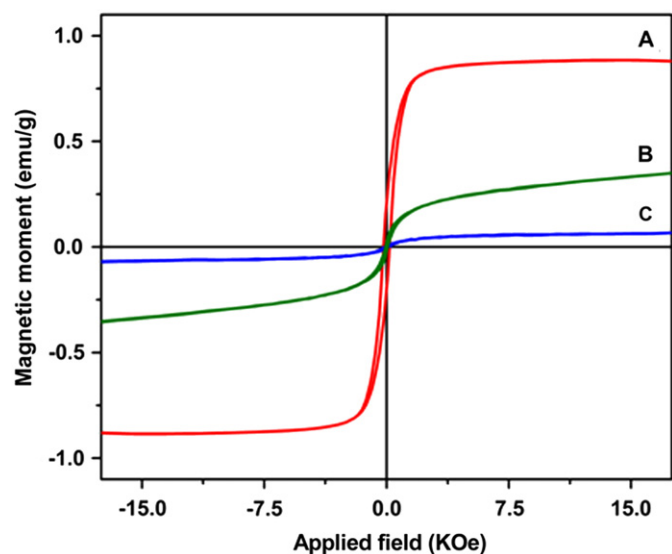
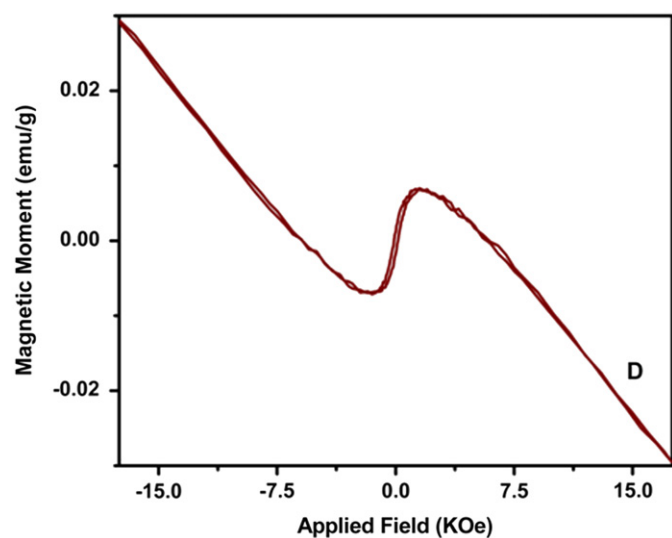**Fig. 3.** M–H curve for doped samples at room temperature (A curve 0.5, B curve 0.2 and C curve 0.1% Fe).

Fig. 4. M–H curve for undoped Cu_2O samples at room temperature (curve D).

Fig. 5. Room temperature Mössbauer spectrum.

present in the samples unintentionally, did not contribute for the ferromagnetism in the doped samples. Also it was observed that ferromagnetic property was dependent on the dopant concentration and as we increase the doping concentration of the Fe ions, there is a marked transition to substantial ferromagnetism in the case of 0.5% doping. Further increment in the Fe concentration beyond 0.5% did not yield any desired result of ferromagnetic behavior, perhaps due to the limited solubility and phase separation.

The ferromagnetic property of the Fe doped samples may be attributed to the presence of the Fe ions in the material, therefore to study about the Fe ions in the samples, iron-57 Mössbauer spectroscopic measurements at room temperature were performed. The presence of the Fe ions in the material, not indicated by the XRD results perhaps due to the low amount, was confirmed by Mössbauer spectroscopy. The de-convoluted spectra exhibit presence of two doublets which represents two different paramagnetic sites of iron ions in the lattice as shown in Fig. 5. Interestingly while it confirms the existence of paramagnetic iron ions, there was no evidence of any magnetic iron ions present in the system
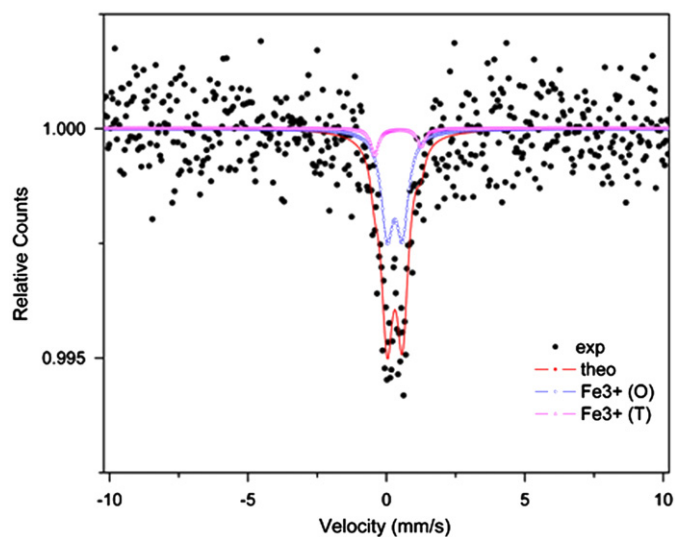
contributing to the ferromagnetic character of the sample as the spectra was devoid of any magnetic sextets (six finger pattern) which represent the presence of magnetic iron sites [16]. The two doublets in the spectra show that the iron impurities are present as Fe^{3+} ions in the octahedral type environment in the neighborhood of six oxygen atoms, perhaps at the face center and tetrahedral type environment in the neighborhood of four oxygen atoms, possibly at the vacant tetrahedral sites of the distorted cubic lattice as presented in Table 1 and indicate the presence of only paramagnetic contribution from Fe ions.

Also the contribution of the magnetic moments of iron ions was estimated for the doped samples. The magnetic susceptibility values were calculated for 0.1%, 0.2% and 0.5% Fe doped concentrations according to the equation, $\chi = n\mu_{eff}^2/3k_BT$ where n is the Fe concentration, and μ_{eff} is equal to $4\,\mu_B$ (per atom) [17]. The values obtained were 0.93, 1.86 and $4.66 \times 10^{-7}\,emu\,Oe^{-1}\,g^{-1}$ for 0.1%, 0.2% and 0.5% Fe concentrations, respectively. Therefore, the total magnetic moments calculated for the doped Fe concentrations were insignificant to account for the observed magnetism by many orders of magnitude. These results clearly suggest that ferromagnetism in the doped samples might have originated from the defects created due to the doped iron ions present in the material [16,18]. Liao et al. [19] have recently reported anomalous ferromagnetism in the Cu_2O nanowires at room temperature purportedly due to the defects in the form of cation vacancies at the surface and the grain boundary. However, their reported values of the coercivity ($\sim 60\,Oe$) and saturation magnetization (of the order of 10^{-5}) are very low as compared to values reported in this present work. Similarly, recently Chen et al. [17] have also shown that ferromagnetic behavior was observed in their Cu_2O samples. Although these samples exhibit saturation magnetization comparable to that of our results in the present study, they have done the measurements at low temperature, i.e. $5\,K$ as compared to our results which are done at room temperature. They have also proved theoretically that cation vacancies in the Cu_2O lattice are the possible cause of the induced magnetic moments [20], leading to the favorable ferromagnetically coupled ground state through the density functional theory (DFT) calculations as magnetism observed in their samples was too large to be accounted for by the magnetic impurities present.

The existence of these defects [21,22] in the Cu_2O nanorods could be supported by the room temperature photoluminescence spectra of the Fe doped samples and the undoped sample (Fig. 6). As the doping concentration of Fe ions increases from 0.1% (curve A), 0.2% (curve B) and 0.5% (curve C) in the samples, the

Table 1
Mössbauer parameters of the Fe doped Cu_2O sample at room temperature.

S. no.	Isomer shift (δ) (mm/s)	Quadrupole splitting (ΔE_Q) (mm/s)	Type of iron ions present
1	0.33	0.58	Fe^{3+} in octahedral type envt.
2	0.40	1.33	Fe^{3+} in tetrahedral type envt.
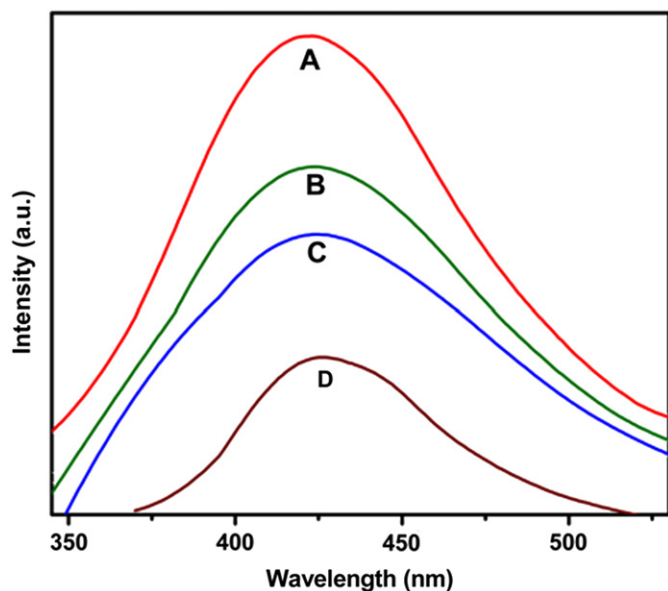
Fig. 6. Photoluminescence spectra at room temperature for doped samples (A curve 0.5, B curve 0.2 and C curve 0.1% Fe) and undoped sample (curve D).

asymmetrical peak becomes broader and simultaneously its intensity also increases as compared to the reference undoped sample (curve D). The asymmetric nature of the luminescence patterns is ascribed to the presence of other inherent emission peaks (due to distributed defect states on the surface and in the interior of a given nanostructured system) at higher wavelengths owing to the asymmetric geometry of the nanosystems. The strong room temperature photoluminescence indicates the high efficiency of photon–electron and/or exciton coupling in the nanorods. As seen from Fig. 6, there is more possibility of having defects with more incorporation of iron ions in the material than the undoped sample due to the enhanced creation of defects because of the dopant ions. It might be suggested that due to the requirement of the charge balance along with the smaller ionic radius of Fe^{3+} in comparison to Cu^+ ions, the presence of iron ions disturbs the long range of the crystallographic ordering which in turn increases the formation of defects in the form of the cation vacancies in the crystal lattice [20] and therefore the origin of magnetism may not result from the Cu $3d$ electrons but instead from the unpaired electrons of O atoms in the immediate vicinity of the cation vacancies. These defects may contribute to magnetic signal, and therefore it is very important to control in the type and number of defects in the crystallographic structure. A more detailed investigation of doped Cu_2O samples with in depth discussion on the induction of defects due to the presence of various dopants like Fe, Mn, Co, etc. and its effect on the magnetism of the sample is underway and will be published soon.

4. Conclusion

Nanorods of Cu_2O doped with Fe impurities were prepared by the polyol method. These samples were found to be single phase

and exhibited ferromagnetic behavior at room temperature. However, no ferromagnetism was found in the undoped sample. Ferromagnetic behavior was found to be dependent on the dopant concentration. The Mössbauer spectra at room temperature for the samples suggested the presence of only paramagnetic iron sites and no ferromagnetic contribution from the iron ions. As the magnetic moment contribution of the doped Fe concentration was too low to account for the observed ferromagnetism, it was suggested that ferromagnetic behavior might have originated from defects created as cation vacancies in the material, existence of whose was endorsed by the room temperature photoluminescence spectrum. Detailed investigations to study the effect of doping transition metal ions like Co, Mn, Ni, etc. on the magnetic properties of cuprous oxide nanoparticles are under way and soon will be published.

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