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Characterization of SnO_2-Coated $CuFe_2O_4$ Nanocomposites

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Nanocomposites are a cohesive class of materials, which have many technological applications due to their excellent properties, realizable within the range of 1–100 nm sizes. Ferrite nanocomposites have been used as the potential candidate materials for photocatalytic and electrocatalytic anodes for oxidation of organic compounds like phenol, anodes for lithium batteries, inert anode for aluminium electrolysis, etc. Recently these are envisaged as an eco-friendly substitute for carbonaceous materials in electrochemical applications. In the present study the $CuFe_2O_4/SnO_2$ nanocomposites have been prepared by a novel combustion method. The TEM figure confirms the nanocrystalline nature of the as-synthesized product. XRD spectra show the well-defined crystalline nature and a phase transition of tetragonal to cubic on increased SnO_2 substitution. The band gap values calculated from the UV-Vis spectra are in the vicinity of semiconducting range. The maximum a.c. electrical conductivity of $1.75 \times 10^{-3}\,S \cdot cm^{-1}$ was obtained for $CuFe_2O_4/5\%$ SnO_2 composition. The impedance spectrum also confirms the semiconducting behavior of the materials.

Keywords nanocomposites, spinel ferrite, X-ray diffraction, electrical conductivity

INTRODUCTION

Nanomaterials, as the name implies, consist of vast materials having minute sizes, at least one dimension in the nanometer range. This covers a wide range of materials such as ceramics, polymers, semiconductors, intermetallics, organometallics, etc. They can be tailor made to the required end use in various shapes, sizes, and morphologies. Since the size of these materials is 1–100 nm and their properties are very critical with the sizes, they can easily be modified and maintained by manipulation of their sizes. The insatiable interest in these materials is due to their unique properties of magnetic molecular recognition, electronic, optical, tunneling, dislocations, interactions, nucleation etc., which are frequently used in emerging areas like aerospace, energy, electronics, magnetic, supramolecules, and superconductors.[1] The introduction of nanomaterials in new fields enables a saving in cost and energy, enhanced performance and environmental benefits. This is really an interesting and interdisciplinary area in which chemists, physicists, engineers, biologists, metallurgists, medical specialists and materials scientists all eagerly engage themselves to get the best out of their own specific field of research and targeted end use. As progress in nanoscience grows quickly, the production of new materials, design, development of new devices and their applications emerge faster into challenging areas. The electrocatalytic effect of these materials can be advantageously utilized for improving the metallurgical process. This paper highlights the preparation and characterization of such a new SnO_2-coated $CuFe_2O_4$ nanocomposites envisaged as clean and catalytic electrodes for metallurgical applications.

EXPERIMENTAL

The wet chemical synthesis is the main route for the preparation of sub-micron size particles. Among these, combustion synthesis is an effective method for the preparation of nanomaterials. The main advantages are use of simple equipment, low temperature process, easily available starting materials, homogeneous mixing, molecular level chemical reaction, uniform particle size distribution and high purity.[2] The $CuFe_2O_4$ nanocomposites coated with SnO_2 (0, 1, 5, 10, 20 wt%) were synthesized using cupric nitrate, ferric nitrate, tin oxide, nitric acid and urea as the starting compounds. The stoichiometric quantities of the above compounds were dissolved in minimum amount of distilled water and the resultant solution was heated continuously. Afterwards the solution

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becomes viscous gel, got ignited automatically giving the voluminous and foamy product of combustion. This has been sintered at 1100°C, keeping in a temperature-controlled furnace at normal atmosphere for 6 h. The crystalline phases of the prepared powders were identified by powder X-ray diffraction technique using an X-ray diffractometer Cu-K_α radiation ($\alpha = 1.5405$ Å). The particle morphology of all the samples was determined by transmission electron microscopy (TEM; JEOL-JEM 100SX microscope) at an accelerating voltage of 200 kV. The TEM specimens were prepared by placing a drop of the sample suspension on a carbon-coated copper grid (400 mesh, Electron Microscopy Sciences) and allowing them to dry in air. High-resolution TEM (HRTEM) images were taken using a JEOL-3010 with 300 kV accelerating voltage. The computer controlled HIOKI 3532 LCR meter (frequency range 42 Hz–5 MHz) has been used for the conductivity and impedance studies at room temperature.

RESULTS AND DISCUSSION

TEM Studies

The presence of nanosized particles of $CuFe_2O_4$ and $CuFe_2O_4/SnO_2$ have been confirmed through TEM and HRTEM analysis. The nanocrystalline nature of $CuFe_2O_4$ with a particle size of approximately 10–20 nm and SnO_2-coated $CuFe_2O_4$ with 20–30 nm are evident from Figures 1a and 1b. The HRTEM images (Figures 2a and 2b) show the well-defined lattice fringes, which confirm the ultrapure crystalline nature of the product. Hence the present study enumerates the possibility of synthesizing nanocomposites of $CuFe_2O_4/SnO_2$ by adopting the urea-nitrate combustion method.

Structural Studies

The XRD patterns of $CuFe_2O_4$ with different concentrations of SnO_2 are shown in Figure 3. Figure 3a shows the XRD pattern of $CuFe_2O_4$ with well-defined and high-intensity peaks matching with the standard (PDF No. 6-545). Figures 3b–3e show the patterns for SnO_2-added $CuFe_2O_4$. A remarkable feature in the patterns is that with increasing addition, the intensities of $CuFe_2O_4$ peaks (311) and (004) are found to decrease continuously. At the same time, a sharp peak (110) and (101) corresponding to SnO_2 is seen to appear, whose intensity increases continuously up to the maximum substitution of 20 wt%. Values of the lattice constants and structural parameters are given in Table 1. The lattice constant values increase with increasing substitution, due to the difference in ionic radii between Cu^{2+}, Fe^{3+}, and Sn^{4+}. The nanocrystalline nature of the synthesized compounds has been calculated using the Debye–Sherror formula $0.9\lambda/\beta\text{Cos}\theta$, where, λ is the wavelength of the target, β is the full width half-maximum of the diffracted (311) plane. The values agreed well with the TEM results.

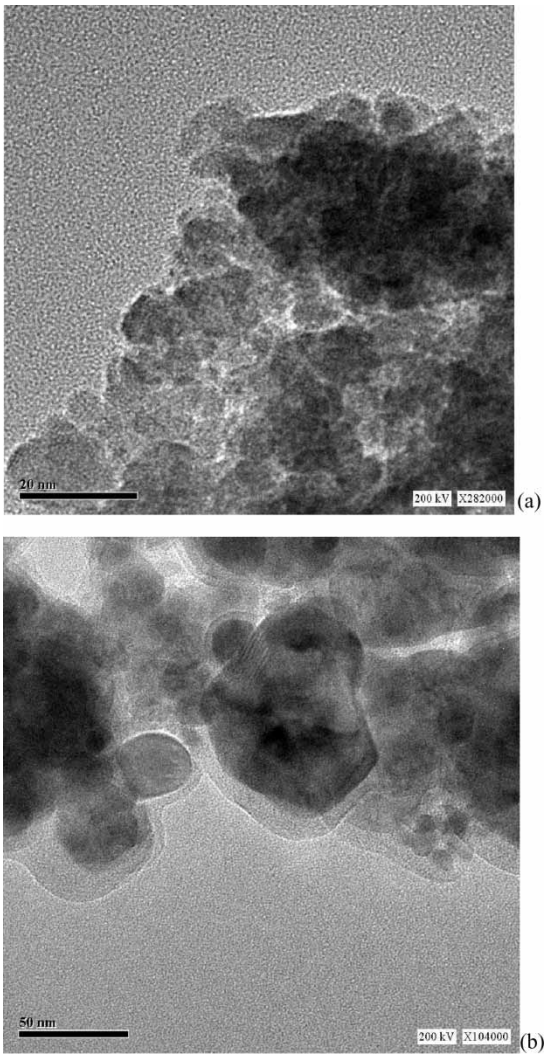

FIG. 1. TEM micrographs of combustion synthesized $CuFe_2O_4$ (a) and SnO_2-coated $CuFe_2O_4$ (b) nanoparticles.

The optical band gap values were calculated from UV-Vis spectra using the formula; $Eg = 1.24/\lambda_{max}$, where λ_{max} is the fundamental absorption edge. The band gap values are 2.63, 2.55, 2.50, 2.91, and 3.07 eV for $CuFe_2O_4$, $CuFe_2O_4/1$ wt% SnO_2, $CuFe_2O_4/5$ wt% SnO_2, $CuFe_2O_4/10$ wt% SnO_2 and $CuFe_2O_4/20$ wt% SnO_2, L respectively. Hence it can be concluded that the synthesized compounds are in the range of semiconductor.[3]

A.C. Conductivity Studies

The relationship between a.c. electrical conductivity and frequency for the copper ferrite without and with addition of SnO_2 is given in Fig. 4. It can be seen that with increase in frequency (log ω) up to 4 kHz a plateau, and a gradual increase, then a sudden spurt at 7 kHz. The same behavior of gradual increase is observed in all the samples. It has also been

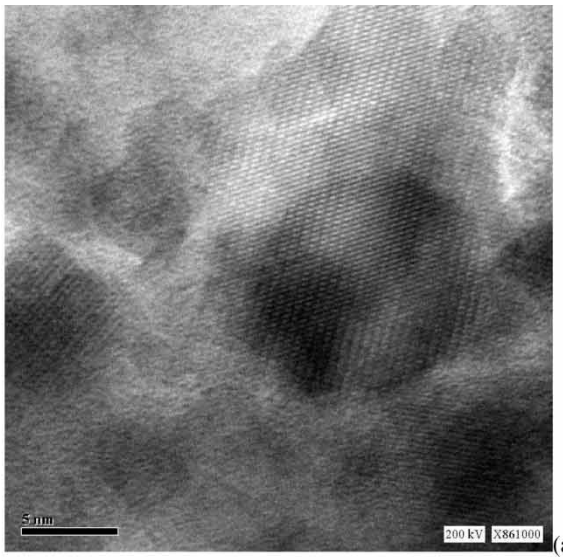

FIG. 2. HRTEM micrographs of combustion synthesized $CuFe_2O_4$ (a) and SnO_2-coated $CuFe_2O_4$ (b) nanoparticles.

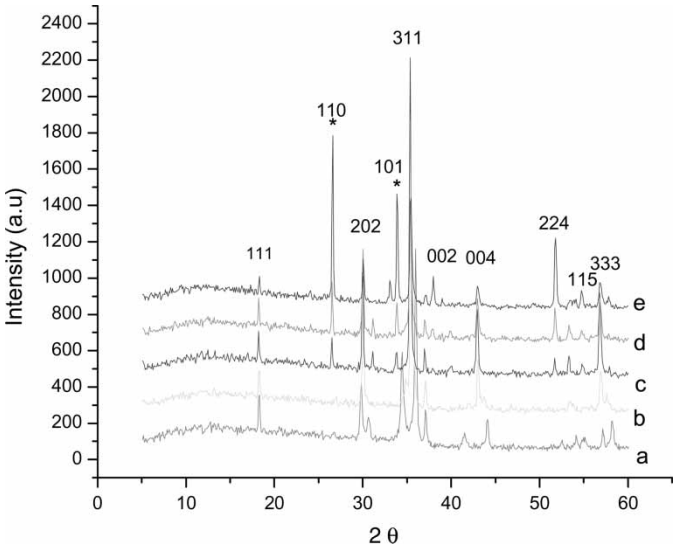

FIG. 3. XRD patterns of $CuFe_2O_4$ (a), $CuFe_2O_4$/1 wt% SnO_2 (b), $CuFe_2O_4$/5 wt% SnO_2 (c), $CuFe_2O_4$/10 wt% SnO_2 (d), and $CuFe_2O_4$/20 wt% SnO_2 (e), (∗) SnO_2.

noticed that parent compound has the lowest conductivity. With addition of SnO_2 the conductivity has been found to increase up to 5 wt% addition. The higher conductivity is resulted only in the $CuFe_2O_4 + 5\%$ SnO_2 composite. All other values lie in between the two. At the frequency of 7 kHz, the conductivity values are 0.0001 to 0.0018. Considering all the compounds the 5wt% SnO_2 is found to be better than other materials. The rate of increase in conductivity with frequency is much higher for the 5 wt% SnO_2 than other compounds. Slowest gain again results for the parent material. These measurements also substantiate the supremacy of $CuFe_2O_4 + 5$ wt% SnO_2 than others in view of its higher conductivity and the rate of conductivity with applied frequency. The high frequency dispersion is noticed to be minimum for the parent compound and maximum for the 5% SnO_2 addition. At high frequency, conductivity dispersion results that may be due to the difference in a hopping

TABLE 1
Crystalline size and unit cell parameters of different composites

Compound	Particle size from TEM (nm)	Grain size from XRD (nm)	Unit cell parameters	
			a (Å)	c (Å)
$CuFe_2O_4$	13	15	8.2740	8.4814
$CuFe_2O_4$/1 wt% SnO_2	—	25	8.3904	8.41895
$CuFe_2O_4$/5 wt% SnO_2	30	33	8.4125	
$CuFe_2O_4$/10 wt% SnO_2	—	51	8.4082	
$CuFe_2O_4$/20 wt% SnO_2	—	58	8.3965	

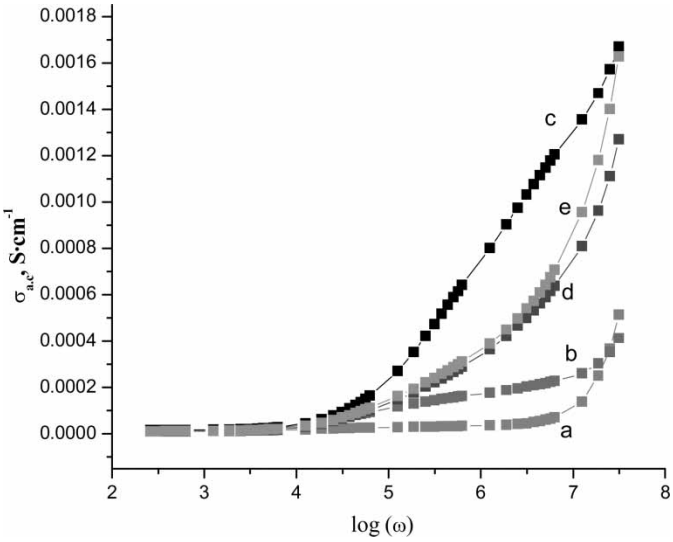

FIG. 4. A.C. electrical conductivity of $CuFe_2O_4$ (a), $CuFe_2O_4$/1 wt% SnO_2 (b), $CuFe_2O_4$/5 wt% SnO_2 (c), $CuFe_2O_4$/10 wt% SnO_2 (d), and $CuFe_2O_4$/20 wt% SnO_2 (e).

mechanism or rate of hopping. This phenomenon is exhibited by many crystalline materials and can be explained on the basis of contribution from both d.c. and a.c. conductivities.[4]

$$\sigma(\omega) = \sigma_{\text{d.c.}} + \sigma_{\text{a.c.}}$$

Since $\sigma_{\text{a.c.}}$ is dependent on frequency, the expression can be written as

$$\sigma\omega = \sigma_{\text{d.c.}} + \text{A}(\omega)^{\text{n}}$$

where A is a conductivity term and n is the temperature dependent constant normally have values between 0 and 1. As observed, the $\sigma_{\text{d.c.}}$ is independent of ω resulting from the drift mobility of free charge carriers. The higher dispersion resulting for 5% SnO_2 is the result of small polaron tunneling mechanism as described earlier. Whereas the decrease of conductivity value with further addition of SnO_2 may be due to reduction of the number of Fe^{3+} ions in octahedral sites, thereby both electron hopping between Fe^{3+} and Fe^{2+} and conductivity are reduced. Moreover as the SnO_2 increases, the grain growth as well as its continuity get disturbed, leading to a barrier to the mobility of the charge carriers, hence, interfering with the normal conducting mechanism. A possibility of higher values than unity has been suggested by Funke et al.[5] at which the conduction is due to localized hopping of the polarons. That frequency is termed as hopping frequency (ω_{p}) of the polarons. The a.c. conductivity is frequency dependent and obeys the Almond–Worz relation

$$\sigma(\omega) = \text{k}\omega_{\text{p}}(1 + \omega/\omega_{\text{p}})^{n}$$

where ω_{p} is the hopping frequency, n is the Jonscher constant, which is assumed to be maximum at high ionic conductivity values due to localized hopping with either translation or rotation of the species.

Impedance Spectra

Impedance measurements enable one to correlate the electrical properties with that of microstructure features of the compounds. The Cole–Cole plots of the SnO_2-added and pure $CuFe_2O_4$ is given in Figure 5, which are characterized by semicircles. Two semicircles resulted for $CuFe_2O_4$ whereas only singles for $CuFe_2O_4 + SnO_2$ materials at 1 to 20 wt%. The double semicircle of $CuFe_2O_4$ indicates the combined contribution from grain interior and grain boundary effects. The bigger semicircle region at low frequencies is for the grain boundary and a small one at high frequency end is for the grains arising from the intragrain phenomenon.[6] The growth, shape and size of the semicircle give important information. The origin of the second semicircle indicates the beginning of intergrains effects on the electrical behavior of the materials. The bulk resistance of the materials calculated from the extrapolation of the center of the semicircle to the real axis (Z') is found to be 4 times higher at low frequency than at high frequency. The single semicircle formed for SnO_2-added $CuFe_2O_4$ clearly indicates a different conduction. The height of the semicircle is noticed to increase for 1, 10, 20 wt%. But for 5 wt% it is found to be less than 1 wt%, but more than $CuFe_2O_4$. Similarly the center of the semicircle shifts towards the higher frequency end giving lower values for the bulk resistance, since $CuFe_2O_4$ has both grain and grain boundary contributions. Considering grain alone, the other materials have higher resistance due to SnO_2 addition. This is due to octahedral preference of Sn^{4+} ions, which

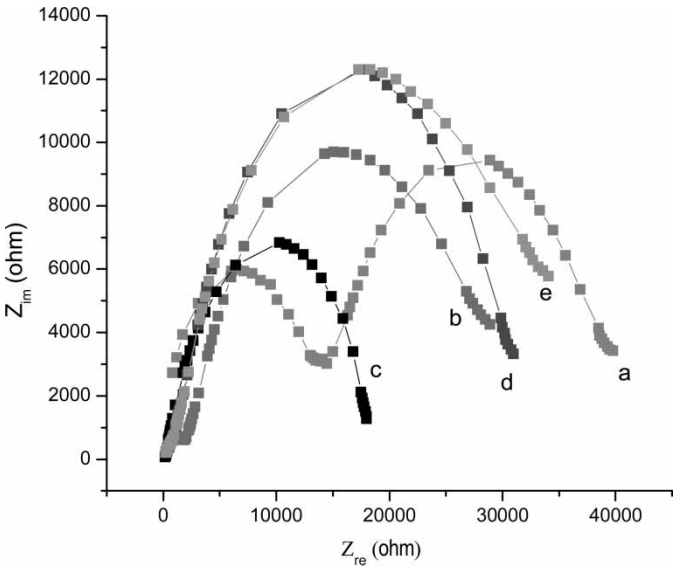

FIG. 5. Impedance spectra of $CuFe_2O_4$ (a), $CuFe_2O_4$/1 wt% SnO_2 (b), $CuFe_2O_4$/5 wt% SnO_2 (c), $CuFe_2O_4$/10 wt% SnO_2 (d), and $CuFe_2O_4$/20 wt% SnO_2 (e).

increases the resistance. Thus $CuFe_2O_4 + 5$ wt% SnO_2 emerges as better material than others in view of its lowest resistance.

It can be concluded that combustion synthesis is found to be one of the simplest and novel methods for preparing nanomaterials. The nanocrystalline nature and coated nanocomposites have been confirmed from TEM and HRTEM analysis. XRD pattern reveals the single-phase compound formation of $CuFe_2O_4$ with tetragonal structure and polycrystalline nature of composites with cubic structure. The band gap values ranging from 2.5 to 3.07 eV indicate the synthesized compounds are semiconductors.

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