Materials Chemistry and Physics 137 (2012) 118–128

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

Copper nano composites functionalized by bis-benzimidazole diamide ligand: Effect of size, co-anion dependent conductivity and band gap studies

Manisha Singla [a], Subash Chandra Mohapatra [b], Sharif Ahmad [b,*]

[a] Dept. of Chemistry, University of Delhi, New Delhi, India
[b] Dept. of Chemistry, Jamia Millia Islamia, New Delhi, India

HIGHLIGHTS

► Nano composites of copper, capped by bis benzimidazole diamide ligand.
► Such copper nano composites have not been used in conductivity studies before.
► Conductance studies for these thus make this work unique.
► The dc conductivity of these composites is much higher than normal.

ARTICLE INFO

Article history:
Received 29 June 2011
Received in revised form
21 June 2012
Accepted 23 August 2012

Keywords:
Composite materials
Chemical synthesis
Electron microscopy
Thermo gravimetric analysis

ABSTRACT

Copper (I) and copper (II) nano composites capped with a bis-benzimidazole diamide ligand were prepared by reverse micelle method and characterized using CHNS, FTIR, ^{1}H NMR, TEM and DLS studies. All particles were spherical ranging between 10 and 70 nm. They displayed a quasi reversible redox wave due to the Cu (II)/Cu (I) reduction process. The E'_{g1} values shift anodically as $NO_3^- < Cl^- < SCN^-$. Electrochemical HOMO and LUMO band gap (E'_{g1}) for the nano composites were +1.80 (NO_3^-), +2.80 (Cl^-) and +4.10 (SCN^-) eV, respectively. However, the optical band gap (E_{g1}) for the nano composites was calculated from their absorption edges and lie between 1.77 and 4.13 eV. Fluorescence studies reveal that nano composites in themselves behave as an enhancer and quencher in respect to ligand, Quantum yield (φ) is varying from 0.008 to 0.02 photon. The activation energies range from 34 to 54 kJ mol^{-1} and are quite low in comparison to that of the free bis-benzimidazole diamide ligand (137 kJ mol^{-1}). The lower activation energies further re-emphasize the nano size of these composites. At room temperature, the dc conductivity lies between 1×10^{-4}–9.33×10^{-4} S cm^{-1} [$NO_3^- > SCN^- > Cl^-$] indicating them to be on the semiconductor insulator interface. The dielectric constant, dielectric loss and the ac conductivity were measured for all nano at room temperature and below the room temperature for the nano composite containing nitrate as co-anion. The conductivity was found to follow the correlated barrier hopping (CBH) mechanism; the exponent factor (s) varies from 0.5 to 1.

1. Introduction

Metal nano particles have gained considerable interest due to their potential applications in diverse fields including catalysis, electronics and magnetic media recordings [1]. Copper is the most widely used material in the world due to its cost effective electrical applications. Copper Nano particles have been synthesized and characterized by many different methods. Stability and reactivity make them much reliable and encourage their use and development in new generation of nano electronic devices [2–5]. Among the various methods used for synthesis of nano materials, surfactants play an important role as stabilizers and size controllers [6–21].

Use of suitable surfactants prevents surface oxidation by protecting the outer surface of metal nano-particles other than those of silver and gold. They also control nucleation of particles and thus act as particle growth terminators. Recently, a number of articles have appeared describing the synthesis of copper nano-particles by various methods [21].

Transition metal nano materials have gained a lot of attention because of their technical applications in areas of material science, catalysis and nano electronics [22,23]. Size dependent magnetic and electrical properties are important for the utilization of these

* Corresponding author. Tel.: +91 11 2698 1717; fax: +91 11 2684 0229.
E-mail addresses: manishasingla@gmail.com (M. Singla), subashcm@gmail.com (S.C. Mohapatra), sharifahmad_jmi@yahoo.co.in (S. Ahmad).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2012.08.049

materials as magnetic/electrical devices [24,25]. These nano particles exhibit superior properties than those of their bulk materials. They also show a high catalytic activity as heterogeneous catalysts [26]. ac conductivity measurements are extensively used to characterize electrical properties of various materials and help in the understanding of the nature of conduction mechanism [27]. Dielectric loss is a manifestation of the fundamental properties of a crystalline and amorphous semiconductor material [28]. The temperature dependence is analyzed in terms of phonon frequencies participating in the corresponding electron–phonon interaction [29].

In molecular material science, there is a current trend to combine physical properties such as magnetism and electrical conductivity in a synergetic way [30] and development is expected to lead to material of high technical interest.

Measurement of ac conductivity, dielectric constant and dielectric loss of semiconductors has been extensively used to understand the conduction process [31,32] and it is a powerful tool for obtaining information about the defect states in amorphous semiconductors. Various models such as the quantum mechanism tunneling (QMT) model [33,34] and correlated barrier hopping (CBH) model [35] have been proposed to explain the ac conduction mechanism. In the correlated barrier hopping (CBH) model the electronic conduction is via bipolaron or mixed polaron hopping process [36].

In this work, copper metal salts are being capped by an organic moiety forming stable nano coordination compounds or nano composites. Till now copper nano composites have not been used for size and co-anion dependent study of conductivity, and the correlation of band gap studies with conductivity, TGA and Cyclic voltammetry of copper nano composites. All surface and bulk properties of nano composites were found to be enhanced as compare with those of normal transition metal coordination compounds, thus distinguishing them into a new class of hybrid compounds.

2. Experimental

2.1. Materials

Glycine benzimidazole dihydrochloride and ligand, *N*,*N*′-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide were prepared following the procedure reported earlier [37]. Freshly distilled solvents were employed for all synthetic purposes. Spectroscopic grade solvents were employed for spectral works. All other chemicals were of AR grade.

2.2. Physical measurements

Transmission Electron Microscopy (TEM) were obtained from USIC, Delhi University, Delhi, India (JEOL 2000 EX electron microscope operating at 200 kV) and TEM micrograph of SCN^- containing Cu (I) nano composite were obtained from All India Institute of Medical Sciences (AIIMS) (Philips Morgagni 268 electron microscope, Megaview III Focus, 1100×, 80 kV).

The light scattering experiments were performed on a Photocor FC. All the measurements were done at a scattering angle of 90° at temperature of 20 °C.

IR spectra of these nano composite particles were obtained in the solid state as KBr pellets on a Perkin Elmer FTIR-2000 spectrometer. The thermogravimetric analysis was performed on a Diamond TG-DTA, Perkin Elmer, USA, system on well ground samples with a heating rate of 10 °C min^{-1} from room temperature to 600 °C. Elementary analysis were obtained from USIC, University of Delhi.

Cyclic voltammograms of all the composites were performed on Micro auto lab type III (M3AVT 70762) and recorded in DMSO/DMF solution with 0.1 M TBAP as a supporting electrolyte. A three-electrode configuration composed of Pt-disk working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode was used for measurements. The reversible one-electron Fc^+/Fc couple has an $E_{1/2}$ of 0.145 V versus an $Ag/AgNO_3$ electrode. ^1H NMR was taken on a 300 MHz Bruker instrument in d_6-DMSO. Fluorescence studies were carried out on FL3-11, Fluorolog-3 spectrofluorometer at IIT, New Delhi.

The dielectric measurements were carried out in a frequency range 100 Hz–1 MHz at room temperature using an Agilent-LCR meter in the metal–insulator–metal (MIM) capacitor configuration. The electrical measurements were done on the powdered sample in the form of a pellet. The composite was finally ground and the resulting powder was compressed into a pellet of 13 mm diameter and 1 mm thickness under a pressure of 5 tonnes cm^{-2}. The pellet was then silver electrode on both sides with a layer of silver paint. The dc conductivity of the nano composite pellet so obtained was studied using Keithley 236 source measure unit. The dielectric measurements were carried out in a frequency range 100 Hz–1 MHz and over a temperature range 150 K–300 K using an Agilent-LCR meter in the metal–insulator–metal (MIM) capacitor configuration. The temperature dependent dielectric studies were carried out using a specifically designed three terminal sample cell. The LCR meter directly provided the values of capacitance (C) and dielectric loss (tan δ). Other parameters like dielectric constant (ε) and the ac conductivity (σ ac) were completed using:

$$\varepsilon' = Ct/\varepsilon_0 A \tag{1}$$

where C is the capacitance (farad); t is the thickness (m); A is the area (m^2); $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1} and

$$\sigma\ \mathrm{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan\delta \tag{2}$$

where f is the frequency (Hz) of the applied electric field.

2.3. Synthesis

2.3.1. Preparation of the ligand

N,*N*′-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide (L)

The bis benzimidazole diamide ligand, *N*,*N*′-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide $C_{24}H_{20}N_6O_2 \cdot 1.25H_2O$ (L), was synthesized by using procedures reported earlier [37]. It was characterized by ^1H NMR and IR spectral studies. This multidentate ligand has been utilized to functionalize the copper metal ions to generate the new nano composites.