Materials Science & Engineering B 228 (2018) 132–141

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

Photocatalytic and ferromagnetic properties of electrically conducting multifunctional Ni/NiO nanocomposites in amorphous carbon matrix

V. Ganeshchandra Prabhu, Abdul Rasheed Paloly, N.G. Divya, M. Junaid Bushiri*

Nanofunctional Materials Lab, Department of Physics, Cochin University of Science and Technology, Kochi, Kerala 682022, India

ARTICLE INFO

Keywords:
Ni/NiO nanocomposites
Raman
Amorphous carbon
Electrical
Magnetic
Photocatalytic

ABSTRACT

NiO rich Ni/NiO nanocomposites in amorphous carbon matrix was synthesized using solution combustion method and characterized with XRD, FTIR, Raman, SEM, TEM, SAED and XPS. Presence of amorphous carbon (sp^2 hybridized) matrix was confirmed from the Raman spectra since compounds were having I_D/I_G ratio higher than 1. Electrical conductivity of the NiO rich Ni/NiO increased with temperature which corresponds to semiconductor nature. Thermal activation energy increased with respect to Ni content in NiO rich Ni/NiO nanocomposites. Sample with higher Ni content showed better photodegradation efficiency in methylene blue which was contributed by surface plasmon resonance (SPR) of nickel nanoparticles. Higher value of room temperature magnetic coercivity of NiO rich Ni/NiO nanocomposites were due to less magnetic interactions between the nanoparticles attributed to decrease of Ni content in the sample. Blocking temperature of Ni/NiO nanocomposites was close to room temperature and it exhibited ferromagnetism.

1. Introduction

Ni/NiO nanocomposites system is subject of research recently because of its variety of applications in the field of catalysis, magnetic recording devices, dye absorption, lithium storage, bioseparations etc. [1–5]. Ni is ferromagnetic (FM) and NiO is antiferromagnetic (AFM), the interaction between FM and AFM would give rise to exchange bias (H_E) [6–9]. There has been great demand for the photocatalytic materials, which can degrade the toxic organic wastes as well as textile dyes. The drawback in the usage of photocatalysts is that, it could not be easily removed after the photocatalytic reaction. On the other hand magnetic composites based photo catalysts can be magnetically separated after its use [10–12]. However, some of the presently available magnetic nanoparticles are prone to oxidation and hence, its magnetic property may get reduced after repeated use. A protective matrix, layer or coating may be best suited to protect these materials from the surrounding environment. It is reported that, polymer like polyaniline can be used as protective covering for iron based nano particles which shows modified physical properties with respect to pristine polymers [13,14]. Carbon is one of the best non-toxic materials which can be used as a protective and supporting system for nanocrystalline multifunctional materials. Metal or metal oxide composites with carbonaceous or polymeric material may have applications such as catalyst, sensors, nanoelectronics, photocatalyst, electric and electrode materials [15–19]. NiO based materials have been previously studied as a typical photocatalysts for the degradation of organic dyes/molecules [20–23]. Interestingly, the combination of metal and semiconductor can vary the photo catalytic properties of materials by modifying the surface properties of the semiconductor [24].

Ni/NiO nanocomposites is an ideal, compatible metal and semiconductor combination system, and it can be synthesized by pulsed laser deposition, reactive ball milling of NiO, partial mechanochemical reduction of NiO, thermal decomposition of nickel acetate and solution combustion synthesis [7,9,25–27] etc. Among these methods, solution combustion synthesis (SCS) is a simple, fast and versatile method, for the synthesis of Ni/NiO [27–29]. In our previous communication, we have reported the synthesis of nickel rich Ni/NiO using SCS and their detailed magnetic properties [6]. The present work focuses on the synthesis of NiO rich Ni/NiO composite system, by changing the fuel to oxidizer ratio used for the synthesis, keeping the volume of HNO_3 as fixed. Electric, photocatalytic and magnetic properties of Ni/NiO nanocomposites is also investigated.

* Corresponding author.
E-mail address: junaidbushiri@cusat.ac.in (M.J. Bushiri).

https://doi.org/10.1016/j.mseb.2017.11.017
Received 21 May 2017; Received in revised form 10 November 2017; Accepted 20 November 2017

2. Experimental

2.1. Synthesis

All the chemicals used for the synthesis were of AR grade (Spectrochem Pvt Ltd. Mumbai, India). Ni/NiO nanocomposites used in the present investigation were synthesized by the solution combustion method [6]. 4 gm of nickel acetate (fuel) and citric acid (oxidizer) were dissolved in 20 ml of deionized water separately and mixed together (fuel to oxidizer ratio 1:1). In the above solution mixture, 30 ml HNO_3 (15.44 M) was added and the pH of the solution was adjusted to 7 by adding ammonia solution. The precursor solution was heated on a hot plate (one hour) to get the experimental sample (Ni-NiO-3). Synthesis of Ni-NiO-4 was done with the above mentioned reactants with the same procedure by keeping the fuel to oxidizer ratio as1:2 (2 gm citric acid and 4 gm nickel acetate).

2.2. Characterization

XRD pattern of samples were done using PANALYTICAL XPERT-PRO X-ray diffractometer with CuKα radiation (1.5404 A°). Raman spectra of the sample were recorded with a Horiba Jobin Yvon Lab RAM HR system (resolution of the order of 3 cm^{-1}) equipped with He-Ne laser (632.8 nm). Fourier Transform Infra Red spectroscopy (FTIR) of the samples was performed using IRAffinity-1-8400S by KBr pellet method. JEOL JSM-6390 LV Model Scanning Electron Microscope (SEM) was used to see the morphology of the samples. X-ray photo-electron spectroscopy (XPS) of the samples was measured by using Kratos AXIS Ultra spectrometer. JEOL JEM 2100 model High Resolution Transmission Electron Microscope (HRTEM) operated at 200 keV was used for the TEM measurements. An Elementar Vario EL III C-H-N Analyser was used for the analysis of carbon, hydrogen, nitrogen present in the samples. The dc conductivity of the pelletized samples with densities 6.509 g/cm^3 (Ni-NiO-1), 6.123 g/cm^3 (Ni-NiO-2), 3.752 g/cm^3 (Ni-NiO-3) and 3.867 g/cm^3 (Ni-NiO-4) were measured using Keithley model 2400 source meter automated with Lab-VIEW software. UV-Vis absorption spectra of the samples were measured with UV-VIS-NIR spectrometer (JASCO-V-570). A Lakeshore make Model 7410 Vibrating Sample Magnetometers (VSM) was used to measure magnetic hysteresis and the temperature dependent magnetization.

2.3. Photodegradation studies

Photodegradation properties of the samples were investigated by taking Methylene Blue (MB) as the model solution under direct sunlight exposure. 0.125 mM MB solution was prepared initially, which was poured into 5 ml borosil bottles with 5 g/L catalyst loading. After each one hour of exposure to solar radiation, optical absorption measurements of remnant MB solution were performed with UV-VIS-NIR spectrometer (JASCO-V-570). The experiment was repeated for 0.05 mM and 0.025 mM of MB with the above described protocol.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD pattern of Ni-NiO-3 has diffraction peaks at 2θ values of 37.23 (1 1 1), 43.30 (2 0 0), 44.50 (1 1 1), 51.93 (2 0 0), 62.97 (2 2 0), 75.44 (3 1 1), 76.33 (2 2 0) and 79.56 (2 2 2) (Fig. 1). Among these, diffraction peaks at 2θ, 37.23, 43.30, 62.97 and 75.44 are corresponding

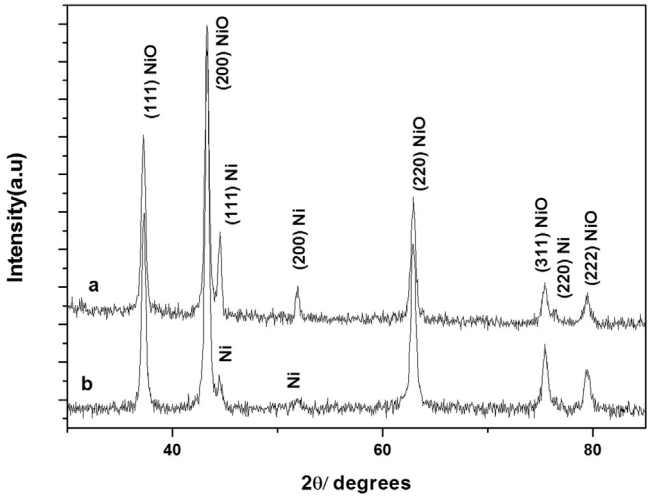

Fig. 1. X-ray diffraction patterns of Ni/NiO nanocomposites synthesized by solution combustion method using (a) 30 ml of HNO_3 with fuel to oxidizer ratio of 1:1(Ni-NiO-3) (b) 30 ml of HNO_3 with fuel to oxidizer ratio of 1:2 (Ni-NiO-4).

Table 1
Raman shift (cm^{-1}) of Ni/NiO nanocomposites synthesized by solution combustion method with different fuel to oxidizer ratios.

N-NiO-1*	N-NiO-2*	N-NiO-3	N-NiO-4	Assignments
189 vw	187 s	189 vw	184 vw	Lattice modes
494 w	488 vs	502 w	499 w	1 LO-NiO
707 vw	707 s	707 vw	707 vw	2 TO-NiO
	1267 w			
	1355 w	1347 s	1352 w	D band
	1405 w			
	1504 vw	1544 sh	1552 sh	G band

vw: very weak, w: weak, s: strong, vs: very strong, sh: shoulder.
* Synthesis of these samples are reported in reference [6].

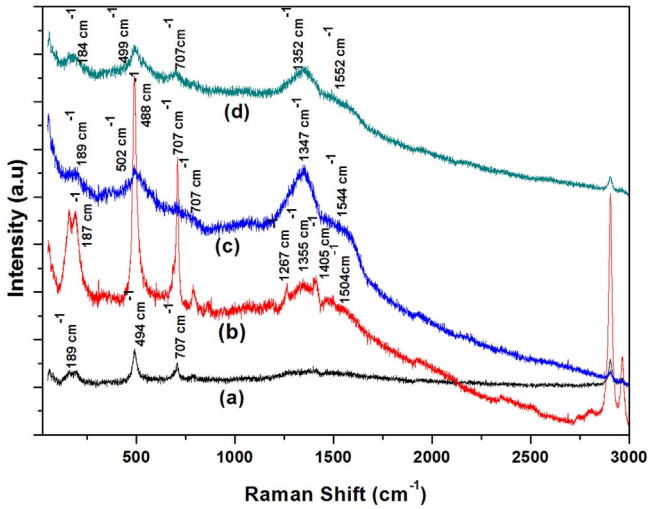

Fig. 2. Raman spectra of Ni/NiO nanocomposites synthesized by solution combustion method using (a) 30 ml of HNO_3 with fuel to oxidizer ratio of 2:1 (Ni-NiO-1) (b) 45 ml of HNO_3 with fuel to oxidizer ratio of 2:1 (Ni-NiO-2) (c) 30 ml of HNO_3 with fuel to oxidizer ratio of 1:1(Ni-NiO-3) (d) 30 ml of HNO_3 with fuel to oxidizer ratio of 1:2 (Ni-NiO-4).