Synthetic Metals 232 (2017) 8–16

Contents lists available at ScienceDirect

Synthetic Metals

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

Research paper

$Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$-graphene nano-heterostructures for various potential applications

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ARTICLE INFO

Keywords:
Spinel ferrite
Reduced graphene oxide (rGO)
Nano-heterostructures
Photocatalysis
Electrical measurements

ABSTRACT

Rare earth Nd^{3+} doped $Mg_{0.8}Ca_{0.2}Fe_2O_4$ nanoparticles were prepared via chemical co-precipitation route. XRD confirmed the cubic structure of all compositions and XRD data was used to determine the lattice constant (a), cell volume (V), crystallite size (D) and porosity. Reduced graphene oxide (rGO) prepared via chemical route was utilized to obtain the $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$-rGO nanocomposite materials. SEM analysis confirmed the well dispersed $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles among the graphene sheets. The photocatalytic degradation rate of methylene blue was higher in the presence of nanocomposite as compared to the bare nanoparticles under visible light irradiation. The enhanced photocatalytic activity of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$-rGO nanocomposite could be related to the decreased charge transfer resistance of composite materials investigated by electrochemical impedance spectroscopic (EIS) analysis. The value of dielectric constant and dielectric loss decreased with the increase in value of Nd^{3+} from 0 to 0.12 mol.

1. Introduction

Nanotechnology is the science of physical and chemical properties of materials that have at-least one dimension in the range of 1–100 nm [1]. Nanotechnology is attracting researchers all over the world since last few decades. Nanomaterials have a broad spectrum of their application almost in every field of daily life. They have applications in medical diagnosis and therapy [2], catalysis [3], telecommunication [4], energy conversion devices, energy storage devices etc [5,6]. The characteristics of materials considerably change at nano-scale as compared to their bulk counter parts [7]. For instance the surface plasmon band appear in UV–vis spectra of metal nanoparticles (Au, Ag, Cu etc), whereas the corresponding bulk metals do not exhibit any plasmon band [8]. The variable oxidation states of transition metal oxides show their applications in modern electronic and other devices [9]. Ferrites are the transition metal oxides with significant Fe contents, magnetic in nature and serve as vital component in many modern electronic devices. Ferrites are classified as soft ferrites and hard ferrites with respect to their magnetic properties. Soft ferrites are the material that magnetized and demagnetized very easily so they are highly permeable. They have verity of applications in biology. Hard ferrites are permanent magnetic materials that possess high coercivity and greater remanance after magnetization and have applications in memory storage appliances etc [10]. Among ferrites spinel ferrites are investigated to modify their properties depending upon their final usage. The general formula of spinel ferrites is MFe_2O_4 (where M is any divalent metal cation and Fe is trivalent metal cation).They are chemically stable, extremely resistive and can be easily prepared by dry as well as wet chemical methods. They can be prepared from cheap raw materials, therefore they are economically cheap and smart materials [11,12]. Spinel ferrites also possess environmental applications. They exhibit the band gap that corresponds to visible light. For instance zinc ferrite exhibits band gap ~ 1.9 eV less than TiO_2. Further $ZnFe_2O_4$ particles are highly stable and cheap [13]. $MgFe_2O_4$ has been investigated extensively. For example Kotlana et al. studied the Lithium doped magnesium ferrites and reported that humidity sensitivity of ferrites increased by Li incorporation because of increasing charge density and pore size [14]. Hankare et al. investigated the variation in magnetic and structural properties of Mg-ferrites with the increase in chromium concentration [15]. Paik et al. reported the kinetics and formation process of

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http://dx.doi.org/10.1016/j.synthmet.2017.07.015
Received 2 January 2017; Received in revised form 8 July 2017; Accepted 19 July 2017
Available online 04 August 2017
0379-6779/

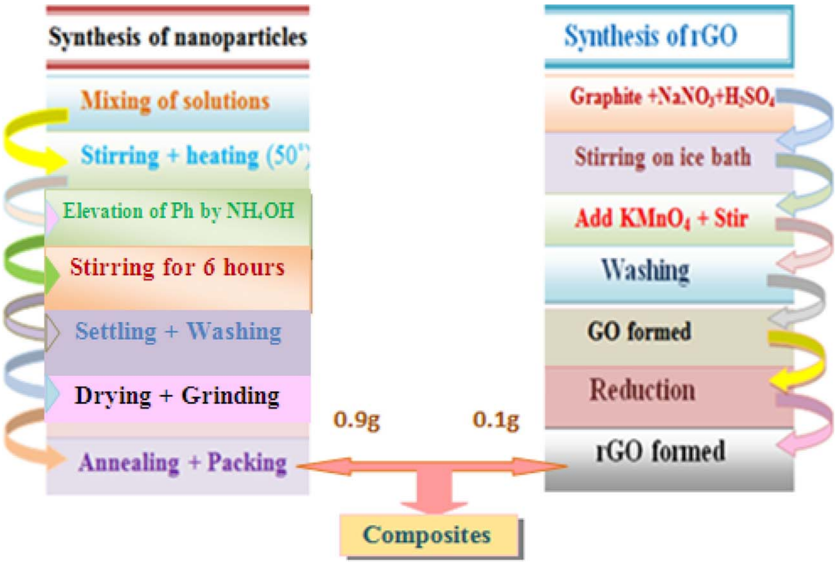

Fig. 1. Schematic illustration of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles synthesis.

magnesium ferrites nanoparticles and studied the temperature dependence on rate constant [16]. Availability of pure water for drinking purpose is the major issue in the world. With the passage of time due to increased population, the problem is increasing continuously [17,18]. The major contaminants present in water are of three types: (a) metal ions in dissolved form (b) organic based impurities and (c) pathogenic contaminants. Many chemical and physical routes are employed to remove these impurities. For example activated sludge process [19], reverse osmosis, photo-catalytic degradation etc [20]. Organic compounds can be removed by photocatalytic decaying into non-toxic compounds like H_2O and CO_2. Semiconductor materials are used for degradation of organic impurities. Titania (TiO_2) was the first material used for photo-catalysis [21]. Use of TiO_2 as a photo-catalyst has many positive as well as negative aspects. It is non-toxic, highly stable photocatalytic material and forms secondary radicals, which degrade the pollutants [22]. The disadvantage of using Titania is that it has band gap ~3.2 eV which lies in the ultra violet region. The major part of sun light is visible and UV is just 3–4% of sunlight. The band gap of a good photocatalyst should be less than 3.2 eV that lie in the visible region (400–800 nm). The significant efforts are being devoted for development of visible light driven photocatalytic materials. Such materials can be obtained by two ways either by minimizing the band gap (~1.9–2.1 eV) by doping TiO_2 with nitrogen, carbon and sulfur in place of oxygen or by mounting new efficient visible light driven photocatalyst. Among various semiconductors materials transition metal oxides are the materials that exhibit absorption in range of 400–800 nm. For example Nb_2O_5, CdS, some oxides of spinel type e.g.$CuCr_2O_4$, perovskites such as $NaTiO_3$, $BaTi_4O_9$ etc. However the major problem in commercialization of these semiconductors is their effective isolation and recovering is costly process. The difficulty can be prevail over by insertion of magnetic particles with semiconductor materials [23]. There is another drawback of using pure semiconductors is fast recombination of electron hole pairs [24]. Graphene is a new class of carbon atoms mono layered structure with sp^2 hybridization. Graphene is mother of all allotropic forms of carbon. When graphene is rolled it gives one dimensional" nanotubes", by wrapping it gives zero dimensional "fullerenes" and by stacking it gives three dimensional "graphite" [25]. Moreover it is light weight, possess great mechanical strength and transparent. The applications spectrum of graphene is very broad. For example Akhavan et al. reported that graphene could enhance the photocatalytic activity of ZnO nanorod films [26]. It has also been reported that the graphene can also be used in bio-medical research [27]. Graphene when mixed with ferrite and other metal oxide nanoparticles may enhance absorption in visible region. It has also been reported to inhibit the recombination photo-excited electron-hole pair [21,28].

In this paper we will discuss the synthesis of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nano-ferrites and their nanocomposites with flake graphene visible light driven photocatalysis and other potential applications.

2. Experimental work

2.1. Chemicals used

$Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles were fabricated by the following precursors/chemicals: Iron nitrate nona-hydrate [Fe $(NO_3)_3.9H_2O$, BDH (AnalaR), 98%], Magnesium acetate [$(CH_3COO)_2Mg.4H_2O$, Merck, 99.5%], Calcium nitrate [$CaNO_3.4H_2O$, Merck, 97%], Neodymium(111) nitrate hexahydrate [($N_3NdO_9.6H_2O$), ALDRICH, 99.9%], Aqueous ammonia [NH_4OH BDH, 35%]. All precursors/chemicals used as received.

2.2. Methods

X-ray powder diffraction (XRD) analysis of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles and composite was recorded on Philip X' Pert PRO3040/60 X-ray diffractometer. It uses CuKα radiation source (λ = 1.54 Å). The dielectric properties of samples were studied in range of 100 MHz to 3 GHz by 4287A RFLCR meter. The DC electrical resistivity was determined using Kiethly 2616 source meter. The catalytic activity of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles and their nano-heterostructures for degradation of methylene blue was monitored by Cary 60 (Agilent) spectrophotometer. The electrochemical impedance spectroscopic analysis (EIS) was conducted on PGZ 402.

2.3. Synthesis of $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles

$Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ nanoparticles were synthesized by co-precipitation method [29]. Schematically, the synthesis has been illustrated in Fig. 1. Following metal salts solutions were prepared in deionised water. The concentrations of all metal salts solutions were kept as: (i) 0.2 M, $Fe(NO_3)_3.9H_2O$ (ii) 0.2 M, $NdNO_3.6H_2O$ (iii) 0.1 M, $Mg(CH_3COO)_2.4H_2O$ (iv) 0.1 M, $CaNO_3.4H_2O$ and (v) 2 M, NH_4OH. Ferrite samples having general formula $Mg_{0.8}Ca_{0.2}Nd_xFe_{2-x}O_4$ (x = 0.00, 0.01, 0.02, 0.04, 0.08 and 0.12) were prepared by mixing stoichiometric amount of all aqueous solutions. All the reaction mixtures were stirred and heated. The heating of all the samples continue until temperature raise up to 50–55 °C. All reaction mixtures pH was