Thermochimica Acta 666 (2018) 103–115

Contents lists available at ScienceDirect

Thermochimica Acta

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

A possible formation mechanism and photocatalytic properties of $CoFe_2O_4$/PVA-SiO_2 nanocomposites

Thomas Dippong[a,*], Dana Toloman[b], Erika-Andrea Levei[c], Oana Cadar[c], Amalia Mesaros[d]

[a] *Technical University of Cluj-Napoca, North University Center of Baia Mare, Department of Chemistry and Biology, 76 Victoriei Street, 430122 Baia Mare, Romania*
[b] *National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donath Street, 400293 Cluj-Napoca, Romania*
[c] *INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath Street, 400293 Cluj-Napoca, Romania*
[d] *Technical University of Cluj-Napoca, Physics and Chemistry Department, Center for Superconductivity, Spintronics and Surface Science, 28 Memorandumului Street, 400114 Cluj-Napoca, Romania*

ARTICLE INFO

Keywords:
Cobalt ferrite
Nanocomposites
Carboxylate precursor
Thermal decomposition
Photocatalysis

ABSTRACT

The paper presents the synthesis of $CoFe_2O_4$ nanocrystallites embedded in PVA-SiO_2 hybrid matrix by a modified sol-gel method. The paper is focused on two aspects: (1) formation of cobalt and iron carboxylate-type precursors (oxalate, lactate, malonate and succinate) in the presence of tetraethylorthosilicate, polyvinylalcohol (PVA) and different diols: 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, and (2) possible decomposition mechanism of carboxylate-type precursors into $CoFe_2O_4$ within the pores of PVA-SiO_2 hybrid matrix. The formation and decomposition of carboxylate-type precursors was studied by thermal analysis coupled with mass spectrometry, while the formation of $CoFe_2O_4$/PVA-SiO_2 nanocomposites (NCs) was investigated by X-ray diffraction and Fourier transformed infrared spectroscopy. The particle size and shape were studied by transmission electron microscopy. At 1000 °C, well-crystallized $CoFe_2O_4$ was evidenced as single phase in G1,2ED and G1,4BD and together with Co_2SiO_4 in G1,2 PD and G1,3 PD. Based on UV–vis absorption spectra, the band gaps of the NCs were evaluated. The photocatalytic activities of the NCs were evaluated by degrading Rhodamine B under UV–vis light irradiation. The reactive radical species produced at the solid-liquid interface were evidenced using electron spin resonance coupled with spin trapping.

1. Introduction

Nanosized cobalt ferrite (CF) has been studied widely due to its chemical stability, mechanical hardness, high electrical resistivity, reasonable cost, excellent dielectric, magnetic and photocatalytic properties [1,2]. The CF's properties are influenced by the synthesis parameters, used reagents, annealing temperature and time, size and morphology of particles. These properties make CF appropriate to a wide range of applications such as lithium ion battery, high-density data storage, magnetic recording, magnetic fluids, hyperthermia therapy, targeted magnetic drug delivery, magnetic separation, biosensors, catalysis, gas detectors, ferro-fluids [3–9]. The application of CF in photocatalysis is based on its low cost and low toxicity together with its magnetic properties that allow magnetic separation from aqueous solutions [5].

Various methods to obtain CF nanoparticles with predefined structural and morphological characteristics have been reported: sol-gel, co-precipitation, microemulsion, hydrothermal, solvothermal, solid state reaction, microwave synthesis, aerosol, ball-milling, ceramic method by firing, reverse micelles and laser ablation [3,4,9]. These methods are effective, but difficult to apply for large-scale production due to their expensive and complicated procedures, high reaction temperatures, long reaction times and involvement of toxic reagents [9]. The sol-gel process provides high quality ceramics and consists in the catalyzed hydrolysis and condensation of alkoxides, leading to a highly viscous gel with an intricate polymer network [10]. The advantage of the gel reaction is both the controlled decomposition of precursors and the prevention of atomization during the heat treatment [4,6]. Furthermore, the reduction of the Co amount in CF's composition will reduce both the production costs and toxicity of such nanocomposites (NCs) [7]. Organic-inorganic hybrid networks such as polyvinylalcohol - silica (PVA-SiO_2), combine the properties of inorganic (biocompatibility, thermal stability, chemical and corrosion resistance, rigidity, nontoxicity) and organic (elasticity, processability, ductility, highly water-permeability) phases and have attracted considerable attention for different applications including catalysis, adsorption, pervaporation, sensors and enzyme encapsulation [11,12].

Transition mixed metal ferrites are good candidates for

---

[*] Corresponding author.
E-mail address: dippong.thomas@yahoo.ro (T. Dippong).

https://doi.org/10.1016/j.tca.2018.05.021
Received 3 February 2018; Received in revised form 4 May 2018; Accepted 24 May 2018

photocatalysis due to their wide band-gap in the visible light spectrum, low cost and corrosion resistance, oxygen storage ability in the crystalline lattice and redox activity [13,14]. Furthermore, ferrites burned under reducing atmospheres form compounds with oxygen defects, facilitate the fixation of oxygen in the existing vacancies. However, their photocatalytic activity is reduced due to the high recombination rate of photogenerated charge carriers, limiting their large-scale applications [15]. This limitation may be overcome using hybridized system, such as CF nanoparticles combined with delocalized conjugated materials (carbon nanotubes, fullerene, graphene and polyaniline) [16].

This paper presents the formation and decomposition of carboxylate precursors to form CF nanoparticles embedded in PVA-SiO_2 matrix by a modified sol-gel method using Co and Fe nitrates, different diols (1,2-ethanediol (1,2ED), 1,2-propanediol (1,2PD), 1,3-propanediol (1,3PD), 1,4-butanediol (1,4BD)), PVA and tetraethylorthosilicate (TEOS). $CoFe_2O_4/SiO_2$-PVA NCs were characterized by thermal analysis coupled with mass spectrometer (TG-MS), differential thermal analysis (DTA), X-ray diffraction (XRD). The shape, morphology and size distribution of the CF nanoparticles in PVA-SiO_2 hybrid matrix were investigated by transmission electron microscopy (TEM). The photocatalytic properties of the NCs were studied by ultraviolet-visible spectroscopy (UV-vis), photocatalysis and electron spin resonance (ESR) coupled with spin trapping.

2. Experimental procedure

$CoFe_2O_4/SiO_2$-PVA (G1,2ED, G1,2PD, G1,3PD and G1,4BD) NCs were prepared by sol-gel method. For synthesis, analytical grade reagents (Merck, Germany) were used without further purification. The average molecular weight (M_w) of PVA was 145.000 g/mol (98% hydrolyzed). *Solution A:* A 5 wt. % PVA solution was prepared by dissolving PVA in deionized water at 85 °C, under vigorous stirring. TEOS ($Si(OC_2H_5)_4$) dissolved in ethanol was added drop-wise under stirring into the PVA solution (PVA:TEOS:H_2O:Ethanol = 0.03:6.5:10:6.5, molar ratio). *Solution B:* Different diols (1,2ED, 1,2PD, 1,3PD or 1,4BD) were added into an aqueous solution of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$) and iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) in molar ratio of diol:Co-nitrate:Fe-nitrate = 8:1:2. Solution A was slowly added to solution B under continuous stirring until complete dissolution. HNO_3 was added to adjust the acidity and the resulting clear solution was exposed to open air for slow gelation (47 days - G1,2ED, 55 days - G1,2PD, 57 days - G1,3PD and 64 days - G1,4BD). The obtained NCs were dried at 40 °C for 4 h and annealed at 200, 600, 800 and 1000 °C for 4 h.

The thermal decomposition was investigated by TG-DTA coupled with a QMS 200 quadrupole mass spectrometer (Residual Gas Analyser - RGA, Stanford Research System) in Pt crucibles, by heating from room temperature to 1000 °C (5 °C/min) under nitrogen flow (20 L/h). The pressure variation with temperature was monitored for CO_2 ($m/z = 44$), CO ($m/z = 28$) and H_2O ($m/z = 18$) evolved during the decomposition process. The formation and decomposition of functional groups were studied by FT-IR using a Spectrum BX II (Perkin Elmer) spectrometer on KBr pellets containing 1% (w/w) sample. UV-vis absorption spectra were recorded with a JASCO V570 UV–vis-NIR spectrophotometer equipped with absolute reflectivity measurement JASCO ARN-475 accessory. The XRD analysis was performed at room temperature, using a Bruker D8 Advance diffractometer, operating at 40 kV, 40 mA with CuKα radiation ($\lambda = 1.54178$ Å). The average crystallites size was calculated using the Scherrer equation (Eq. (1)) [17].

$$D_{hkl} = \frac{0.9\,\lambda}{\beta\cos\theta} \tag{1}$$

Where D is crystallites size, β is the broadening of full width at half the maximum intensity (FWHM) in radian, θ is the Bragg angle, λ is the X-ray wavelength.

Transmission electron microscopy (TEM) observations carried out on a Hitachi HD2700 electron microscope were used to examine the size, shape and clustering of the nanoparticles, while the particle size distributions were determined using UTHSCSA ImageTool Software. The magnetic measurements were performed with a vibrating sample magnetometer (Cryogenic Limited). A 2 T maximum magnetic field was used for the room temperature hysteresis loops. The generation of reactive oxygen species (ROS) was monitored by ESR coupled with a spin trapping probe using a Bruker E500 ELEXSYS X-band (9.52 GHz) spectrometer, at room temperature. 10 mg sample was dispersed in 1 mL dimethyl sulfoxide (DMSO), homogenized in an ultra-sound bath (30 s), followed by addition of 0.2 mol/L 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The samples were prepared just before measurement and transferred into a quartz flat cell optimized for liquids measurements. The photodegradation of Rhodamine B (RhB) was carried out in a Laboratory-Visible-Reactor system using a 400 W halogen lamp (Osram) [18]. 10 mg catalyst was suspended in 10 mL aqueous solution of RhB (10^{-5} mol/L) and stirred for 30 min in the dark to achieve the adsorption equilibrium on the catalyst surface. Each degradation experiment was continuously conducted for 240 min. At every 60 min, 3.5 ml aliquots suspension were withdrawn and analyzed by recording the maximum absorbance of RhB at 554 nm, using a JASCO V570 UV-VIS spectrophotometer. The photocatalytic activity (degradation) was calculated using Eq. (2).

$$\text{Degradation (\%)} = \frac{A_0 - A}{A_0}\,x\,100 \tag{2}$$

Where A_0 and A is the absorbance of RhB at 554 nm before and after exposure to simulated solar light, respectively.

3. Results and discussion

The TG-DTA (Fig. 1a) and TG-MS (Fig. 1b) analyses revealed that the decomposition of precursors takes place in 4 successive stages (2 endothermic and 2 exothermic processes). Generally, the first stage occurs in the temperature range of 65–130 °C with a mass loss of 15–20 wt.% and is attributed to the elimination of residual water (physically adsorbed water, moisture) and to the formation of Fe^{3+}-carboxylate precursors. The second stage is observed between 140–220 °C and corresponds to the elimination of coordinated water and the formation of Co^{2+}-carboxylate precursors. This transformation is accompanied by a mass loss of 13–17 wt.% depending on the diol chemical structure. The main decomposition stage starts around 200 °C with a sharp and massive mass loss of 32–39 wt.%, attributed to the decomposition of the carboxylate groups. Due to the different acidity of Co and Fe aquacations ($pKa_{[Fe(NO3)3]} = 2.22$, $pKa_{[Co(NO3)2]} = 12.2$), nitrates react individually with the diol [19]. The TG-MS revealed the formation of H_2O ($m/z = 18$), CO ($m/z = 28$) and CO_2 ($m/z = 44$) during the thermal decomposition. The curves corresponding to $m/z = 18$ fragment confirm the water release up to 350 °C due to the dehydration processes and to pyrolysis of organic matrix. The evolvement of CO_2 in the temperature range 200–600 °C confirms both the decomposition of Fe and Co-carboxylate salts and the structural changes in the hybrid PVA-SiO_2 matrix. It is well known, that during the carboxylate-type precursor decomposition, the formation of CO and CO_2 occurs simultaneously. In our case, the decrease of $m/z = 28$ curve up to 340 °C corresponding to CO can be observed. This behavior can be explained by the consumption of the CO for partial reduction of Fe^{3+} to Fe^{2+} and Co^{2+} to Co° and reoxidation to Co_3O_4 [20].

For G1,2ED, the DTA curve shows 2 distinct endothermic effects attributed to Fe^{3+}-oxalate ($T_{max} = 111$ °C) and Co^{2+}-oxalate formation ($T_{max} = 169$ °C), according to Eq. (3) (n = 0). The decomposition of precursors appears as 2 distinct exothermic effects between 240–304 °C ($T_{max} = 282$ °C) for Fe^{3+}-oxalate (Eq. (4), n = 0) and between 305–460 °C ($T_{max} = 340$ °C) for Co^{2+}-oxalate (Eq. (5), n = 0). For G1,3PD the DTA curve shows 4 effects: 2 endothermic effects at $T_{max} = 100$ °C attributed to Fe^{3+}-malonate and at $T_{max} = 168$ °C