Applied Clay Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Heteronuclear nanoparticles supported hydrotalcites containing Ni(II) and Fe(III) stable photocatalysts for Orange II degradation

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ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form 9 August 2016
Accepted 17 August 2016
Available online xxxx

Keywords:
Hydrotalcites
Metal nanoparticles
Supported catalysts
Sol-immobilization
Photocatalysis

ABSTRACT

Hydrotalcites containing Ni(II) and Fe(III) was synthesized using co-precipitation method to demonstrate their use as a support material for the homogeneous deposition of Au and Au-Pd nanoparticles via sol-immobilization. Detailed characterization performed by UV–Vis, ATR-FTIR, TGA, Mössbauer spectroscopy, SEM, Cryo-TEM, BET analysis evidenced the structural, morphological and textural properties of the passive support and decoration of nanoparticles on the surface of LDH and evidenced the property to be used as photocatalysts. These materials proved to be efficient photocatalysts for the degradation of environmentally important Orange II dye (OII) as a model pollutant. Different experimental parameters influencing the photocatalytic activity viz., catalyst dosage, initial dye concentration and reusability of the catalyst were studied. Langmuir-Hinshelwood model was used to analyze the kinetics of the photocatalytic process. Heteronuclear Au-Pd nanoparticles immobilized on $NiFeCO_3$ LDH was found to be the best photocatalyst degrading about 95% of the dye (25 mg/L) after 60 min and this activity remains to be nearly the same after recycling the catalyst. This enhancement in the activity was attributed to the presence of Au-Pd Nps, with specific surface area (80 m^2/g), and band gap (2.7 eV). Our study shows the prepared photocatalyst anticipates being a promising candidate for other photocatalytic applications.

1. Introduction

Layered double hydroxides (LDH) are a type of anionic clays consisting of brucite-like layers compensated by charge-balancing anions in the interlayers. They belong to the group of hydrotalcite like minerals. These materials are based on the general formula $(M(II)^{1-x}M(III)^{x}(OH)_2)^{x+}(A^{n-}{}_{x/n}).mH_2O$, where M(II) and M(III) are the divalent (Mg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} etc.) and trivalent (Al^{3+}, Cr^{3+}, Ti^{3+}, Fe^{3+}, etc.) metal cation, respectively. A^{n-} is the exchangeable interlayer (CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}, F^-, etc.) anion (Allmann, 1968; Taylor, 1973; Miyata, 1975). LDH materials possess interesting property to accommodate simple to complex anions in the interlayers that may be organic, inorganic, carboxylate, oxoanion, coordination compounds and polyoxometalates (Newman and Jones, 1998). These lamellar materials drives increasing interest because of their high specific surface area, good anion exchange capacity, expansion properties, low-cost and environmentally benign in areas of catalysis, photocatalysis, catalyst supports, adsorbents, composites, anion exchangers, electrochemical reactions, medicine, etc. (Evans and Duan, 2006; Gomes-Silva et al., 2009, Gunjakar et al., 2011; Lange et al., 2013, Paušová et al., 2015; Liji Sobhana et al., 2016). The LDH support was designed to have Fe in the LDH host layers so as to increase the surface area and prevent the fast recombination of photogenerated electron–hole pair, which increases the photocatalytic activity (Mingfei et al., 2011). Moreover the divalent Ni cation can play significant role with its partially filled 3D orbital towards photocatalysis (Baliarsingh et al., 2013). Although the structure of LDH has the ability for high light absorption in the spectral range, the photocatalytic efficiency is practically low for its applications (Verónica et al., 2008). This is due to the fast recombination of the charge carriers which remains to be a bottleneck problem to improve the semiconductor efficiencies. The most favorable way to overcome this challenge is to decorate the surface of the semiconductors (LDH) with metal

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http://dx.doi.org/10.1016/j.clay.2016.08.016
0169-1317/

nanoparticles (Au, Ag, Pd, Pt, etc.) as they exhibit unusual redox activity by readily accepting electrons from a suitable donor which delays the recombination and thereby increasing the photocatalytic efficiency (Chen et al., 1998; Cozzoli et al., 2005). It should be also noted that the use of metal nanoparticles alone could prove much more catalytic efficiency, however, the reusability of the nanoparticles cannot be achieved as the phase is homogeneous (McNamara et al., 2002). Therefore, supporting the metal nanoparticles on solid supports proves to be superior in offering a heterogeneous and economically viable material, as the catalyst could be filtered and reused again and again.

Bimetallic nanoparticles display unique optical, magnetic properties because of their high surface area-to-volume ratio, which directly results from their very small particle size, can improve the catalytic activity (Valden et al., 1998, Campbell et al., 2002). Among the various bimetallic systems used, alloying of gold with palladium leads to a significant enhancement in activity for their applications (Enache et al., 2006, Edwards and Hutchings, 2008). The deposition of stabilized nanoparticles synthesized by colloidal method onto catalytic supports is highly advantageous because of their precise control of particle size and retaining the structure. In the light of this, we consider this approach to mutually benefit LDH and metal nanoparticles which results in better photocatalyst material.

These materials can be helpful in treating the discharge of untreated dye effluents from textile, leather, and paper, cosmetic and plastic industries which are major sources of environmental pollution all over the world mainly corrupting rivers, lakes and oceans. There are many types of dye being used in the industries of which most of them are toxic, mutagenic and carcinogenic. Therefore, it is inevitable to concentrate on the careful and efficient way to dispose these pollutants. Several types of physical (evaporation, distillation, sedimentation, and adsorption) and chemical (chlorination, ozonation) methods have been employed for the color removal from wastewater. The above said methods greatly limit their use because of their high cost. Photocatalysis has emerged as a promising, efficient and cheap technique to degrade wastewater pollutants (Fernández et al., 2004). This technique involves the use of semiconductors and light as energy source to potentially degrade a wide range of pollutants without producing harmful by-products. Widely known semiconductors include TiO_2, ZnO, SnO_2, CeO_2, Fe_2O_3, ZrO_2, Al_2O_3 and SiO_2 for their photodegrading ability (Mohapatra et al., 2006, Evgenidou et al., 2007, Seftel et al., 2008). In the recent years, layered double hydroxides and their derived structures, has received much attention for photocatalysis owing to their semiconductor properties (Gomes-Silva et al., 2009, Gunjakar et al., 2011; Paušová et al., 2015).

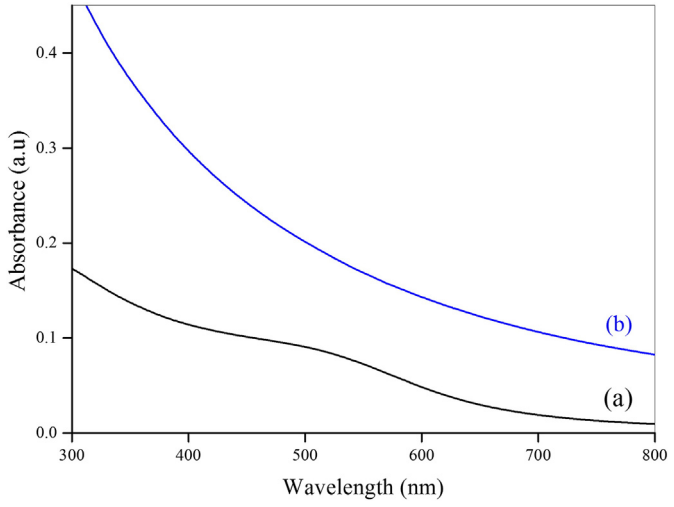

Fig. 1. UV–vis spectra for the formation of nanoparticles (a) Au (b) Au-Pd.

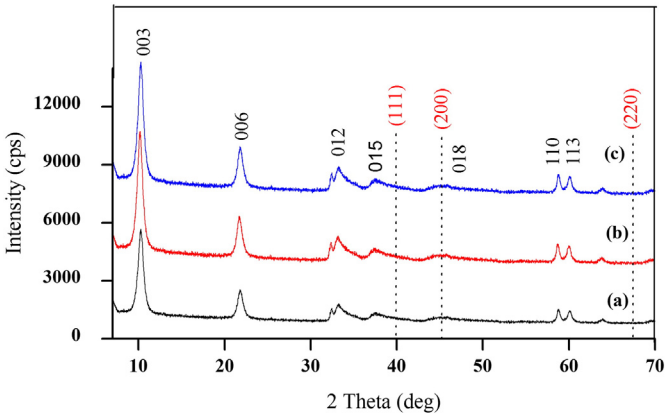

Fig. 2. XRD diffractogram of as-synthesized LDH particles and metal Nps iinmobilized materials (a) LDH. (b) LDH-Au. and (c) LDH-Au-Pd. Reflections from 111, 200, 220 are from the Au, Au-Pd Nps. The reflections are not distinguishable as the amount of total metal loading is 1%. However, the nanoparticles are clearly visible through cryo-TEM images.

LDH materials can be synthesized with the cationic ratios (M^{2+}:M^{3+}) 1:1, 2:1, 3:1 and 4:1. Out of these, 2:2 and 3:1 are the most common ratios used in practice to synthesize a material with most preferable cation ordering patterns (Krivovichev and Yakovenchuk, 2012). Therefore, we have attempted to design a LDH support material to have Ni and Fe in the cationic layers in the ratio 3:1. In this article, we have explored the use of sol-immobilization of Au, Au-Pd nanoparticles onto $NiFeCO_3$ LDH synthesized by co-precipitation method for their photoactivity against model pollutant OII dye.

2. Experimental part

All the reagents were analytical grade and used without further purification.

2.1. Preparation

2.1.1. Synthesis of $NiFeCO_3$ LDH

An aqueous solution of metal salts (Ni and Fe nitrates with ratio 3:1) was added dropwise at a rate of 1 mL·min^{-1} to a flask containing anionic solution containing Sodium Carbonate (2 M). Simultaneously, a solution of NaOH (2 M) was added dropwise to maintain the pH of co-precipitation medium at 11. The synthesis was performed at room temperature and under constant magnetic stirring to ensure homogeneity of the reaction medium. The resultant slurry obtained was subjected to microwave hydrothermal treatment at 100 °C for 1 h. The particles were then washed several times with distilled water to attain neutral pH 7 and to remove the unbound impurities. The sample was then dried at 105 °C for 19 h, crushed to a fine powder to yield the yellow powder, the support material namely $NiFeCO_3$ LDH.

2.1.2. Synthesis of supported metal catalyst

A standard sol-immobilization method was employed to prepare the nanoparticles (1% Au, 1% Au-Pd) supported on $NiFeCO_3$ LDH (Su et al., 2012). Poly vinyl alcohol (PVA, 1 wt% aqueous solution, Aldrich, MW = 10,000, 80% hydrolyzed) was used as a protective ligand during

Table 1
The prepared samples will be denoted as follows in this article.

Sample	Material synthesized	Sample ID
1	$NiFeCO_3$	LDH
2	1%Au/$NiFeCO_3$	LDH-Au
3	1%AuPd/$NiFeCO_3$	LDH-Au-Pd

Please cite this article as: S.S, L.S., et al., Heteronuclear nanoparticles supported hydrotalcites containing Ni(II) and Fe(III) stable photocatalysts for Orange II degradation, Appl. Clay Sci. (2016), http://dx.doi.org/10.1016/j.clay.2016.08.016