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Research paper

Preparation and analysis of multi-layered hybrid nanostructures

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ABSTRACT

In this study, we report a simple and efficient (bath ultrasonication) method for the preparation of multi-functional layered hybrid nanostructures using graphene oxide (GO) and modified Mg-Al layered double hydroxides (LDH) [LDH@GO]. The functional composition, crystalline nature, layered surface morphology and thermal behavior of the hybrid nanostructures of LDH@GO were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, Field-emission scanning electron microscopy, Transmission electron microscopy, elemental analysis and thermo gravimetric analysis. The results confirmed the formation of layered hybrid nanostructures of LDH@GO showing a significant increment in the spacing between GO sheets due to the incorporation of LDH. Also hybrid nanostructures of LDH@GO have better thermal stability as compared to pristine GO.

1. Introduction

The field of material science and nanotechnology has blossomed over the last two decades due to various applications from medical to industrial sectors and from laboratory to market (Das and Prusty, 2013). But some of nanomaterials (NM) were observed with their aggregation due to the high specific area (Bourlinos et al., 2009; Mishra et al., 2011; Mali et al., 2014; Mishra et al., 2012a, 2012b; Esmaeili and Entezari, 2014; Angelopoulou et al., 2015) and also these NM were reported with specific use. On the other side, alloying or hybridizing the two or more NM can give multifunctional properties of the resulting hybrid nanostructures (NS) and also they can be used in many applications. The combination of multi-dimensional NM or layered NS were used to prepare hybrid nanostructures with many advantages due to each kind of NM or NS (Bouakaz et al., 2015; Oraon et al., 2015; Alsharaehn et al., 2016; Chen et al., 2016; He and Hen, 2016; Pino et al., 2016; Kavinkumar and Manivannan, 2016; Zhao et al., 2016). These kinds of hybrid nanostructures with exceptional properties are effective and they were reported for the potential applications (Latorre-Sanchez et al., 2012; Lonkar et al., 2015). Many hybrid materials were reported, which can be made using different NS. But recently organic-inorganic hybrid NS have shown considerable attention (Mishra et al., 2011; Chatterjee and Mishra, 2013a, 2013b). Among the various organic NS materials, graphene oxide (GO) has a tremendous interest in a scientific research. Because GO is two dimensional (2D) and conducting layered NM and it consists of one atom-thick planar sheets of sp^2-bonded honeycomb structure of carbon atoms (Low et al., 2015). GO possesses extraordinary mechanical, thermal, electronic and physical properties, (Hansora et al., 2015; Lonkar et al., 2015), more importantly it contains a range of reactive oxygen functional groups (e.g., hydroxyl groups) (Yan et al., 2016a, 2016b). Therefore, GO was used to prepare organic-inorganic hybrid NS (Wu et al., 2011; Nandi et al., 2013; Esmaeili and Entezari, 2014; Yadav et al., 2014; Angelopoulou et al., 2015, Low et al., 2015; Jain and Mishra, 2016). Many scientists have prepared hybrid NS using different metal and inorganic NM filled with GO, e.g., Titanium oxide–graphene (He and Hen, 2016; Pino et al., 2016; Zhao et al., 2016), Manganese-nickel mixed oxide/graphene (Latorre-Sanchez et al., 2012), Organomontmorillonite/graphene (Bouakaz et al., 2015; Oraon et al., 2015), Calcium carbonate/GO (Zhou et al., 2016), Silver nanoparticle/GO (Kavinkumar and Manivannan, 2016), Cobalt oxide nanoparticles/reduced GO (Alsharaehn et al., 2016), Zinc oxide nanorods/graphene (Chen et al., 2016),Vanadium dioxide nano flowers decorated on GO (Kang et al., 2016) and novel boehmite/GO nano-hybrids (Zhang et al., 2016). Graphene based polymer hybrid nanocomposites were also reported (Acharya et al., 2007; Das and Prusty, 2013; Nandi et al., 2013; Chakraborty et al., 2014; Yadav et al., 2014; Angelopoulou et al., 2015; Bouakaz et al., 2015; Oraon et al., 2015; Yan et al., 2016a, 2016b). But recently in the field of inorganic NM, layered double hydroxide (LDH) has emerged as the most powerful NM for the preparation of multifunctional hybrids for various applications (Yuan and Shi, 2012). The LDH, a family member of inorganic layered NM, have recently attracted considerable attention because of their wide applications (Olfs et al., 2009; Ladewig et al., 2010; Chakraborty et al., 2012; Yuan and Shi, 2012; Lonkar et al., 2013; Menezes et al., 2014; Yang et al., 2014a, 2014b; Zazoua et al., 2014). The chemical composition of LDH is generally

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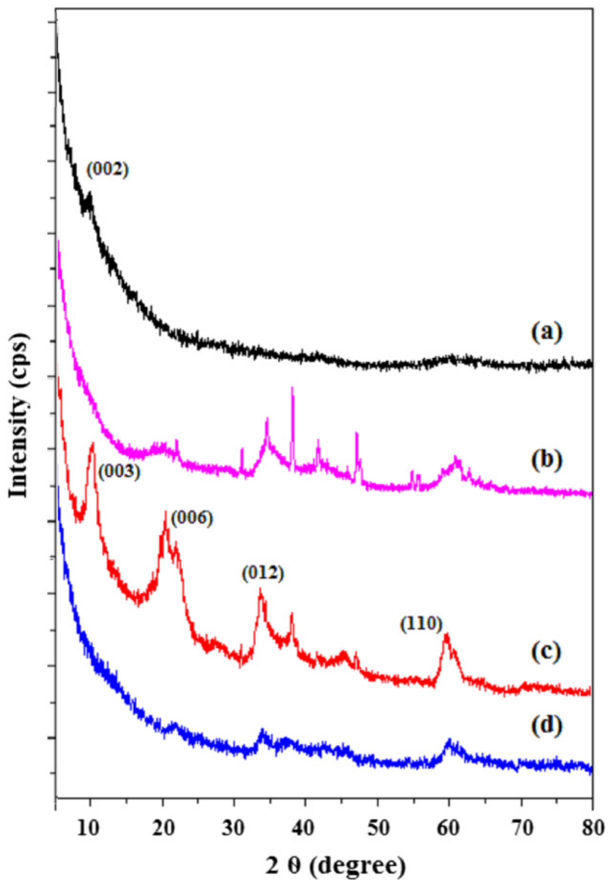

Fig. 1. XRD diffraction pattern of (a) GO (b) Calcined Mg-Al LDH (c) Modified Mg-Al LDH (d) Hybrid layered NS of Mg-Al-LDH@GO.

described by the formula: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}\,[A^{n-}]_{x/n}\cdot mH_2O$. Usually, M^{2+} is a divalent metal (Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Co^{2+} or Fe^{2+}), M^{3+} is a trivalent metal (Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} or Ni^{3+}) and A^{n-} is a *n*-valent anion group (e.g. $CO^{2-}{}_3$, NO_3^-, PO_4^{3-}, SO_4^{2-} or Cl^-). The M^{2+}/M^{3+} ratio, also known as χ, usually lies in the range of $0.1 \leq \chi \leq 0.5$. LDH afford space between the two layers and becomes suitable host for intercalation of planar transition metal complex catalyst containing porphyrin, phthalocyanine or Schiff base ligands (Sun et al., 2015). The LDH have a high anion exchange capacity and large surface area due to their structural configuration (Olfs et al., 2009; Basu et al., 2014). The nanostructures of these minerals are brucite-like positively charged layers resulting from the partial substitution of original Mg^{2+} by Al^{3+} ions. The LDH can absorb inorganic as well as organic anions, which make them attractive materials for technological applications in different areas (Olfs et al., 2009). Recently, graphene decorated layered metal hydroxides like LDH (with different metal) compositions were studied in order to diminish their stacking interactions and to limit the aggregation in graphene nanosheets (Garcia-Gallastegui et al., 2012; Latorre-Sanchez et al., 2012; Tang et al., 2012; Wen et al., 2013; Lonkar et al., 2015). In the present study, we report a simple method for preparation of multifunctional hybrid NS of Mg-Al-LDH@GO by bath ultra-sonication technique. Multi-layered hybrids of LDH@GO were analyzed by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Field-emission scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), Elemental analysis (EDX) and thermo gravimetric analysis (TGA) to investigate their functional composition, crystalline nature, layered surface morphology, elemental analysis and thermal behavior.

2. Experimental

2.1. Materials

For the synthesis of Mg-Al–LDH, magnesium nitrate ($Mg\ (NO_3)_2\ 6H_2O$) and aluminum nitrate ($Al(NO_3)_3\cdot 9H_2O$) (98% purity) were purchased from Rankem, India. Sodium carbonate (anhydrous), Sodium hydroxide and sodium dodecyl sulfate (SDS) were also purchased from Rankem, India and Sigma Aldrich, India respectively. For the synthesis of graphene oxide (GO), fine powder of graphite (98% purity) was purchased from Loba Chem, India. Hydrogen peroxide (H_2O_2), Sulfuric acid (H_2SO_4) hydrochloric acid (HCl), sodium nitrate ($NaNO_3$) were purchased from Merck, India, while potassium permanganate ($KMnO_4$) was purchased from Rankem, India. All the chemicals were of analytical reagent grade and used without any further purification. Double distilled water was used throughout the experiments.

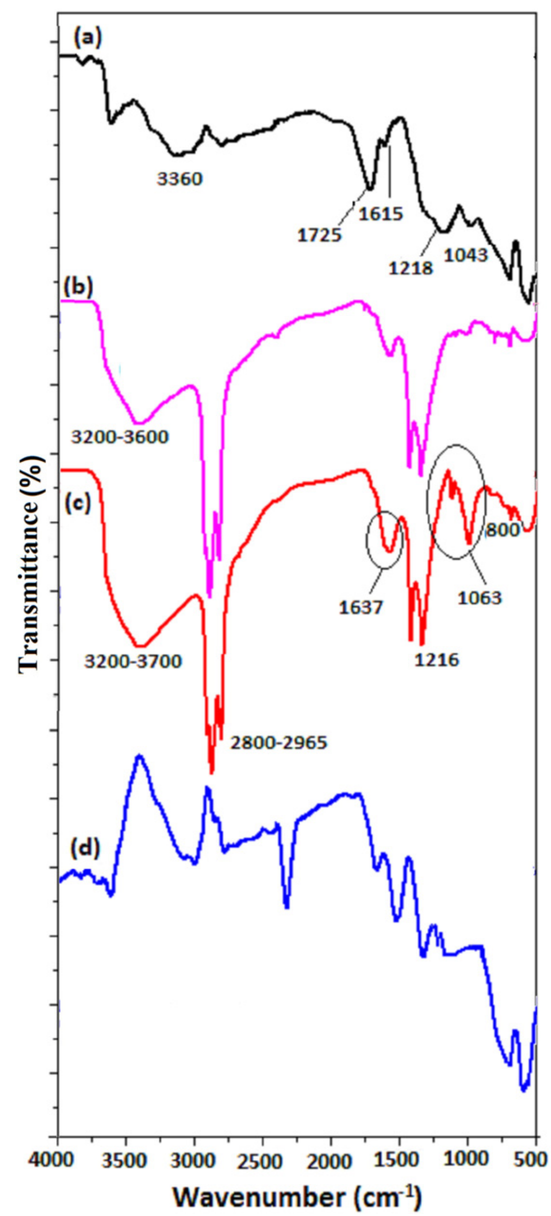

Fig. 2. FTIR spectra of (a) GO (b) Calcined Mg-Al LDH (c) Modified Mg-Al LDH (d) Hybrid layered NS of Mg-Al-LDH@GO.

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