Chemical Engineering Journal 292 (2016) 207–223

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Review

Graphene/layered double hydroxide nanocomposite: Properties, synthesis, and applications

Yong Cao*, Guoting Li, Xinbao Li

Institute of Environment and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, PR China

HIGHLIGHTS

- Graphene and LDHs have similar structure and complementary property.
- Graphene/LDH nanocomposite is synthesized.
- The synergistic effect is formed between graphene and LDHs in nanocomposite.
- Graphene/LDH shows better performance than pure graphene or LDHs alone.
- Future research directions of graphene/LDH are highlighted.

ARTICLE INFO

Article history:
Received 17 November 2015
Received in revised form 22 January 2016
Accepted 23 January 2016
Available online 9 February 2016

Keywords:
Graphene
Layered double hydroxides
Nanocomposite
Synthesis
Application

ABSTRACT

Although both graphene and layered double hydroxides (LDHs) have similar two-dimensional lamellar structure, most of their properties are distinct and just complementary. Besides, both graphene nanosheets and LDH nanosheets encounter the common problem of aggregation during the process of application. In view of these, combination of both exciting materials together to form a novel nanocomposite can take full advantages of each kind of materials, which is an effective way for the preparation of multifunctional materials with extraordinary properties. The properties of graphene, LDHs, and the combined nanocomposite are described first. Then, the routes for the synthesis of this nanocomposite, including self-assembly of the exfoliated graphene nanosheets and LDH nanosheets, in situ growth of LDHs on graphene sheets, and in situ growth of graphene within or on LDHs are presented. The obtained graphene/LDH nanocomposite shows excellent performance as a multifunctional material for its promising applications in the fields of energy storage, catalysis, environmental protection, drug delivery, and material science. At the end, the possible future research directions on this emerging nanocomposite are highlighted.

Contents

---

* Corresponding author.
E-mail address: caoyangel@126.com (Y. Cao).

http://dx.doi.org/10.1016/j.cej.2016.01.114
1385-8947/

1. Introduction

Exploring hierarchical nanocomposites with multifunctional properties through combining various building blocks together into a well-designed structure has always been a hot topic for material science. The combination of various building blocks with distinct physical and chemical properties into composites with hierarchical structure can usually inherit full advantages of the component materials, or even lead to the formation of multifunctional materials with unexpected properties for unique applications [1]. Among various building blocks, graphene and layered double hydroxides (LDHs) have been intensively investigated recently. On one hand, graphene is a two-dimensional (2D) sp^2-hybridized carbon nanostructure that has been of great interest in the physics, chemistry, and material communities throughout the world since discovered by Geim and Novoselov [2]. Graphene is the "thinnest" known material, and it exhibits extraordinary elections, mechanical, thermal, and optical properties that have made it a critical material in the 21st century [3]. Graphene holds a great promise for use in energy storage materials [4], drug delivery systems [5], biosensors [6], polymer composites [7], liquid crystal devices [8], supercapacitors [9], nanoelectronics [10], and other areas. As an ideal kind of building block, graphene is commonly used for the design of hybrid composites that can exhibit high performance and multifunction by combining the advantages of graphene and other functional nanomaterials. However, a big barrier which limits graphene application is that graphene sheets tend to form irreversible agglomerates or even restack to form graphite through π–π stacking and van der waals interactions if the sheets are not well separated from each other [11]. In order to overcome this barrier, a growing exploration to modify graphene surface and immobilize, anchor or embed nanoparticles or other materials onto graphene in different arrangements has been exerted [12,13]. On the other hand, LDHs being known for more than 150 years also with 2D lamellar structure are among the most studied advanced functional materials and have been widely applied in the fields of material science, catalysis, environment protection, biology, and energy in recent years [14–16]. The general formula of LDHs can be represented as $[M^{2+}_{1-x}M^{3+}{}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} may be cations of Mg^{2+}, Co^{2+}, Ni^{2+} and M^{3+} may be Al^{3+}, Fe^{3+}, Cr^{3+}, etc. And A^{n-} can be an interlayer anion such as CO_3^{2-}, SO_4^{2-}, and NO_3^-. The x is defined as the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$ and generally has a value ranging from 0.2 to 0.33 [17]. Graphene and LDHs exhibit unique but distinguish physical and chemical properties, which are complementary to a certain extent. Therefore, many efforts have been devoted on the exploration of a hierarchical nanocomposite with improved or extended properties from the combination of graphene and LDHs based on their synergistic effect [18].

This paper highlights the recent research progress and achievements on the hierarchical nanocomposite derived from graphene and LDHs. Firstly, the properties of graphene, LDHs, and the hybrid composite are briefly summarized. Then the synthesis routes are illustrated to give the basic material chemistry for the fabrication of the hierarchical nanocomposite. The applications of this nanocomposite in the fields of energy, catalysis, materials science, and environment are introduced. Finally, the possible future research directions are pointed out.

2. Properties of graphene, LDHs, and their hybrid nanocomposite

2.1. Properties of graphene

The term 'graphene' refers to a single layer of graphite, with sp^2-hybridized carbon atoms arranged in an hexagonal lattice and partially filled π-orbitals above and below the plane of the sheet. Graphene has attracted extensive attentions for its excellent mechanical, electrical, and thermal properties, such as a large theoretical specific surface area (2630 m^2/g) [19], high Young's modulus (~1.0 TPa) and tensile strength (130 GPa) [20], much lower band gap (0 eV), high electrical (~10^6 S/cm) [21], and thermal conductivity (3000–5000 W/m/K) [22]. Due to the chemical inertness of carbon atoms, graphene shows a lack of chemical reactivity. However, defects exist on the surface or at the edge of graphene, which is easy to be oxidized and functionalized [23,24]. Graphene oxide (GO), the functionalized graphene with oxygen-containing chemical groups (e.g. hydroxyl, epoxy and carboxyl) on its basal planes and edges, is one of the most important derivatives of graphene. After being reduced or thermal treatment, almost all the functional groups containing oxygen can be eliminated and GO is transformed into reduced graphene oxide (rGO). The functionalization of graphene either by covalent or noncovalent methods decorates it with functional groups, which not only improves its solubility, but also gives to its chemical reactivity. Functionalized graphene has been widely investigated as a great candidate for high-performance supercapacitor, catalyst, adsorption, drug delivery, etc [24–26].

2.2. Properties of LDHs

LDH is a class of anionic clays. The lamellar structure of LDHs is based on positively charged brucite-like sheets with anions and water molecules intercalated between the layers. The specific surface area of as-obtained LDHs is ranging from 20 to 120 m^2/g [27]. After calcination, LDHs can be converted into layered double oxides (LDOs) with mixed metal oxides or spines as the main component. An important property of LDO is the "memory effect", which means that this calcined product can reconstruct LDH original layered structure via rehydration and simultaneous incorporating of anions into the interlayer from aqueous solution. The LDOs with fine dispersion of metal cations and high surface area act as good catalysts for various chemical reactions [28]. Besides, LDHs are also widely explored as catalyst supports due to the strong interactions between LDHs and the arranged metals [29].

LDHs have many attractive properties, such as composition flexibility, anion exchangeability, and biocompatibility [14–16]. Among them, one of the most important properties for LDHs is their excellent anion exchangeability. Almost all kinds of anions can be intercalated into the interlayer space of LDHs through coprecipitation or anion exchange process. The interlayer anions