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Research Paper

Developing stretchable and graphene-oxide-based hydrogel for the removal of organic pollutants and metal ions

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ABSTRACT

It remains challenging to process the industrial wastewater of high consistence of organic pollutants and difficult decomposition of heavy metal ions. In this study, we develop a functional nanocomposite hydrogel with a highly photocatalytic Fenton reaction activity for the degradation of organic pollutants and adsorption for the heavy metal ions. The hydrogel is made up of Fe_3O_4 nanoparticles, reduced graphene oxide (RGO) and polyacrylamide (PAM), which is prepared by a two-step chemical synthetic method, and exhibits the outstanding mechanical strength, Photo-Fenton activity, adsorptive property and reversibility. For the degradation of organic dyes, the Fe_3O_4/RGO/PAM hydrogel can degrade the 20 mg/L Rhodamine B (RhB) for 90% within 60 min under visible light irradiation, and even after 10 times cycle test, the degradation rate for RhB still keeps at 90%. Meanwhile, it can degrade the actual sewage of fine chemical wastewater, whose COD (Chemical Oxygen Demand) decreases from 10400 to 2840 mg/L after one hour's visible irradiation. For the synchronous removal of organic pollutants and heavy metal ions over hydrogel, the degradation data of 20 mg/L RhB can be up to 90% with 20 min under visible light irradiation, and the removal rate of various metal ions can reach up to 34.8%–66.3% after continual two days' adsorption. This study provides a new pathway to process the industrial wastewater of high consistence and difficult decomposition.

1. Introduction

The wastewater coming from electrolysis, electroplating, pesticide, medicine, paint, paper making, printing and dyeing, textiles and other chemical industries has done great harms to the ecological environment. That because the industrial wastewater always contains the organic pollutants and heavy metal ions, which are difficult to be degraded by the power of nature. Several traditional approaches like Fenton reaction [1,2], biological treatment [3,4], membrane technology [5], extraction [6], electrodialysis process [7] etc. have a certain effect on the treatment of organic pollutants or heavy metal ions. However, there is less report on the pollution treatment technology for the synchronous removal of organic pollutants and heavy metal ions. Polymeric hydrogels are the typical fascinating and versatile soft materials with wide potential applications in drug delivery and tissue engineering [8–11], releasing matrices for drug delivery [12], cell modulating substances [13], as well as the adsorption of heavy metals [14]. The network structure of hydrogels provides a 3D environment with high water retention, tunable mechanical properties and nutrients [15], which has a large application potential in the environment. Unfortunately, the majority of polymeric hydrogels suffers from poor mechanical performance, which is difficult to be recycled and greatly limits its practical applications.

Recently, much attention has been paid to prepare the hydrogels with superior mechanical properties [16]. Commonly, there are three types of recipes to prepare the hydrogels, which are equipped with high strength, including a topological (TP) gel [17], a double network (DN) gel [18], and a nanocomposite (NC) gel [19]. Among of them, nanocomposite gels are considered to effectively enhance the mechanical properties of hydrogels. For instance, the nanocomposite gels with a unique organic-inorganic network structure would have the extraordinary mechanical property [20]. Nowadays, graphene oxide (GO) has been no doubt one of the hottest research topic among chemists, ascribed to its low cost for mass production and good dispersibility in water [21–24]. Meanwhile, its abundant oxygen-containing groups, *i.e.* hydroxyl, epoxide and carboxyl groups make it favorable candidates for improving the mechanical strength of the polymeric hydrogels. Ye et al. [25] have reported super tough graphene oxide (GO)-poly(acrylic acid) (PAA) nanocomposite hydrogels by using Fe^{3+} ions as cross-linkers. In regard with this, the GO-PAA nanocomposite hydrogels exhibit superior

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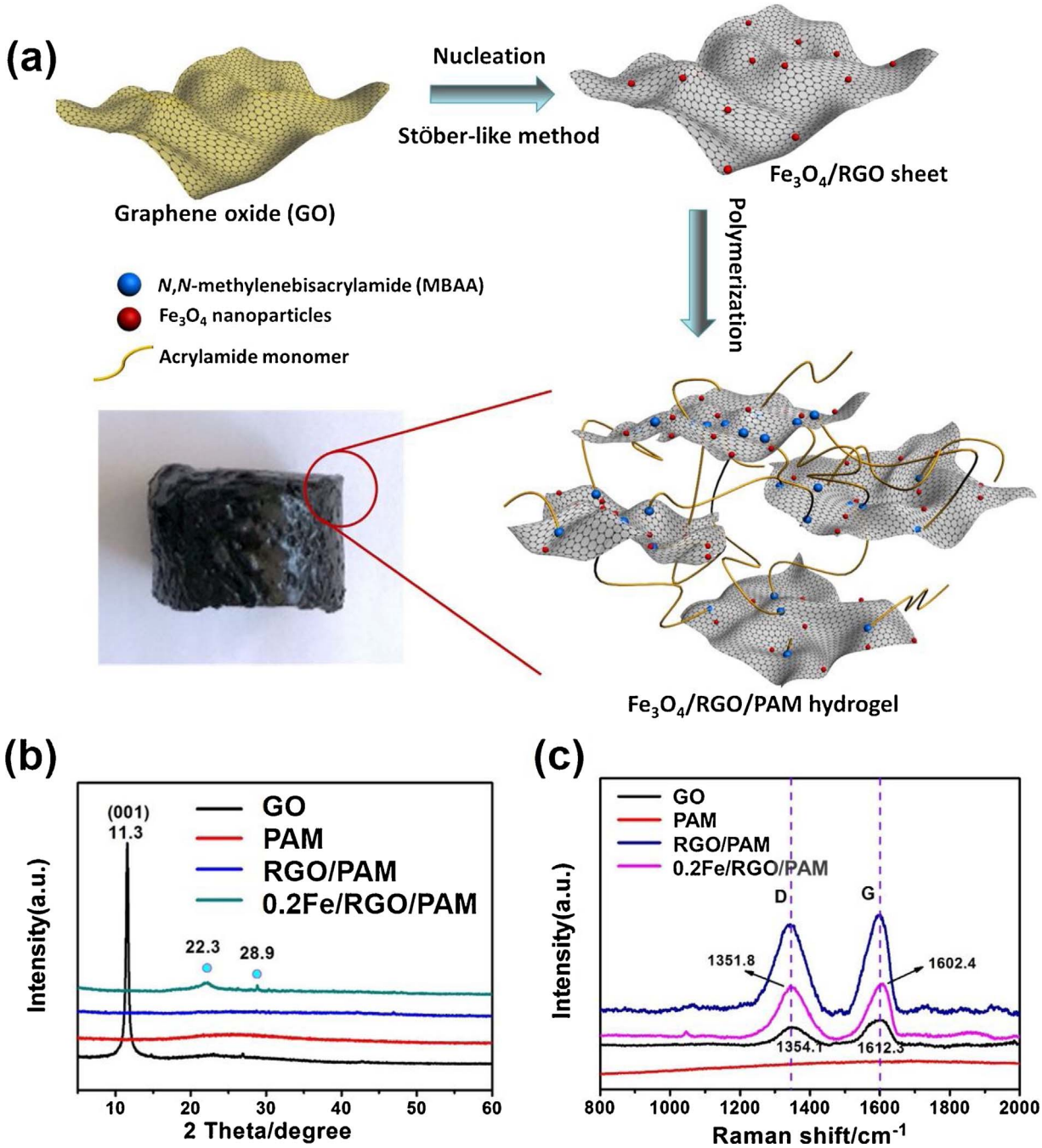

Fig. 1. (a) Schematic steps of preparation of Fe_3O_4/RGO/PAM hydrogels, and the corresponding (b) XRD and (c) Raman spectra of hydrogels.

toughness (tensile strength = 777 kPa, work of extension = 11.9 MJ m^{-3}) and stretchability (elongation at break = 2980%). In 2012, Liu et al. [26] prepared polyacrylamide (PAM)/graphene oxide nanocomposite hydrogels (PGH) with GO nanosheets as cross-linkers, via in situ free radical polymerization of acrylamide in an aqueous suspension of GO. On the basis of that, Yu et al. [27] proposed a facile approach to prepare a new kind of elastic GO/PAM hydrogels with exceptional mechanical behavior by combination of the characteristics of conventional double-network hydrogel and nanocomposite hydrogel, thus obtaining highly elastic and super-stretchable GO/PAM hydrogels. Under this circumstance, the majority of work correlated with PAM hydrogels is to enhance its mechanical property. It is well known that GO itself has a huge surface area, good chemical stability, and graphitized basal plane structure, thus allowing it to have strong p-p interactions with the aromatic moieties present in many organic molecule dyes [28]. Yin et al. [29] prepared graphene oxide (GO)/sodium alginate (SA)/polyacrylamide (PAM) (GO/SA/PAM) composite hydrogels, which were successfully applied in dye adsorption, including cationic dyes (R6G, MB, MG, and BG) and anionic dyes (CA, MO, BR and RB). However, the majority of the researches based on GO hydrogels focus on the adsorption of organic pollutions. PAM is a type of water-soluble polymer and widely used in industrial water treatment. And it is considered as non-toxic, economic and efficient, has undoubtedly of great potential application prospect [30]. And polyacrylamide (PAM) is composed of large numbers of amide side groups, which is beneficial for the adsorption of heavy metal ions. Although GO/Fe_3O_4 based hydrogels have been reported, Fe_3O_4/RGO/PAM hydrogel is much more efficient to adsorb heavy metals. This is because of the chemical adsorption, ascribed to the metal-NH_2 complex [31]. In the strict sense of the word, the toxicity of pollutants remains