

Reduced Graphene Oxide-Based Silver Nanoparticle-Containing Natural Hydrogel as Highly Efficient Catalysts for Nitrile Wastewater Treatment

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In this work, a new natural hydrogel containing reduced graphene oxide (RGO) supporting silver (Ag) nanoparticles composite were successfully prepared and tested as catalyst for waste water treatment. The formed hydrogels contain a network structure of cross-linked nanosheets decorated with metal nanoparticles. The reported method is based on in situ co-reduction of GO and Ag acetate within the natural hydrogel matrix to form RGO-based composite gel, carried on with a 'green' process. The silver nanoparticles were homogeneously and uniformly dispersed on the surface of the RGO nanosheets. The hybrid acts as catalyst for the reduction of organic pollutants in an aqueous environment, while the natural hydrogels hinders the intrinsic aggregation of the nanofiller, due to the protection of the formed 3-D network, preserving the catalytic activity. Interestingly, the as-prepared catalytic composite matrix structure can be easily handled, e.g. for separation from an aqueous environment after the reaction, suggesting the potentially large-scale applications of the RGO-based nanoparticle-containing composite hydrogels for nitrile compounds removal and wastewater treatment. The morphology of our composite has been investigated by using: X-ray diffraction, transmission electron microscopy, thermogravimetric analysis coupled with a mass spectrometer, Raman and Infrared Spectroscopy. The catalytic performance has been evaluated by recording the reaction progress with a UV-vis Spectrometer.

1. Introduction

Hydrogels are 3-dimensional hydrophilic cross-linked polymer networks, capable of absorbing large water amount (Brannon-Peppas, 1990; H. Gulrez et al., 2011). The networks are usually built up by homopolymers or copolymers and are insoluble, due to chemical or physical interactions within the structure. The physical interactions can be crystallites (Peppas and Merrill, 1976), entanglements (Lee et al., 2008), or weak forces such as hydrogen bonds (Kabanov and Papisov, 1979) and Van Der Waals forces (Khutoryanskiy, 2007). Environmentally sensitive hydrogels (Peppas, 1991) have the capacity to change morphology, due to the external conditions. In particular, these polymers show drastic changes in their swelling behaviour and mechanical strength by changing pH or ions present in the surrounding media. This property can be used in a wide range of biomedical applications such as dental adhesives, controlled release devices and biocompatible materials (W. Oppermann, 1992). Recently, it has been demonstrated that low-dimensional carbon materials can be incorporated within the hydrogels, increasing the number of potential applications of this class of hybrid materials, as in the case of graphene oxide (GO), graphene (Zhu et al., 2010) and carbon nanotubes (CNTs) (Popov, 2004). GO-based hydrogels have been assembled by adding a gelator, namely any substance capable of forming a gel, into an aqueous dispersion of GO. The gelator used is either a polymer (Bai et al., 2011), a natural complex molecule (Aderibigbe et al., 2014), a small organic molecule (Adhikari et al., 2012) or ions (Jiang et al., 2010). In these gels, the main bonding interactions for gelation are hydrogen bond, π - π interaction or electrostatic forces. A hydrogel composed by GO sheets and DNA long chain molecules, that exhibits excellent adsorbing capacity and self-healing properties has been reported (Xu et al., 2010), while Huang studied the selectively reversible gel-sol transition of glucono- δ -lactone -graphene oxide hydrogels

(Huang et al., 2012), Guo developed a GO-based gel by using polyethylenimine as gelator and used it as dye adsorbent for wastewater treatment (Guo et al., 2015), Cong and his coworkers produced macroscopic multifunctional graphene-based hydrogels by an iron ion induced self-assembly process (Cong et al., 2012). Recently, the opportunity to develop functionalized graphene-based hydrogels with metal nanoparticles has got remarkable attention because of possible applications in several fields, including energy conversion, catalysis, fuel cells and others. For example, Lin and coworkers produced graphene-metal NPs based hydrogels for several applications such as formic acid oxidation (Zhang et al., 2011) and sensing for organophosphate pesticide (Wang et al., 2011). Hydrogels containing graphene sheets decorated with gold nanoparticles have been used as catalyst for the reduction of p-nitrophenol and p-nitroaniline (Adhikari et al., 2012). Du produced graphene/Au gel that showed good electrocatalytic activity and was used to fabricate an amperometric sensor towards uric acid with good sensitivity (Du et al., 2014). Here we propose a 'green' approach for the synthesis of a hydrogel containing reduced graphene oxide functionalized with noble metal nanoparticles. In this report, we present the formation of GO based macromolecular hydrogels in the presence of spermine (N,N'-Bis(3-aminopropyl)-1,4-diaminobutane, C₁₀H₂₆N₄) and the in situ simultaneous reduction of GO and formation of silver (Ag) nanoparticles by a 'green' approach with vitamin C (L-ascorbic acid). Silver nanoparticles are uniformly formed and deposited on the reduced graphene oxide surface in a single step within the hydrogel media to form a nanohybrid system. This hydrogel compound has been used as a reusable catalyst for the mineralization of bromoxynil, a nitrile herbicide especially effective in the control of weeds in cereal, corn, sorghum, onions, flax, mint, turf, and on non-cropland (The Agrochemicals Handbook, 1991). Chronic exposure for more than one year in humans caused symptoms of weight loss, fever, vomiting, headache, and urinary problems in one documented case (Buhl et al., 1993). In the United States it is distributed as a restricted use pesticide in toxicity class II, classified as group C possible human carcinogen and not available for homeowner use (U.S. EPA, 1999). In this work, we have developed a hybrid gel based on a silver decorated graphene to catalyze the reduction of bromoxynil by UV light in water media. Although bromoxynil is removed from water by usual waste water treatment, the simplicity and elegance of our catalytic reduction make this method suitable for large scale application. Indeed, our hydrogel acts as a heterogeneous catalyst, is easy to handle and is easily removable from the reaction media after the end of the process and this makes our catalyst reusable several times.

2. Experimental

2.1 Materials

Graphite powder (synthetic, 99.9 %, SIGMA ALDRICH), sulfuric acid (H₂SO₄, 95-97 %, SIGMA ALDRICH), potassium permanganate (KMnO₄, ≥ 99 %, SIGMA ALDRICH), hydrogen peroxide (H₂O₂, 30 %, SIGMA ALDRICH), L-ascorbic acid (vitamin C, ≥ 99 %, SIGMA ALDRICH), AgNO₃: silver nitrate, ≥ 99.9 %, SIGMA ALDRICH, sodium hydroxide (NaOH, ≥ 98 %, pellets, SIGMA ALDRICH), ethanol (reaction grade, ≥ 99.8 %, Fluka Analytical), spermine (N,N'-Bis(3-aminopropyl)-1,4-diaminobutane, ≥ 97 %, SIGMA ALDRICH), bromoxynil (Pestanal®, analytical standard, SIGMA ALDRICH), double-distilled water (Fluka Analytical).

2.2 Synthesis method

The most significant challenge in the preparation of graphene is to overcome the strong exfoliation energy of π-stacked layers in graphite (Sarno et al., 2014). Graphite oxide consists of a layered structure of 'graphene oxide' sheets that are strongly hydrophilic such that intercalation of water molecules between the layers readily occurs (Buchsteiner et al., 2006). Therefore, graphite oxide can be completely exfoliated to produce suspensions of graphene oxide (GO) by simple sonication (Park and Ruoff, 2009). In this work, GO has been prepared following a modified Hummers method (Wu et al., 2010). In a typical experiment, 2 g of pure graphite powder is added to 46 ml of H₂SO₄ in 250 ml volumetric flask. With magnetic stirring, they are mixed together in ice bathing. Then, 8 g of KMnO₄ are added gradually under stirring, keeping the temperature of the mixture is kept to be below 10° C by cooling. The whole adding procedure should last for more than 1 hour to avoid intense exothermic reaction. After 1 h 30 min of mixing the system is heated up to 35-40° C for 30 min to initiate the oxidation process. Upon oxidation and intercalation the volume of graphite expands and leads to an increasing system viscosity. Then, the mixture is diluted with 100 ml of distilled water. Since the addition of water in concentrated sulfuric acid medium releases a large amount of heat, the addition is performed in an ice bath to keep the temperature below 100° C. After adding all of the 100 ml of water, the mixture is stirred for 1 hour and is, then, further diluted to approximately 300 ml with water. After that, 20 ml of H₂O₂ are added to the mixture to remove residual KMnO₄. The mixture releases a large amount of bubbles and the color turns into a brilliant yellow. Finally, the mixture is washed by centrifugation, repeatedly, to remove metal ions and the acid. The resulting dispersion is dried and a solid graphite oxide is obtained. The graphite oxide has been re-dispersed in water and sonicated well to obtain GO, and the pH of the solution has been adjusted to 7 with

a proper amount of a NaOH solution. Then, the hybrid gel is synthesized. At first, 50 μl of aqueous solution of AgNO_3 , with a concentration of 240 mg/ml, has been added to 0.8 mL of aqueous dispersion of GO, with a concentration of 12 mg/ml, and has been stirred and sonicated. Then, 0.2 mL of ascorbic acid, with a concentration of 240 mg/ml, was added to the mixture, and the solution is centrifugated and sonicated well. Then, a solution of 0.2 ml of spermine (4.8 mg/mL) was added dropwise under centrifugation. The solution was then heated, firstly at 40 $^\circ\text{C}$ for 1 h and then at 90 $^\circ\text{C}$ for 15 min. At the end of reaction the solution turned from black to grey, and a solid cluster floating on the surface was found. We believe that during the low temperature step the interactions between GO and spermine are generated, leading to a crosslink gel structure, while in the step at 90 $^\circ\text{C}$ the concurrently reduction of GO and metal particle deposition have occurred.



Figure 1 a) hydrogel floating in water; b) swelling effect of acid and basic media on the network

2.3 Catalytic study

The reduction of bromoxynil has been investigated with UV-vis spectroscopy and GC (Gas chromatography). The reaction has been carried out in water, at 25 $^\circ\text{C}$, under UV light, with a wavelength of 325 nm for 1 hour with and without the catalyst and the two results have been compared.

3. Results and discussion

3.1 Ionic gelation and pH effect

Biologically active polyamine, spermine is involved in cellular metabolism and it is found in all eukaryotic cells. At physiological pH, spermine exists as a protonated form with four positively charged amino groups. This polyamine is basic in nature and exists, as polyammonium ions at physiological pH (Dudley et al., 1926). Having N-containing basic functionalities, spermine can accept protons from the COOH groups of the GO sheets to participate in the acid-base type electrostatic attraction. Moreover, nitrogen (N)-containing functionalities of spermine can form hydrogen bonds with hydroxyl groups ($-\text{OH}$) of GO sheets. Spermine can act as a strong binder between GO sheets through hydrogen bonding and acid-base type of interactions and create with GO a complex network. Water molecules can be immobilized within the network obtained from the GO sheets and the binder molecules to form an ionic hydrogel. Ionic hydrogels are swollen polymer networks containing ionic moieties that show sudden or gradual changes in their dynamic and equilibrium swelling behaviours as a result of changing the external pH. Anionic materials contain pendant groups such as carboxylic acid or sulfonic acid. In these gels, ionization occurs when the pH of the environment is above the pK_a of the ionizable group (Katchalsky, 1949). As the degree of ionization increases (increased system pH), the number of fixed charges increases, resulting in increased electrostatic repulsions between the chains. This, in turn, results in an increased hydrophilicity of the network and greater swelling ratios. Conversely, cationic materials contain pendant groups such as amines (Scranton et al., 1995). These groups ionize in media at pH levels below the pK_b values of the ionizable species. Thus, in a low pH environment, ionization will increase, causing increased electrostatic repulsions. The hydrogel will become increasingly hydrophilic and will swell to an increased degree. There are many advantages using ionic materials over neutral networks. For example, the swelling forces developed in these systems will be increased over the nonionic materials. This increase in swelling force is due to the localization of fixed charges on the pendant groups. As a result, anionic gels in media above their pK_a levels and cationic gels in media below their pK_b values reach degrees of swelling an order of magnitude higher than nonionic materials (Yui et al., 2004). In view of these consideration, we choose to work at neutral pH in order to have: (a) the spermine existing as polyammonium

salts, (b) the carboxylic groups of GO deprotonated (c) avoid swelling effects (figure 1b). Indeed, all ammine groups of spermine accept hydrogens ion in a media with a pH less than 7.9 (Woster, 2006), while, for carboxylic groups of GO, the pK of ionization values are 4.3 and 6.6, where the lower value correspond to carboxyl group with hydroxyl groups in an ortho-position that allows the carboxylate anion to be stabilized by H-bonding, and hence, these groups are more acidic (Konkena and Vasudevan, 2012). This results, in ionic interaction between spermine salts and deprotonated GO, leading to the desired network, allowing the structure to swell a large amount of water, producing our hybrid hydrogel.

3.2 Thermogravimetric analysis

The thermal decomposition behavior has been investigated using a thermo-analyzer (Q600, TA Instruments). The measurement has been carried out in air flow, between RT and 1000 °C. The weight loss takes place in three temperature regions. Between room temperature and about 150 °C, the weight loss can be attributed to water entrapped in the gel network, indicating that 20 % in weight of the gel is water. The second weight loss (150-300 °C) can be attributed to spermine molecules, in particular two peaks can be pinpointed, probably due to the presence of external amino groups that are removed before the organic chains. The fringed spectra in the range 330-400 °C is mainly due to the thermal decomposition of graphene backbone, since the oxidation is not instantaneous (presence of defects and oxo-groups). The decomposition of graphene occurs at temperature less than graphene alone, due to the presence of silver that acts as catalyst. The residue at the end of thermal decomposition is silver oxide. Taking in account the presence of oxygen, the silver content in the gel is around 17 %.

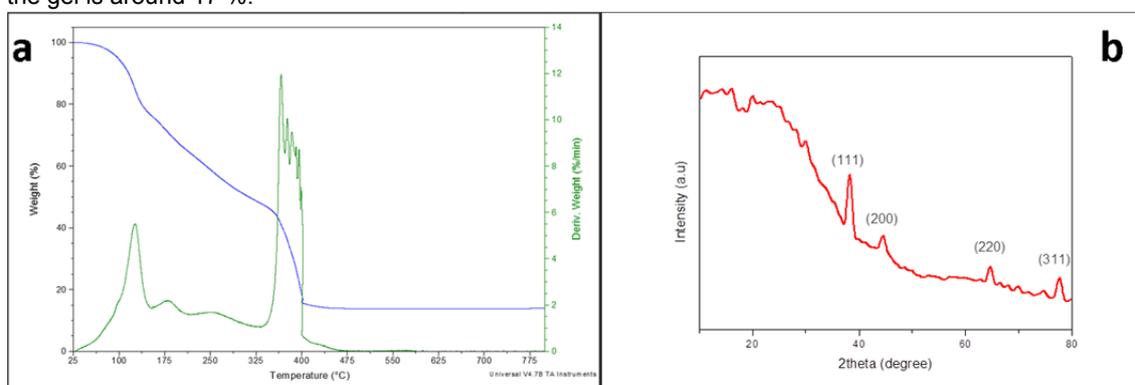


Figure 2 a) TG analysis of as-prepared gel; b) XRD spectrum of as-prepared gel

3.3 XRD characterization

XRD measurements have been performed using a Bruker D8 X-ray diffractometer (USA) with CuK α radiation. As expected, the XRD spectra presents a fringed shape, due to the intercalation of a large number of spermine and water molecules between the graphene layers. This feature is more pronounced in the range 10-30 2theta, where usually graphitic compounds show their signals. On the other hand, signals at higher 2theta, namely shorter atomic distances, confirm the crystallinity deposited on graphene surface or dispersed in the network. In figure 2b, in the range 40-80 degree, it is possible to pinpoint 4 peaks at 38.08°, 44.32°, 64.45° and 77.43°, corresponding to (1 1 1), (2 0 0), (2 2 0) and (2 2 2) planes, respectively (JCPDS File No.: 01-1167). This states that the as-prepared particles are crystalline with a face-centered cubic (fcc) structure (Xu and Hu, 2012). The particles size has been evaluated by the Sherrer formula:

$$d = \frac{k\lambda}{\beta \sin \theta}$$

Where k is structural constant, λ is the wavelength of X-Ray, d is the size of the nanoparticle and β is full width at half maximum. Using this formula, the average particle size (diameter) is 16 nm, evaluated with all 4 peaks for confirmation.

3.4 Bromoxynil reaction

The as-prepared gel has been tested as catalyst for the decomposition of bromoxynil under UV light. We prepared two water solutions with a concentration of bromoxynil of $3.6 \cdot 10^{-6}$ M, named S1 and S2. S1 was exposed for 1 hour to UV light. Then, 23 mg of as-prepared gel was added to S2 solution and exposed to UV light for 1 hour. The solution were tested with a UV-vis spectrometer, before and after the UV treatment. Figure 3 shows the results. Without catalyst, no reaction occurs, indeed the spectrum remains the same, meaning that the bromoxynil remains in the solution. With catalyst, the peaks shift to lower wavelengths, meaning that bromoxynil has been transformed in a different compound. This compound has been identified

as dimethyl 3-hydroxyphthalate, as suggested by Yuan (2008) and his group. GC analysis suggests a reaction pathways that includes diethyl phthalate as intermediate of reaction.

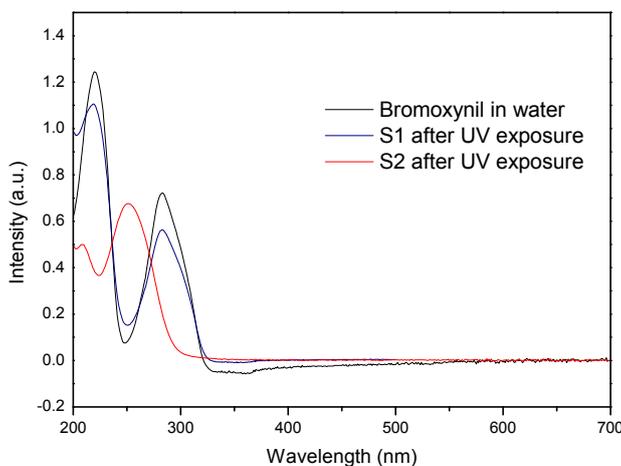


Figure 3 UV spectra before and after UV exposure.

4. Conclusion

A new natural hydrogel containing reduced graphene oxide supporting silver nanoparticles composite was successfully prepared and tested. The pH of the synthesis media has been optimized to have a gel structure formed by a polyammonium salts of spermine and deprotonated GO. The network formation and the silver deposition have been performed in a single step. The result is a solid gel easy to be handle and suitable to be used as heterogeneous catalyst. This catalyst has been tested for the mineralization of bromoxynil, a noxious pesticide, mostly used in agriculture. The results show that bromoxynil is degraded to dimethyl 3-hydroxy phthalate, showing the complete removal of bromine from the aromatic structure.

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