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Preparation of a Fe_3O_4 -Au-GO nanocomposite for simultaneous treatment of oil/water separation and dye decomposition[†]

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A nanocomposite capable of simultaneously controlling multiple water pollutants (soluble organic dye and insoluble chemical solvent) has been obtained. The Au and Fe₃O₄ nanoparticles (NPs) were modified on a graphene oxide (GO) surface via light reduction and covalent attachment. The obtained Fe₃O₄-Au-GO nanocomposite has magnetic driving ability and catalytic applications. The nanocomposite can form emulsions after wrapping an insoluble and volatile organic solvent inside; moreover, the multilayer graphene shell structure may delay volatilization of the solvent, ensuring that the oil droplets are collected efficiently and completely by the Fe₃O₄-Au-GO nanocomposite. At the same time, the Au NPs on the surface of the composite can effectively catalyze the decomposition of an organic dye in water and the recovery of the nanocomposite catalyst can also be realized using an external magnetic field. The simultaneous treatment of nonsoluble oil (organic solvents) and organic dyes in water can be realized by the Fe₃O₄-Au-GO nanocomposite. Therefore, based on surface modification of GO, one material with two types of water pollution treatment functions was realized. This provides a new way for the simultaneous treatment of oil separation and dye decomposition, and the assembled structure may result in emulsions to give new applications in fuel cells and other fields.

Introduction

Environmental pollution, especially water pollution, has become a worldwide problem. Owing to the rapidly increasing utilization and transportation of oils and chemical solvents, oil leakages have attracted a lot of attention considering its potential to cause severe water pollution.^{1,52} Oil spillage or organic pollutants are generally not soluble in water, which not only cause huge losses, but also seriously threatens the safety of the surrounding human population and environment. Meanwhile, organic dye pollution is also one of the causes of environmental pollution, such as organic dyes from the textile industry, paper industry and pharmaceutical industry.^{2,3} Dyes are well known to influence water quality. Most dyes are toxic and carcinogenic. Therefore, over the past few decades, how to control and collect leaked oil droplets efficiently and completely, and how to deal with the pollution of organic dyes have caused extensive research interest.⁴

In response to these problems, many methods have been used to deal with water pollution. For the treatment of oily wastewater, various approaches have been used including air flotation,⁵ coagulation,⁶ absorption⁷ and membrane filtration.⁸ Most of these technologies suffer from the limitations of a complex operation process, high energy costs, low efficiency and time consumption.9 Therefore, novel efficient materials for the treatment of oil/water separation are highly desired. For dye pollution treatment, techniques including biological, chemical and physical techniques have been developed.¹⁰⁻¹² In all of these pollution treatment methods, most methods only work for one particular type of pollution, even using adsorption, it is still difficult to realize the simultaneous treatment of insoluble solvents and soluble materials. For example, only for organic solvents or for organic dyes. A nanocomposite that can treat a variety of pollutions simultaneously with rapid processing times (for example: easy volatilization of insoluble organic solvents and organic dye in water) is very necessary.

Graphene oxide (GO) has good dispersion and can be easily functionalized because the GO sheets are heavily oxygenated with hydroxyl and epoxy functional groups on their basal planes and carboxyl groups at the edges of the sheets.^{13,14,50} The hydrophilic oxygen-containing groups and hydrophobic basal plane of GO give it amphipathicity to act as a Pickering stabilizer.¹⁵ GO is expected to show excellent ability to stabilize emulsions due to its asymmetric surface wettability. It can create highly stable Pickering emulsions of organic solvent-like colloidal particles and disperses insoluble solids in water-like molecular surfactants,⁴⁰ so it will be effectively inhibit the

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diffusion of the organic substances into the air, avoiding secondary pollution. Indeed, Pickering emulsions stabilized by GO have drawn significant attention owing to their unique 2D structures and the amphiphilic surface properties of GO,¹⁶ but investigations on GO to prepare Pickering emulsions for oil/water separation and recovery of water pollution treatments are still limited.

Noble metals such as Pt, Pd and Au have always attracted a significant amount of attention owing to their unique properties,¹⁷ especially in catalysis.^{18,19,49} With the presence of oxygen containing functional groups, the hydrophilic properties of GO result in it being well dispersed in water and provide a versatile platform for further chemical modification, with PAA (poly-acrylic acid) or noble metals. These modified metal-GO catalysts have the advantages of higher catalytic activity and better recyclability than that offered by the pure metal nanoparticles, owing to the electron transfer across their interface as well as their heterogeneous properties.^{20,21} Among these noble metals, Au nanoparticles (NPs) have attracted a considerable amount of attention because of their unique physical and chemical properties, their good catalytic properties and lower price compared to platinum. Many approaches for the preparation of Au-GO nanocomposites have been attempted, such as chemical reduction processes²² and physical vapour deposition.²³ Au NPs can be dispersed over graphene sheets using these chemical and physical methods, however, these processes usually involve highly toxic chemicals, high temperatures or manipulations that are complicated. Some of them might cause contamination in the nanocomposites, thereby reducing the electron transfer capacity.^{24,48} Accordingly, there has been considerable interest in developing a facile, green and environment-friendly strategy for the synthesis of Au-GO nanocomposites.^{25,26} Here, Au NPs can be obtained by light reduction of an HAuCl₄ solution, thereby reducing the chemical pollution generated and cost. Based on these reasons, we chose Au NPs as the catalytic agent combined with GO as a solution to organic dyes pollution. GO and emulsions or metal-GO catalysts are all difficult to recycle. Magnetic nanoparticles such as Fe₃O₄ NPs have been successfully applied to various applications, such as the separation of biomolecules, magnetic field assisted transport, medical imaging via magnetic field control and heterogeneous catalysis.²⁷ Therefore, the combination of GO with Fe₃O₄ NPs can solve the problem of difficult recovery.

In this paper, through light reduction and covalent bonding we obtained a Fe_3O_4 -Au–GO nanocomposite with the ability of forming emulsions, which can realize oil/water separation, magnetic driving ability and catalytic application *via* the surface modification of GO. This nanocomposite is the same as pure GO, which can form emulsions at an oil/water surface and cause the oil (insoluble and volatile organic solvent) to be wrapped inside. The multi-layered graphene shell structure can delay the volatilization of the solvent and recovery of the emulsions can be realized using an external magnetic field. At the same time, the Au NPs on the surface of the composite can effectively catalyse the decomposition of an organic dye in water and the Fe_3O_4 NPs ensure the composite catalysts may be recycled. The treatment of non-soluble organic solvents and organic dyes in water can be realized simultaneously by adjusting the concentration of the Fe_3O_4 -Au-GO nanocomposite. Therefore, based on the modification of the surface of graphene, one material with two kinds of pollution treatment functions was realized. This provides a new way for the simultaneous treatment of multiple pollutants.

Experimental details

Preparation of the Au-GO nanocomposite

Au NPs decorated GO was synthesized using the chemical method described by Xiong *et al.* with some modification.²⁸ First, an amount of GO was dispersed in water after cleaning, then 2 mL of $HAuCl_4 \cdot 4H_2O$ (0.01 M) solution was added to the GO solution and stirred evenly. After a period of static mixing (more than 48 h), the purified mixture was dispersed into the water.

Preparation of the Fe₃O₄-Au-GO nanocomposite

1 ml of the pre-synthesized Fe_3O_4 NPs was added into solution, the solution was stirred for 2 h to obtain the centrifugal solid dispersed into an aqueous solution.

Preparation of the emulsions

The Fe₃O₄-Au-GO nanocomposite was dissolved in water and after mixing evenly, a certain amount of organic solvent was slowly added. Then, the mixture was shocked, after 2 min, the mixed solution was static and observed.

Catalytic experiment

First, the GO and Fe₃O₄–Au–GO nanocomposite solutions with the same absorption strength were configured. At the same time, a small amount of sodium hydroxide was added to a *p*-nitrophenol solution and the spectral shape observed. Subsequently, the same amount of GO and Fe₃O₄–Au–GO nanocomposite solutions were added to an equivalent of amount of 4-AP and the change in the spectral shape observed.

Results and discussion

In order to obtain GO with magnetic and catalytic properties, we modified Fe_3O_4 and Au NPs on the surface of GO.²⁹ The experimental procedures are shown in Fig. 1(A). The Au NPs can be reduced slowly under the action of natural light and temperature, and combined with the GO surface, the process also can be achieved by adding a certain amount of reducing agent to shorten the reaction time. The sample is shown in Fig. 2(A). It can be found that the Au NPs were dispersed on the surface of GO and no obvious aggregation was observed. The Au NPs size follows a Gaussian distribution in the range of 4–14 nm and the average particle size was about for 9 nm.



Fig. 1 (A) The main procedure used for the preparation of the Fe_3O_4 -Au-GO nanocomposite and its application in oil/water separation and catalysis (B).



Fig. 2 (A) TEM image of the Au–GO nanocomposite; the inset is the SAED pattern of the Au NPs. (B) TEM image of the Fe_3O_4 –Au–GO nanocomposite. (C) The size distribution of the Au NPs of Au–GO nanocomposite. (D) EDX spectrum of the Fe_3O_4 –Au–GO nanocomposite.

As obtained from the SAED pattern of the Au NPs shown in Fig. 2(A inset) we can see the individual Au NPs exist in the form of a single crystal. In order to obtain the magnetic material, Fe₃O₄ NPs were modified on the surface of GO. Fe₃O₄ NPs were prepared according to our previous method,³⁰ its surface was coated with PAA, so it can be easily combined with the -COOH and other oxygen containing functional groups found on the surface of the GO. The pre-synthesized Fe₃O₄ NPs size was in the range of 50-150 nm. The results after modification are shown in Fig. 2(B). From the TEM images it can be found that the two kinds of nanoparticles were effectively combined with GO with no obvious aggregation. The EDX spectra shown in Fig. 2(D) confirmed the two elements Fe and Au can be measured on the modified GO surface. In addition, from the TEM images of the emulsion shown in Fig. 3(D), it can be seen clearly that the nanoparticles appear only within the scope of the globular structure, indicating that the nanoparticles were anchored on the GO surface and



Fig. 3 (A) Images of the Fe₃O₄–Au–GO water solution after adding toluene two times. (B) Microscope photographs of the emulsions formed by the Fe₃O₄–Au–GO nanocomposite before and (C) after the partial volatilization of toluene with magnetic control (D) and (E) TEM images of the emulsion after volatilization of toluene. (F) Agglomeration of emulsions caused by an external magnetic field. (G) Hysteresis loops recorded for Fe₃O₄ and the Fe₃O₄–Au–GO nanocomposite.

assembled with GO. Therefore, without surfactants and capping agents, the Au and Fe_3O_4 NPs were modified on the GO surface by means of photo-reduction and chemical bonding methods.

XRD (X-ray diffraction) was conducted to confirm the structural changes during the Fe₃O₄-Au-GO nanocomposite synthesis. The crystalline nature of the Fe₃O₄ NPs and Au NPs in the Fe₃O₄-Au-GO nanocomposite was confirmed by XRD. As shown in Fig. S1(A),[†] there was no obvious peak of graphene for the dark line and a new broad diffraction peak at 24.5° appeared in the Fe₃O₄-Au-GO nanocomposite (Red line); this diffraction peak was quite close to the typical diffraction peak of graphite at 26.6°, implying the successful reduction of GO to graphene.^{31,32} The Fe₃O₄-Au-GO nanocomposite showed major diffraction peaks at 38.36°(111), 44.64°(200) and 64.78° (220) for the Au NPs, which were in good agreement with facecentered cubic crystalline Au (JCPDS 04-0784) and have the diffraction peaks at 19.8°, 30.46°, 33°, 42.6°, which can be ascribed to the $(1 \ 1 \ 1)$, $(2 \ 2 \ 0)$, $(3 \ 1 \ 1)$, $(4 \ 0 \ 0)$ plane of Fe₃O₄, respectively,³³ according to the standard data of Fe₃O₄ (JCPDS 19-0629). This confirms that the Au NPs were produced and clearly shows the successful anchoring of the Au NPs and Fe₃O₄ NPs onto the GO surface.

Raman spectroscopy is a non-destructive technique to characterize carbonaceous materials, and it often be used to detect the surface of GO. As presented in Fig. S1(B), \dagger the Raman spectra of both GO and Fe₃O₄-Au-GO have two strong peaks at 1346 cm⁻¹ and 1604 cm⁻¹, which correspond to the

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D and G bands, respectively.³⁴ It is well-known that the G band is ascribed to the E_{2g} phonon of sp² hybridized C atoms, while the D band is associated with structural defects, amorphous carbon or edges that can break the symmetry and selection rule.³⁵ The intensity ratio of the D band to G band (I_D/I_G) is regarded as a reflection of the degree of graphitization of carbonaceous materials and the defect density. The intensity ratio of Fe₃O₄-Au-GO (0.803) was higher than that intensity ratio of GO (0.668), indicating the presence of localized sp³ defects within the sp² carbon network after the reduction of the exfoliated GO. The increased (I_D/I_G) value demonstrates the efficient removal of oxygenated functional groups from GO after the Au NPs and Fe₃O₄ NPs were attached.³⁶

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elements of the Fe₃O₄-Au-GO nanocomposite. The high-resolution C 1s curve of GO, three different peaks centered at binding energies of 284.6, 286.6, and 287.8 eV were assigned to C=C, C-O and C=O, respectively.³⁷ Meanwhile, the peak intensity of the oxygen containing groups in the Fe₃O₄-Au-GO nanocomposite (Fig. S2(B)[†]) are remarkably decreased when compared to GO (Fig. S2(A)[†]) indicating that the oxygen-containing groups were effectively removed upon attachment of the Au NPs and Fe₃O₄ NPs. As shown in Fig. S2 (A inset),† C 1s, O 1s, Fe 2p and Au 4f existed distinctly. The Au 4f peaks were at binding energies of 84.1 and 87.78 eV (Fig. S2(C)[†]) and can be attributed to Au $4f_{7/2}$ and Au $4f_{5/2}$, which are possibly attributed to physical absorption and incomplete reduction of Au³⁺ by light indicating the successful attachment of the Au NPs on the GO nanocomposite surface. In addition, the high-resolution Fe 2p spectrum presents two peaks at 711.5 and 724.8 eV, which are attributed to Fe $2p_{3/2}$ and Fe 2p_{1/2} of Fe₃O₄ respectively, further confirming the attachment of Fe₃O₄ on the GO surface.³⁸ The amount of Au NPs and Fe₃O₄ NPs immobilized on the Fe₃O₄-Au-GO nanocomposite was found to be about 1.6 and 1.8 wt%, respectively.

The treatment of oil pollutants is a relatively troublesome problem, most oil contained organic solvents will float on the surface of water and are volatile in the air. Here we use the modified GO to solve this problem, GO sheets can stabilize oil droplets in water by adsorption at the oil-water interface, forming Pickering emulsions.^{39,40} In order to know whether the modified GO can also assemble in the oil/water interface, the following experiments were performed. After the addition of toluene in a Fe₃O₄-Au-GO nanocomposite solution, there will be obvious stratification; toluene was in the upper layer as shown in Fig. 3(A1), through a simple concussion, the nanocomposite pre-dissolved in water appeared in the toluene layer (Fig. 3(A2)), when the liquid was stable, further toluene was added, as shown in Fig. 3(A3), and lower solution of the external solution was an aqueous solution and the mixture was continued to be shocked. As shown in the Fig. 3(A4), the mixture displays obvious stratification and the original toluene layer volume was significantly larger, indicating that if the composite materials were sufficient, the organic solvent can be fully enwrapped. The upper solution volume changes slightly after

stabilization (Fig. 3(A5)) and the organic solvent droplets are stable in water for months in an airtight environment. Based on this, we believe that the shell structure can inhibit the volatilization of the internal oil. The upper solution was observed by microscopy and from Fig. 3(B) we can clearly see the existence of droplets, after a period of time, with toluene volatilization the spherical shell structure was observed in Fig. 3(C), which indicates that the droplets formed by the Fe₃O₄-Au-GO nanocomposite enwrapped the toluene. We found in the experiments that 2.6 mg GO could realize an up to 2.9 mL of toluene package and the package efficiency was 96.6%. Through the TEM images shown in Fig. 3(D and E), we were able to clearly see the shell structure of the single emulsion formed by the Fe₃O₄-Au-GO nanocomposite, the nanoparticle distribution within the scope of the shell structure and no obvious aggregation phenomenon. This confirmed that the GO with nanoparticles are connected. Fig. 3(F) shows the magnetic control performance of the emulsions, the effect of the emulsion will obviously be gathered together under an external magnetic field. The magnetic properties of Fe3O4 and the Fe₃O₄-Au-GO nanocomposite were investigated at room temperature with an applied field of $-20\,000 \le H \le 20\,000$ A m⁻¹. As shown in Fig. 3(G), the S-shape curves in the magnetic hysteresis loops exhibit negligible coercivity (H_c) and remanence, revealing their super-paramagnetic behavior. The magnetization of the composite (12 emu g^{-1}) was decreased when compared to pure Fe_3O_4 (53emu g⁻¹), which was related to the doping ratio of the nanoparticles in the composite. In summary, the Au and Fe₃O₄ NPs modified GO also can form Pickering emulsions at the interface of water and oil as GO, the organic solvent is wrapped inside, the stable structure can restrain the volatilization of the solvent and the existence of super- paramagnetic Fe₃O₄ NPs make sure the droplets can be collected under an external magnetic field.

In order to confirm that the composite can be formed in a variety of organic solvent interfaces, that is, in order to verify the general applicability of the assembly and the stability of the assembly, toluene, cyclohexane, *n*-butyl alcohol, propyl acetate, acetyl acetone in the same proportion, were added to the same concentration of Fe₃O₄-Au-GO nanocomposite aqueous solution and observed at different times. As shown in Fig. 4(A(a-e)), the several organic solvents all float on water, after the same frequency and time shocking, the stratification phenomenon disappeared and after standing for a period of time, toluene and cyclohexane show a faster reappearance stratification. With increasing time propyl acetate and n-butanol also reformed layers, but acetyl acetone showed no obvious stratification after 90 min. This phenomenon was related to the nature of the solvent itself and the proportion of the assembly. The package efficiency of the 5 kinds of solvent in Fig. 4 were all above 97% and for acetyl acetone reached 98%. The relationship between the volume of the assembly with time in the reaction is shown in Fig. S3.† After 90 min, the upper solution was observed using microscopy and we found that the sizes of the several solvent emulsions were different, which may be related to the polarity of the solvent itself. It was



Fig. 4 (A–D) The different time photographs of the Fe_3O_4 –Au–GO water solution after adding the same amount of (a) toluene, (b) cyclohexane, (c) butyl alcohol, (d) propyl acetate and (e) acetyl acetone. (E) Microscope photographs of the emulsions assembled with the different organic solvents.

found that in the air, small droplets of *n*-butanol will quickly mix together, indicating that the assembly of *n*-butanol was not stable in the air. However, there were no significant changes in the size of the assemblies and the emulsions stability was proved after the assembly; a stable assembly was beneficial to inhibit the volatilization of the solvent and realize magnetic recovery. Based on the above results, we believe that the Fe₃O₄-Au-GO composite structure can form emulsions with high stability in the presence of multiple types of solvents. This is very beneficial for the treatment of various types of organic solvents and the discovery may be of some reference value for the preparation of graphene assemblies with different specific surface areas.

The catalytic activity of Au-Fe₃O₄-GO was evaluated using the catalytic reduction of 4-nitrophenol (PNP) into 4-aminophenol (4-AP). PNP is a commonly used chemical intermediate with high toxicity and thus, the elimination of PNP from industrial wastewater is essential. This reaction is usually used to evaluate the catalytic performance of noble metal catalysts.41-44 The original aqueous solution of PNP shows a typical absorption peak at 317 nm and its color is light yellow, upon the addition of NaBH₄, the aqueous solution of PNP turns to a yellow colour and the absorption peak red-shifts to 400 nm, corresponding to the formation of 4-aminophenolate under alkaline conditions.45 In order to distinguish the dye concentration change caused by GO was reduced to graphene, a small amount of NaBH4 was added and used after no further bubble generation. The reduction process was monitored by recording the intensity of the absorption peak at 400 nm associated with 4-AP. At the same time, in order to distinguish

the dye concentration changes by GO, we used pure GO as a reference and in order to distinguish the concentration change of dye dilution, we add the same amount of water with the GO solution to detect the dilution of PNP. As shown in Fig. 5(A), after adding the same amount of GO solution and water, after a short period of time, the dye concentration decreased substantially. With an increase in time, the addition of GO tube walls will have air bubbles attached, the dye concentration will be reduced by 13.4%; upon the continued addition of excess NaBH₄ the dye concentration decreased significantly with the total decrease being about 73.4%, which may be caused by NaBH₄ decomposition during the process of GO reduction, partial decomposition NaBH₄ reacted during the dye reaction causing the dye to be restored. It is worth noting that the GO after the reaction was difficult to be re-used. However, upon the addition of Fe₃O₄-Au-GO, the dye concentration decreased by 90%, the color of the solution did not significantly change showing that the solution of GO was not significantly reduced, which was due to the effective electron transfer from graphene to theAuNPs;^{46,47} upon the continued addition of excessive NaBH₄, there are a large number of bubbles in the mixture solution and the dye concentration was reduced by 99% after stability. Fig. 5(B) shows the color changes of the Fe₃O₄-Au-GO mixture before and after the addition of excess NaBH₄, the reason for the black is that oxygen containing groups which did not connected to NPs of the GO surface were reduced. Even so, after the reduction, the Fe₃O₄-Au-GO nanocomposite still has a catalytic effect. However, the amount of NaBH4 added can be adjusted to minimize the reduction of Fe₃O₄-Au-GO in the catalytic decomposition of PNP. The catalytic efficiency of multiple cycles was about 99%, 99% and 97%, and the changes in the catalytic efficiency may be due to the loss of the complex substance during its recovery. The magnetic recovery performance of the Fe₃O₄-Au-GO nano-



Fig. 5 (A) The UV spectra of PNP reduction caused by GO and the Fe_3O_4 -Au-GO nanocomposite. (B) The Fe_3O_4 -Au-GO nanocomposite and PNP mixed solution before (left) and after (right) the addition of excess NaBH₄, (C) The aggregation of the nanocomposite materials under the action of an external magnetic field.

composite is shown in Fig. 5(C). After the reaction is completed, the composite material can be recovered by applying an external magnetic field. In summary, the GO surface loaded nanoparticles can be achieved after the degradation of the dye catalyzed the degradation of low $NaBH_4$ concentration and recycling.

Conclusions

In conclusion, the Fe₃O₄ and Au NPs were modified by natural light reduction and covalent attachment to the GO surface, then the nanocomposite with magnetic response and catalytic ability was obtained. This method does not use a chemical reductant, so it is green and of low cost. The Fe₃O₄-Au-GO nanocomposite can create highly stable Pickering emulsions of multiple type organic solvents, enwrap the organic solvent inside and can retard the volatilization speed, which is conducive to the efficient and rapid collection and treatment of organic pollutants. At the same time, the high catalytic activity and water solubility make the nanocomposite have unique advantages in the treatment of water-soluble organic dye pollutants. In this way, the composite materials we can make are able to simultaneously realize the treatment of different types of pollutants (water insoluble oil and dve pollution). It is of great value to control the pollution of the regional environment and the three-dimensional structure formed by droplets in the emulsion may have potential applications in the field of batteries and other fields.⁵¹

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