Facile synthesis of uniform magnetic graphitic carbon for an efficient adsorption of pentachlorophenol†

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Uniform core–shell structured magnetic graphitic carbon (Fe3O4@SiO2@g-C) nanospheres were fabricated via a two-step Stöber coating strategy, followed by a carbonization process in N2 atmosphere. The resultant composites possess a large magnetic susceptibility (25 emu g\(^{-1}\)) and a high graphitization degree, making it an excellent magnetically separable adsorbent for the removal of pentachlorophenol.

Pentachlorophenol (PCP) is an important chlorinated aromatic organic compound that is widely used as a pesticide, a disinfectant, and a wood preservative. As a result, the concentration of PCP in the aquatic system is continuously increasing year by year. In addition, long-term exposure to PCP, even at very low level concentrations, can cause severe harmful effects on the liver, kidneys, lungs and nervous system of human beings.1 Therefore, the development of an efficient technology to treat PCP is necessary. Till now, commonly used strategies include biological degradation, membrane filtration, adsorption, and advanced oxidation technology.2 Among them, adsorption has been considered as one of the most practical and reliable technologies because of several advantages such as low cost, high efficiency, and simplicity in operation.3 Recently, graphitic carbon (g-C) – based materials are of vital importance in this field for their special structure, high rigidity and good chemical stability.4 However, they are very difficult to separate and regenerate during application, especially in a slurry operating system. To address this issue, magnetic separation provides a very convenient approach for removing and recycling magnetic particles such as magnetite, ferrite, and barium ferrite by applying external magnetic fields. It has been demonstrated that the incorporation of magnetic components into the adsorbent can greatly enhance the separation and recovery.5 To date, several methods (laser assisted irradiation,6 thermal plasma,7 microwave heating,8 chemical vapor condensation,9 and hydrothermal10) have been used for the synthesis of this type of material. However, most of these methods are associated with some disadvantages such as involving relatively harsh reaction conditions, requiring high energy cost, producing materials with aggregated structures, etc. Therefore, to develop a facile method to synthesize uniform magnetic g-C with a high adsorption performance for PCP is very much desired.

Herein, uniform core–shell structured magnetic g-C nanoparticles (Fe3O4@SiO2@g-C) have been fabricated via a two-step Stöber coating method, followed by a carbonization process. The introduction of a rigid silica layer between Fe3O4 core and graphitic carbon shell is to help prevent leaching of Fe3O4, as well as increase the thermal stability of the resultant core–shell material during the carbonization process. After treated at 850 °C in N2 gas, the magnetic g-C possesses a well-defined core–shell structure with a large magnetic susceptibility (25 emu g\(^{-1}\)) and a high graphitization degree. Finally, the magnetic g-C is used as an adsorbent, showing an excellent adsorption capacity for PCP. Moreover, the adsorbent can be easily recycled within 30 s by using an external magnetic field and the constant adsorption ability is retained even after 5 cycles.

The synthesis strategy for the core–shell structured magnetic g-C nanospheres is depicted in Fig. 1. First, the uniform magnetite particles were coated with a nonporous silica layer through a general Stöber coating approach in the presence of tetraethyl orthosilicate (TEOS) (denoted as Fe3O4@SiO2). Then, a layer of resorcinol-formaldehyde (RF) resin was deposited onto the silica layer through interface polymerization of resorcinol and formaldehyde catalyzed by ammonium hydroxide due to the strong electrostatic attraction between resorcinol derivatives and NH3+ absorbed on Fe3O4@SiO2 (defined as
**Fe₃O₄@SiO₂@RF**

Finally, the resultant composites were carbonized in N₂ at 850 °C (designated as Fe₃O₄@SiO₂@g-C).

The obtained Fe₃O₄ particles possess a uniform spherical shape with an average diameter of ~130 nm (Fig. 2A). The particles exhibit excellent dispersibility in polar solvents such as water and ethanol because of numerous citrate groups anchored on the surface, facilitating the subsequent coating. The Fe₃O₄@SiO₂ nanospheres after the first Stöber coating process shows a relatively smooth surface with a diameter of ~190 nm (Fig. 2B). TEM images reveal that a silica layer with a thickness of ~30 nm is uniformly coated onto the magnetic core, resulting in a well-defined core–shell structure. The further Stöber coating leads to the formation of sandwich-like Fe₃O₄@SiO₂@RF nanospheres with an average diameter of 250 nm, indicating the presence of ~30 nm thick carbon layer (Fig. 2C). Notably, when the core–shell Fe₃O₄@SiO₂@RF samples after being carbonized at 850 °C in nitrogen, discrete and uniform nanospheres are well retained (Fig. 2D). However, the delocalization of Fe₃O₄ cores was observed, which is possibly resulted from the recrystallization of Fe₃O₄ but inhibited by the outer silica shell. The energy-dispersive X-ray (EDX) of the magnetic g-C (Fig. S1†) clearly showed the characteristic peaks of titanium, carbon, silica and oxygen, suggesting the possible coexistence of Fe₃O₄, SiO₂, and carbon. In addition, the iron peaks at 2θ = 44.6 and 49.6° were detected, which is possibly due to the inhibition effect of silica towards the crystallization of Fe₃O₄. The formation of iron in the composites could be attributed to the reducibility of carbon. Notably, this is good for the formation of magnetic g-C with a large magnetic property because iron (200 emu g⁻¹) typically exhibits a larger magnetization than the magnetite (50–80 emu g⁻¹). Unlike the Fe₃O₄@SiO₂@g-C sample, the XRD pattern of the core–shell Fe₃O₄@g-C sample shows intense crystalline diffraction peaks at 2θ = 33.7 and 42.6°, in accordance with FeO crystals (diamagnetic), which gives a bad effect on the magnetic property of the resultant composites, further revealing the priority of coating a silica interlayer. To check the graphitic character of the resultant composites, the Raman spectra was recorded in the range of 500–2500 cm⁻¹ (Fig. 3B). In the Raman spectra of the resultant composites, the appearance of two prominent peaks D (1368 cm⁻¹) and G (1590 cm⁻¹) are assigned to the disordered hybridized carbon atoms (A₁g) and the stretching vibrations of sp² bonds of perfect graphite crystals (E₂g mode), respectively. It is widely believed that the intensity ratio of the D and G bands, I_D/I_G, is a measure of the crystallinity of carbon.¹⁴

The relatively small I_D/I_G ratio of magnetic g-C over other samples indicates the low density of the disordered sp² – hybridized carbon atoms, suggesting a high graphitization degree of the magnetic g-C.

The performance of the resultant magnetic g-C composites for the adsorptive removal of PCP was evaluated at pH 6.8 (Fig. 4A). As a control, the adsorption performances of PCP in the presence of pristine Fe₃O₄@RF and Fe₃O₄@g-C-450 were also tested, exhibiting the adsorption capacity of 3.0 and 4.8 mg g⁻¹,
FTIR spectra, the peak at 3425 cm⁻¹ which was demonstrated by FTIR spectra (Fig. 4B). In the aromatic emerging organic pollutants (Fig. S3), the adsorbent can also be used to effectively remove the core–shell structured magnetic g-C via a successive Stöber coating strategy, which is facile, mild and effective. The resultant Fe₃O₄@SiO₂@g-C nanospheres possess well-defined core–shell structure with a large magnetic susceptibility (∼25.0 emu g⁻¹), a relatively large BET surface area (25.7 m² g⁻¹), and a high graphitization degree. Then, it was demonstrated as an adsorbent for the removal of PCP, showing an excellent adsorption capacity (55 mg g⁻¹), which is much higher than that of the previous magnetic adsorbent (35–50 mg g⁻¹). In addition, it exhibits an excellent reusability (adsorption capacity remaining constant after 5 cycles) and fast magnetic separation capacity (magnetic separation time < 30 s). This study paves a great way to synthesize and design a magnetic adsorbent for efficiently removal of PCP.

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Notes and references


