Research Article

Preparation of Graphene Oxide Decorated $\text{Fe}_3\text{O}_4@\text{SiO}_2$ Nanocomposites with Superior Adsorption Capacity and SERS Detection for Organic Dyes

Song Yang,¹ Tian Zeng,¹ Yaling Li,¹ Jun Liu,¹
Qian Chen,¹ Ji Zhou,¹ Yong Ye,¹ and Bin Tang^{2,3}

¹Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials and Key Laboratory for the Synthesis and Application of Organic Functional Molecules of Ministry of Education and College of Chemistry & Chemical Engineering, Hubei University, Wuhan 430062, China

²School of Textile Science and Engineering, Wuhan Textile University, Wuhan 430073, China

³Institute for Frontier Materials, Deakin University, Geelong, VIC 3216, Australia

Correspondence should be addressed to Ji Zhou; zhouji@hubu.edu.cn and Bin Tang; bin.tang@deakin.edu.au

Received 23 July 2015; Revised 19 September 2015; Accepted 28 September 2015

Academic Editor: Giuseppe Compagnini

Copyright © 2015 Song Yang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The fast detection and removal of organic dyes from contaminated water has become an urgent environmental issue due to their high toxicity, chemical stability, and low biodegradability. In this paper, we have developed graphene oxide decorated $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$) as a novel adsorbent aiming at the rapid adsorption and trace analysis of organic dyes followed by surface enhanced Raman scattering (SERS). The structure and morphology of the nanocomposites were characterized by transmission electron microscopy (TEM), Fourier infrared spectrometry (FT-IR), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM). The obtained nanocomposites were used to adsorb methylene blue (MB) in aqueous solution based on π - π stacking interaction and electrostatic attraction between MB and GO, and the adsorption behaviors of MB were investigated. Moreover, the obtained nanocomposites with adsorbed dyes were separated from the solution and loaded with silver nanoparticles for SERS detection. These nanocomposites showed superior SERS sensitivity and the lowest detectable concentration was 1.0×10^{-7} M.

1. Introduction

The organic dyes are widely used in the textile industry for dyeing fibers, leathers, paper, and so forth. However, the contaminated water containing the residual dyes from textile dyeing and finishing factories is considered as a significant source of environmental pollution due to their high toxicity, chemical stability, and low biodegradability. Therefore, there is an increasing demand for the development of effective and environmentally benign approaches for the trace detection and fast removal of organic dyes from contaminated water.

Surface enhanced Raman scattering (SERS), which can provide rich structural information of most molecules with high sensitivity and selectivity, has been considered as a promising technique for the trace detection and analysis of complex real-world samples. It has been shown to be

a reliable platform for a number of fast and accurate analyses, including environmental pollutants [1, 2], food toxins [3, 4], and bioanalysis [5]. The enormous enhancement of Raman signal is originated dominantly from the electromagnetic amplification on noble metal nanostructures. However, the low concentration of targets and the spectral interference of the complex composition severely limit the SERS analysis, especially for the rapid detection in the field. Thus, a pretreatment procedure to isolate and enrich the targets was generally required prior to the instrumental determinations.

Graphene oxide (GO), a product of graphite from an oxidation process, is a chemically modified two-dimensional atomically thick carbon network containing hydroxyl and epoxy functional groups on its large surfaces. Owing to the large delocalized π -electron system and the rich oxygen contained groups, GO is characterized with high capacity

and selectivity and strongly hydrophilic, which shows high adsorption capacities for organic dyes in aqueous solution, especially for benzene-containing compounds [6]. Therefore, GO has been paid extensive attention as a superior adsorbent for its potential applications for environmental remediation and pollution treatment. However, GO was normally separated from the sample solution through high-speed centrifugation for about 30 min, which is energy-intensive and troublesome. To ease the separation procedure, magnetic nanoparticles (Fe_3O_4 nanoparticles) have been widely introduced to functionalize a hybrid material with GO, which could serve as a magnetically recoverable adsorbent by taking advantage of the magnetic functionality of Fe_3O_4 . Wang et al. [7] used magnetic graphene nanoparticles as adsorbent to extract neonicotinoid insecticides and then was determined by HPLC. Lin et al. [8] prepared graphene oxide functionalized magnetic particles and utilized the particles to remove tetracycline antibiotics including tetracycline, oxytetracycline, chlortetracycline, and doxycycline from environmental waters.

In this work, GO decorated $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was synthesized by a facile and efficient approach. Fe_3O_4 nanoparticles were firstly synthesized by using a solvothermal method, followed by coating with silica through a sol-gel process. The obtained $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was further functionalized with (3-aminopropyl) trimethoxysilane (APTMS), and then GO sheets were assembled on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ through electrostatic interactions. Subsequently, the magnetic adsorbent was added to the methylene blue (MB) (chosen as a typical organic dye) aqueous solution and silver nanoparticles were loaded on the nanocomposites for SERS analysis. Herein, the Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite microspheres could simultaneously result in dual functions of both fast enrichment and local surface plasmon resonance. The nanocomposites exhibited superior SERS sensitivity and the lowest detectable concentration was 1.0×10^{-7} M.

2. Experimental Section

2.1. Reagents. GO was bought from Nanjing Xianfeng Company (Nanjing, China). AgNO_3 (>99%), trisodium citrate ($\geq 99.0\%$), methylene blue (MB), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate anhydrous (NaAc), 2-propanol, ethylene glycol, and tetraethylorthosilicate (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol, ammonium hydroxide, and toluene were purchased from Tianjin Bodi Chemical Co., Ltd. (3-aminopropyl) trimethoxysilane (APTMS) was purchased from Aladdin Chemistry Co., Ltd. (China). All chemicals were of analytical grade and used as received. Deionized water was obtained from Hangzhou Wahaha Co.

The stock solution containing 1.0×10^{-3} M of MB was prepared by dissolving the required amounts of the solid in aqueous solution. Working solutions were prepared by diluting the stock solution with appropriate amounts of water.

2.2. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ Microspheres. The magnetic Fe_3O_4 nanoparticles were synthesized following the

typical solvothermal reaction, as reported by Deng et al. [9]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.24 g) and NaAc (8.64 g) were dissolved in 120 mL of ethylene glycol. The mixture solution was sonicated (100 W) vigorously for 30 min and then allowed to react at 200°C for 8 h in teflon-lined stainless-steel autoclaves. The Fe_3O_4 nanoparticles were collected by an external magnetic field, washed with ethanol, and dried in 60°C vacuum drying box. The obtained Fe_3O_4 nanoparticles were then coated with silica shell by sol-gel process to prevent the microsphere from agglomeration and oxidization. Fe_3O_4 nanoparticles (600 mg) were dispersed in 50 mL of 2-propanol and 12.8 mL of water with the aid of ultrasonication. Then, 10 mL of ammonium hydroxide and 4 mL of TEOS were added in the dispersion, and the mixture was stirred at room temperature for 10 h. The product was washed with water and ethanol several times and dried in 60°C vacuum drying box. The obtained magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were then dispersed in 50 mL of toluene, followed by the addition of 4.0 mL of APTMS. The mixture was refluxed for 10 h under nitrogen atmosphere to obtain amino-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$). The product was magnetically separated from the mixture solution using a magnet and was then washed with ethanol and deionized water. 0.7 g $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ was then dispersed in 100 mL of water with the aid of ultrasonication, and the preparation of 100 mL of GO aqueous solution (0.5 mg/mL) was poured into the dispersion. The mixture was stirred vigorously for 2 h at room temperature. The obtained $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was washed with water for several times and dried in 60°C vacuum drying box.

2.3. Adsorption Test of MB on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. Adsorption studies were carried out by batch process. The effects of the pH of the MB solution, the amount of adsorbent, and the contact time were investigated. Firstly, the effect of pH on adsorption of MB was studied over a pH range of 2.0–12.0 with a contact time of 1 h. The pH was adjusted by adding aqueous solutions of 0.1 M HCl or 0.1 M NaOH. The different amounts of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ ranging from 3.0 to 14.0 mg were then applied to adsorb the targets from the sample solutions. For the kinetic study, 5.0 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was added into 20 mL of MB solutions of desired initial concentrations (1×10^{-5} M). The influence of the contact time was conducted by changing the shaking time from 1.0 to 65 min. For adsorption isotherm, 5 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was added to 10 mL of MB solution at concentrations ranging within 7.47–37.39 mg/L and shook at 27°C for 1 h. After adsorption equilibrium, the concentrations of dye were determined by using a BWTEK BRC642E CCD Arrays spectrometer with BDS 100 light source. The removal rate (1) of MB and the adsorption capacity (2) of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ were assessed by the following equations:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100, \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V, \quad (2)$$

where q_e is the amount of dye adsorbed on adsorbent at equilibrium (mg g^{-1}); C_0 and C_e are the initial and equilibrium

FIGURE 1: TEM images of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$.

concentrations of MB in the solution (mg L^{-1}), respectively; V is the volume of solution (L); m is the mass of absorbent (g).

2.4. SERS Measurement of Methylene Blue on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ Microspheres. For the SERS analysis, 5 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was added into 20 mL of MB solutions of different concentrations (1×10^{-5} , 1×10^{-6} , and 1×10^{-7} M, adjusted with NaOH to pH 8.0). After vigorous shaking for 40 min, the magnetic microspheres with adsorbed MB molecules were separated by an external magnet and mixed with 15 mL silver colloid followed by vigorous stirring for 3 h. The Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ microspheres were then transferred onto a clean glass slide. The SERS analysis was then performed on a Renishaw inVia Raman microscope system (Renishaw plc., Wotton-under-Edge, UK). A 50x/N.A. 0.75 objective and a 532 nm DPSS laser excitation source (120 mW, 0.5%) were used in all measurements. The spectra within a Raman shift window between 200 and 1800 cm^{-1} were recorded using a mounted CCD camera with integration time of 10 s through single scan.

2.5. Characterization. TEM images of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ were obtained with a Hitachi H-8100 microscope operated at 200 kV. X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Magnetic property was performed on a JDAW-2000C&D vibrating sample magnetometer (VSM, Changchun, China) at room temperature. Fourier transform infrared (FTIR) spectra were measured with a Thermo Scientific Fourier transform infrared spectrometer (Nicolet iS10). Zeta potentials were measured on a Nano-ZS zetasizer (Malvern Instruments, Worcestershire, UK).

3. Results and Discussion

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ Nanocomposites. TEM images of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ are presented in Figure 1. As shown in Figure 1(a), the Fe_3O_4 nanoparticles are well dispersed and uniform in shape and size, and the mean diameter is about 372 nm. Figure 1(b) shows that SiO_2 had been assembled on the surface of Fe_3O_4 with a thinner

FIGURE 2: FTIR spectra of GO, Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$.

smooth layer. The smooth SiO_2 shell played an important role in protecting the magnetic nanoparticles against oxidation and covalently attaching with other functionalized nanomaterials. The average diameter of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ is about 383 nm which is bigger than Fe_3O_4 nanoparticles in Figure 1(a). From Figure 1(b), it can also be seen that the sheet-like structure with the smooth surface and wrinkled edge shows the major characteristic of GO [10]. The TEM images can be considered as the direct evidence that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was fabricated successfully.

Figure 2 shows the FTIR spectra of GO, Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. The bands at 3410 and 1620 cm^{-1} are assigned to the -OH stretching vibration due to the existence of surface hydroxyl and H_2O . For all the nanomaterials, absorption peaks at 580 cm^{-1} were observed, ascribed to the Fe-O vibration from the magnetite phase [11]. Two typical signatures for silica are exhibited to $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. A strong broadband at 1094 cm^{-1} corresponds to the Si-O-Si asymmetric stretching vibration and a weak band at 477 cm^{-1} is assigned to C-Si-O vibration [12, 13], reflecting the coating of silica on the magnetite

FIGURE 3: XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$.

surface. After the amination reaction, several minor peaks in the region $2800\text{--}3000\text{ cm}^{-1}$, corresponding to the C-H stretching vibration of the hydrocarbon chains of the grafting APTMS, are observed [14]. For GO, peaks at 1619 , 1386 , and 1069 cm^{-1} are assigned to the H-O-H bending, =C-H vibration, and C-O stretching, respectively. Due to the ultralow content of GO in the core-shell hybrids, the peaks of GO are a little weak in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ spectral curve.

The phase structure and crystallization of the magnetic microspheres were identified with XRD (Figure 3). For Fe_3O_4 , diffraction peaks with 2θ at 30.1° , 35.5° , 43.1° , 57.0° , and 62.9° were observed, which correspond to the crystal planes of (220), (311), (400), (511), and (440), respectively, of crystalline face-centered cubic Fe_3O_4 nanoparticles (JCPDS file number 19-0629). The same series of characteristic peaks were also observed for $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$, indicating the stability of the crystalline phase of Fe_3O_4 nanoparticles during silica coating and surface GO. Wide diffraction peaks at 22.3° can be viewed from $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$, which is a typical feature of amorphous SiO_2 . After coating GO, the peaks exhibit no obvious changes compared to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres, which might be related to the thinness of the shell GO layer.

In order to monitor the changes in the surface characteristics of the as-prepared nanocomposites during the surface modification process, the zeta potential at different stages of surface modification was measured. The average zeta potentials of the Fe_3O_4 nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$, were measured to be 18.7 , -13.5 , 26.7 , and -11.4 mV , respectively. The prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres are negatively charged due to the silanol groups on the surface, and the strongly positive zeta potential of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ microspheres may be the result of the presence of the high amine content in the shells. Upon GO self-assembly on the microspheres, the zeta potential fell from ca. 26.7 mV to ca. -11.4 mV , which demonstrates successful GO coating. For $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$, the hybrid materials with

FIGURE 4: Magnetic hysteresis loops of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ (the insets show the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ aqueous solution before and after magnetic separation by an external magnet).

negative surface charges are suited for the enrichment of the cationic dyes due to the electrostatic effect.

The magnetic properties of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ were measured by VSM at room temperature (Figure 4). The curves present a hysteresis loop, which suggests that all of these nanoparticles exhibit ferromagnetic behavior. The magnetic saturation values are 78.3 , 47.6 , and 40.5 emu/g for Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. The decrease in the overall magnetization values indicates that the Fe_3O_4 surface is covered with nonmagnetic materials such as SiO_2 and GO. Moreover, the suspensions of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ microspheres can be rapidly concentrated on the side of the glass vial (see the insets in Figure 4). When the magnet was removed, the nanocomposites were well dispersed again in aqueous solution after shaking, demonstrating that the nanocomposites featured with highly efficient magnetic manipulation when used as adsorbents for removal of dyes from aqueous solution under relatively low external magnetic field.

3.2. Adsorption Equilibrium and Kinetics of MB on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. Organic dyes, as common pollutants from wastewater, were one of the most detected targets in water analysis. Due to its known strong adsorption onto solids, MB often serves as a model compound for removing dyes and organic contaminants from aqueous solutions [15]. Figure 5(a) shows the high adsorption capability of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ nanocomposite. When dispersed into MB solution ($1.0 \times 10^{-5}\text{ M}$), the nanocomposite can still be separated entirely from the suspensions, leaving a colorless solution within a few minutes. In a typical adsorption experiment, the effects of the pH of the sample solution, the amount of adsorbent, and the contact time were investigated to improve the adsorption efficiency. Figure 5(b) shows the effect of the sample pH on the adsorption capacity of MB on

FIGURE 5: (a) Photographs of MB solution treated with Fe₃O₄@SiO₂-GO and the response to an external magnetic field. The effect of (b) the sample pH value, (c) the amount of sorbent, and (d) the contact time on the adsorption capability of MB.

the Fe₃O₄@SiO₂-GO in the pH range between 2.0 and 12.0. The adsorption capacity of MB obviously increases in basic solution. Above pH 8.0, the MB removal percentage has no great change and reached 93%. This observation is consistent with the pH-sensitive electrostatic interaction between the highly negatively charged oxygen groups in GO and the positively charged molecules [16, 17]. Thereby, the sample solution pH was adjusted to 8.0 for the adsorption. The effect of different dosages on MB removal was also carried out, and the result was shown in Figure 5(c). It is observed that the MB removal percentage increases with increasing adsorbent dose. It is due to the fact that increasing adsorbent dose serves to increase the surface area and the number of active sites for adsorption. Based on the above results, 5 mg of Fe₃O₄@SiO₂-GO was selected for the following studies. Figure 5(d) shows plots of the removal percentage of MB on Fe₃O₄@SiO₂-GO versus contact time. The results indicated that the adsorption

efficiency increased when the contact time increased from 1.0 to 40 min, and no significant change is observed from 40 to 60 min. As shown, MB adsorption on the Fe₃O₄@SiO₂-GO is a fast process and reaches the equilibrium in 40 min. The fast adsorption may be attributed to (i) the electrostatic attraction between the negatively charged surface oxygen-containing groups and cationic MB and (ii) the π - π interactions between the MB molecules and the aromatic rings of graphene [18].

In order to inspect the mechanism of the adsorption of MB onto Fe₃O₄@SiO₂-GO, kinetics analysis was studied. Two common kinetic models, pseudo-first-order (3) and pseudo-second-order models, were applied to analyze the experimental data:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303}, \quad (3)$$

FIGURE 6: Pseudo-first-order kinetics (a) and pseudo-second-order kinetics (b) of MB adsorption on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite.

TABLE 1: Adsorption kinetic parameters for MB adsorption on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite.

Kinetic model	Kinetic parameters	
Pseudo-first-order model	$q_{e,\text{exp}}$	14.14
	$q_{e,\text{calc}}$	9.96
	k_1	0.0945
	R^2	0.9801
Pseudo-second-order model	$q_{e,\text{exp}}$	14.14
	$q_{e,\text{calc}}$	14.37
	k_2	0.017
	R^2	0.9992

where q_t is the amount of dye adsorbed on adsorbent at different time (mg g^{-1}); k_1 is the adsorption rate constant (min^{-1}):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (4)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

Figures 6(a) and 6(b) show the linear plots of $\ln(q_e - q_t)$ versus t and t/q_t versus t , respectively. All the nonlinear fitting results are calculated and listed in Table 1. The determination coefficients R^2 of the pseudo-second-order are higher than those of pseudo-first-order rate model, indicating that the adsorption kinetic model of MB onto $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ fits the pseudo-second-order model well.

To further comprehend the adsorption progress, we employ the Freundlich (5) and Langmuir (6) isotherm models to fit the experimental data:

$$\ln q_e = \ln k_F + \left(\frac{1}{n}\right) \ln C_e, \quad (5)$$

FIGURE 7: Langmuir isotherm for the adsorption of MB onto $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$.

where k_F (L g^{-1}) is the Freundlich constants related to adsorption capacity and $1/n$ is the adsorption intensity:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m}, \quad (6)$$

where q_m is the maximum adsorption capacity; k_L is related to the energy of adsorption (L mg^{-1}).

The adsorption isotherm plots for MB adsorbed on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ are presented in Figure 7 and the simulation results are listed in Table 2. The results show that the correlation coefficient (R^2) of the linear for Langmuir model is higher than Freundlich models. As the good fit with Langmuir model indicates, the monolayer coverage of MB on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ surfaces is the main sorption mechanism.

3.3. Investigation of SERS Sensitivity to MB. On the basis of the electromagnetic mechanism of SERS donated by silver

TABLE 2: Parameters for Langmuir and Freundlich isotherm models.

Langmuir model			Freundlich model		
$q_{m,max}$ (mg/g)	k_L (L/g)	R^2	k_F (L/g)	$1/n$	R^2
44.05	1.478	0.9993	23.07	0.1866	0.5497

FIGURE 8: (a) Raman spectrum of MB solid, (b) Raman spectrum of MB adsorbed on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ microspheres, and (c) SERS spectrum of MB on the Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$.

nanoparticles, the Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite microspheres may be good substrates for the sensitive detection of organic dyes. Figure 8(b) displays the Raman spectrum of MB (1×10^{-5} M) adsorbed on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$. Compared with the Raman spectrum of MB solid (Curve (a) in Figure 8), some weak characteristic Raman bands of MB were observed in Curve (b) due to the effective enrichment. After loading with silver nanoparticles, it is easily seen in Curve (c) in Figure 8 that the Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ microspheres have superior SERS sensitivity to MB molecules. The feature peaks from 400 to 1700 cm^{-1} are attributed to MB Raman signals [19–21]. Among the SERS bands, the band at 1623 cm^{-1} is strongest, which is the C-C stretching mode. The bands at 470 and 504 cm^{-1} can be assigned to C-N-C skeletal bending. Those bands at 1394, 1439, and 1462 cm^{-1} belong to C-N stretching and C-C asymmetric stretching mode. The band at 953 cm^{-1} is assigned to the $\rho(\text{CH}_2)$ rocking vibration.

Figure 9 shows the SERS spectra of MB adsorbed onto the Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite microspheres with different concentration (10^{-7} M – 10^{-5} M). As can be seen from the graph, MB with 10^{-5} M displayed obvious characteristic peaks with strong signal intensity. For dye molecules at 10^{-6} M , the G bands of graphene oxide at about 1600 cm^{-1} may overlap the signature band of MB (1623 cm^{-1}) and the bands located at 1623 cm^{-1} obviously blue shifted, but some vibration bands can still be distinguished. For 10^{-7} M dye molecule, strong background signal from GO is observed, and only the band at 953 cm^{-1} can be distinguished. It is concluded that the lowest detectable concentration for MB could be achieved at 10^{-7} M , which is improved at least

FIGURE 9: SERS spectra of MB with different concentration obtained from Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ composite microspheres.

10 times compared with the lowest concentrations detected using GO/Ag materials [22]. It suggested that the superior adsorption capability of the graphene oxide decorated magnetic microspheres may contribute towards the excellent SERS enhancement.

4. Conclusions

In summary, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ magnetic nanocomposites were successfully prepared by a facile solvothermal method. The prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ was then used as a superior adsorbent for the enrichment of MB in aqueous solution. After grafting the silver nanoparticles onto the surface of the nanocomposites, the Ag-loaded magnetic-based microspheres can serve as both the dye adsorbents and the enhancement nanoprobe. The testing results show that MB in the solution with a concentration as low as 10^{-7} M could be detected. Thus, it can be anticipated that the bifunctional Ag-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO}$ microspheres would have great potentials for the field-based environmental monitoring and remediation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (nos. 21003034 and 51403162) and the Educational Commission of Hubei Province of China (nos. T201101 and Q20131002).

References

- [1] Y. J. Ye, J. Chen, Q. Q. Ding et al., “Sea-urchin-like $\text{Fe}_3\text{O}_4@\text{C}@\text{Ag}$ particles: an efficient SERS substrate for

- detection of organic pollutants,” *Nanoscale*, vol. 5, no. 13, pp. 5887–5895, 2013.
- [2] M.-J. Han, J. M. Hao, Z. H. Xu, and X. G. Meng, “Surface-enhanced Raman scattering for arsenate detection on multilayer silver nanofilms,” *Analytica Chimica Acta*, vol. 692, no. 1-2, pp. 96–102, 2011.
 - [3] X. Wang, Y. P. Du, H. Zhang et al., “Fast enrichment and ultra-sensitive in-situ detection of pesticide residues on oranges with surface-enhanced Raman spectroscopy based on Au nanoparticles decorated glycidyl methacrylate-ethylene dimethacrylate material,” *Food Control*, vol. 46, pp. 108–114, 2014.
 - [4] Y. X. Hu, S. Feng, F. Gao, E. C. Y. Li-Chan, E. Grant, and X. Lu, “Detection of melamine in milk using molecularly imprinted polymers–surface enhanced Raman spectroscopy,” *Food Chemistry*, vol. 176, pp. 123–129, 2015.
 - [5] L. J. Liang, D. S. Huang, H. L. Wang et al., “In situ surface-enhanced Raman scattering spectroscopy exploring molecular changes of drug-treated cancer cell nucleus,” *Analytical Chemistry*, vol. 87, no. 4, pp. 2504–2510, 2015.
 - [6] H. Yan, H. Wu, K. Li et al., “Influence of the surface structure of graphene oxide on the adsorption of aromatic organic compounds from water,” *ACS Applied Materials & Interfaces*, vol. 7, no. 12, pp. 6690–6697, 2015.
 - [7] W. N. Wang, Y. P. Li, Q. H. Wu, C. Wang, X. H. Zang, and Z. Wang, “Extraction of neonicotinoid insecticides from environmental water samples with magnetic graphene nanoparticles as adsorbent followed by determination with HPLC,” *Analytical Methods*, vol. 4, no. 3, pp. 766–772, 2012.
 - [8] Y. X. Lin, S. Xu, and J. Li, “Fast and highly efficient tetracyclines removal from environmental waters by graphene oxide functionalized magnetic particles,” *Chemical Engineering Journal*, vol. 225, pp. 679–685, 2013.
 - [9] H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen, and Y. D. Li, “Monodisperse magnetic single-crystal ferrite microspheres,” *Angewandte Chemie*, vol. 44, no. 18, pp. 2782–2785, 2005.
 - [10] L. Li, L. Fan, M. Sun et al., “Adsorbent for chromium removal based on graphene oxide functionalized with magnetic cyclodextrin-chitosan,” *Colloids and Surfaces B: Biointerfaces*, vol. 107, pp. 76–83, 2013.
 - [11] M. Yamaura, R. L. Camilo, L. C. Sampaio, M. A. Macêdo, M. Nakamura, and H. E. Toma, “Preparation and characterization of (3-aminopropyl)triethoxysilane-coated magnetite nanoparticles,” *Journal of Magnetism and Magnetic Materials*, vol. 279, no. 2-3, pp. 210–217, 2004.
 - [12] A. Z. M. Badruddoza, M. T. Rahman, S. Ghosh et al., “ β -cyclodextrin conjugated magnetic, fluorescent silica core-shell nanoparticles for biomedical applications,” *Carbohydrate Polymers*, vol. 95, no. 1, pp. 449–457, 2013.
 - [13] Y. B. Zeng, Y. Zhou, L. Kong, T. Zhou, and G. Shi, “A novel composite of SiO₂-coated graphene oxide and molecularly imprinted polymers for electrochemical sensing dopamine,” *Biosensors and Bioelectronics*, vol. 45, no. 1, pp. 25–33, 2013.
 - [14] L. Chen, S. G. Chai, K. Liu et al., “Enhanced epoxy/silica composites mechanical properties by introducing graphene oxide to the interface,” *ACS Applied Materials & Interfaces*, vol. 4, no. 8, pp. 4398–4404, 2012.
 - [15] B. H. Hameed, A. T. M. Din, and A. L. Ahmad, “Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies,” *Journal of Hazardous Materials*, vol. 141, no. 3, pp. 819–825, 2007.
 - [16] S.-T. Yang, S. Chen, Y. Chang, A. Cao, Y. Liu, and H. Wang, “Removal of methylene blue from aqueous solution by graphene oxide,” *Journal of Colloid and Interface Science*, vol. 359, no. 1, pp. 24–29, 2011.
 - [17] L. H. Ai, C. Y. Zhang, and Z. L. Chen, “Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite,” *Journal of Hazardous Materials*, vol. 192, no. 3, pp. 1515–1524, 2011.
 - [18] M. Vinothkannan, C. Karthikeyan, G. G. kumar, A. R. Kim, and D. J. Yoo, “One-pot green synthesis of reduced graphene oxide (RGO)/Fe₃O₄ nanocomposites and its catalytic activity toward methylene blue dye degradation,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 136, part B, pp. 256–264, 2015.
 - [19] E. N. Aybeke, Y. Lacroute, C. Elie-Caille, A. Bouhelier, E. Bourillot, and E. Lesniewska, “Homogeneous large-scale crystalline nanoparticle-covered substrate with high SERS performance,” *Nanotechnology*, vol. 26, no. 24, pp. 245–302, 2015.
 - [20] S. D. Roy, M. G. J. Ghosh, and J. Chowdhury, “Adsorptive parameters and influence of hot geometries on the SER(R) S spectra of methylene blue molecules adsorbed on gold nanocolloidal particles,” *Journal of Raman Spectroscopy*, vol. 46, no. 5, pp. 451–461, 2015.
 - [21] G.-N. Xiao and S.-Q. Man, “Surface-enhanced Raman scattering of methylene blue adsorbed on cap-shaped silver nanoparticles,” *Chemical Physics Letters*, vol. 447, no. 4–6, pp. 305–309, 2007.
 - [22] G. H. Ding, S. Xie, Y. Liu, L. Wang, and F. G. Xu, “Graphene oxide-silver nanocomposite as SERS substrate for dye detection: effects of silver loading amount and composite dosage,” *Applied Surface Science*, vol. 345, pp. 310–318, 2015.