Mussel Inspired Preparation of Functional Silica Nanocomposites for Environmental Adsorption Applications

Qiang Huang^{a, #}, Meiyang Liu^{a, #}, Junyu Chen^a, Ke Wang^b, Dazhuang Xu^a, Fengjie Deng^a, Hongye Huang^a, Xiaoyong Zhang^{a, *}, Yen Wei^{b, *}

a Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

b Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing, 100084, P. R. China.

These authors contributed equally to this work

Abstract

Surface modification of nanomaterials with polymers is an effective route to render new functions and improve the performance of the final nanocomposites. Here, a facile method was developed to fabricate polyacrylic acid (PAA)-grafted monodisperse SiO₂ nanoparticles (SiO₂-PDA-PAA) through a combination of mussel inspired chemistry and Michael addition reaction. To obtain the products, the SiO₂ nanoparticles were first coated with polydopamine (PDA) through self-polymerization of dopamine under rather mild conditions. The PDA thin films can then be further conjugated with amino-terminated PAA, which was synthesized by chain transfer free radical polymerization using cysteamine hydrochloride as a chain transfer agent and acrylic acid as a monomer. The SiO₂-PDA-PAA nanocomposites were characterized via transmission electron microscopy, Fourier transform infrared spectroscopy, thermal gravimetric analysis, and X-ray photoelectron spectroscopy. The effect of contact time, solution pH, temperature and methylene blue (MB) concentration on the removal of MB were investigated. The results demonstrated that SiO₂-PDA-PAA showed significant improvement in adsorption efficiency towards MB. The kinetics and isotherm studies showed that pseudo-second-order and Langmuir isotherm models were well fitted the experimental data. The values of thermodynamics parameters such as entropy change (ΔS^0), enthalpy change (ΔH^0) and Gibbs free energy (ΔG^0) were calculated based on the Van't Hoff equation. The negative values of thermodynamic parameters indicated that the adsorption of MB was a feasible, spontaneous and exothermic process. In summary, we developed a facile method to fabricate SiO₂-based polymer nanocomposites, which showed obviously enhanced adsorption capability towards MB.

Key words: Mussel inspiration; Michael addition reaction; SiO₂ nanocomposites; Methylene blue; Self-polymerization of dopamine.

1. Introduction

SiO₂ nanoparticles are one of the most important inorganic nonmetallic nanomaterials and possess many unique properties including high thermo-stability, excellent optical and electrical properties, and good mechanical properties.[1] These remarkable features mean that SiO₂ nanomaterials can be used as desiccants, catalyst supports[2], separation agents[3], drug carriers[4, 5] and adsorbents[6-11] as well as a tool to remove pollutants. However, unmodified SiO₂ nanoparticles lack functional groups, which results in limited adsorption capability for these SiO₂ nanoparticles. Therefore, several surface modification methods such as layer-by-layer assembly and grafting copolymerization have been reported to overcome this issue.[12-17] However, most of these methods have some deficiencies and limitations including a challenging experimental procedure, complex and expensive instruments, long reaction time and stringent reaction conditions. Hence, it is highly desirable to explore a facile and effective strategy for surface modification of SiO₂ nanoparticles.

Mussel-inspired modification is a novel strategy for surface modification and was first reported by Waite et al. in the 1980s.[18] Afterwards, Lee et al. demonstrated that dopamine (DA) could form polydopamine (PDA) films onto a wide range of inorganic and organic materials through self-polymerization in alkaline aqueous solution.[19-24] Thus, mussel-inspired chemistry has been regarded as a new route for surface modification for various materials and surfaces. For example, Fei et al. reported a method to synthesize PDA-coated carbon nanotubes with tunable thickness by adjusting the polymerization time.[25] Sung et al. developed a one-step, solution-based surface chemical method to modify super hydrophobic surfaces via a mussel-inspired surface coating.[26] Yang et al. demonstrated a method to prepare a layer of protective shell on the surface of yeast cells combined with covalent conjugate and self polymerization of DA.[27] We reported the preparation of carbon nanotubes, graphene oxides and SiO₂ nanoparticle-based nanocomposites through mussel-inspired chemistry.[28-37] Because of the universal and strong adhesion of PDA towards various substrates, mussel-inspired chemistry has been extensively investigated for different applications.[38-40] However, the surface modification of SiO₂ nanoparticles with polymers through mussel-inspired chemistry is rarely reported. The utilization of these polymer-modified SiO₂ nanoparticles for removal of environmental pollutants has not yet been reported.

Herein, we report a facile method for the surface modification of SiO₂ nanoparticles via mussel-inspired chemistry and a Michael addition reaction (**Scheme 1**). The SiO₂ nanoparticles were prepared according to a slightly modified Stöber method. The SiO₂ nanoparticles were coated on PDA films via self-polymerization of DA. The PDA films are a platform for the secondary reactions. Amino-terminated PAA were synthesized from free radical polymerization and contained many carboxyl functional groups. This was immobilized on the surfaces of the SiO₂ nanoparticles via a Michael addition reaction. The successful preparation of functionalized SiO₂ nanocomposites was confirmed by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Batch experiments were carried out to study the adsorption performance of functionalized SiO₂ nanocomposites for the removal of methylene blue (MB) from aqueous solution. In addition, the adsorption kinetics, isotherms and thermodynamics of the adsorption process were also investigated.

Scheme 1 Schematic showing the preparation of SiO₂-PDA-PAA through a combination of mussel-inspired chemistry and Michael addition reaction.

2. Experimental

2.1. Materials and methods

2.1.1 Materials

All chemical reagents were used as received without further purification. All solvents were of analytical grade. Tetraethyl orthosilicate (TEOS) (> 98%) was used to prepare monodisperse SiO₂ nanoparticles. Acrylic acid (AA) (> 98%), ammonium persulfate (APS) (> 98.5%), dopamine hydrochloride (> 98%) and methylene blue were all purchased from Aladdin industrial Co. Ltd. (Shanghai, China). Ammonia (28%), tris-(hydroxymethyl)-aminethane (Tris) (> 99%) and cysteamine hydrochloride (CSH) (98%) were all supplied by Tianjin Heowns Biochem. Co. Ltd.

2.1.2 Synthesis of monodisperse SiO₂ nanoparticles

The SiO₂ nanoparticles were synthesized according to the Stöber method.[41-44] In a typical synthesis procedure, 36 mL ammonia (28%) was mixed with 124 mL ethyl alcohol and 50 mL deionized water. Then, 18 mL TEOS was rapidly added into the mixture ammonia solution. After being stirred at room temperature for 6 h, the mixture was centrifuged at 6000 r/min for 5 min. The sediments were then washed with deionized water three times to remove unreacted reagents. A white powder was obtained and dried in vacuum oven at 60 °C for 8 h.

2.1.3 Synthesis of PAA

The amino-terminated PAA was synthesized using chain transfer free radical polymerization, in which AA was selected as the monomer and CSH as chain transfer agent. Briefly, 1.136 g (10 mmol) CSH, 4.564 g (20 mmol) APS and 14.412 g (200 mmol) AA were dissolved in 500 mL polymerization flask by deionized water. The mixture was stirred under nitrogen atmosphere at 80 °C for 24 h. The PAA was dialyzed with running water overnight to remove small molecules. The amino-terminated PAA was then precipitated with acetone and dried at 60 °C under vacuum.

2.1.4 Preparation of SiO₂-PDA-PAA

The functional SiO₂ nanocomposites (SiO₂-PDA-PAA) were prepared by combining mussel-inspired chemistry and a Michael addition reaction.[45] The typical procedure was described as follow: 2.0 g SiO₂ nanoparticles and 6.0 g DA were dispersed into 500 mL (10 mM) Tris buffer solution and stirred constantly at room temperature for 8 h. The mixture was centrifuged at 8000 r/min for 10 min. The sediments were washed with deionized water three times. The SiO₂-PDA composites were dried in a vacuum at 60 °C. A secondary reaction occurred on the surface of the SiO₂-PDA. The SiO₂-PDA (2.0 g) and 6.0 g of PAA were added to 100 mL 10 mM Tris buffer solution. This mixture was stirred for 8 h at room temperature, and the final products were separated by centrifugation at 10000 rpm and dried at 60 °C in a vacuum oven.

2.1.5. Characterization of adsorbents

The size and morphology features of the SiO₂ samples were characterized by TEM (Hitachi-7650B, Japan). FT-IR spectra were recorded on a Nicolet 380 Fourier transform spectrometer instrument from 4000-400 cm⁻¹ in transmission mode. TGA was performed under nitrogen atmosphere at a flow rate of 100 mL/min using a SDTQ600 TGA instrument. The heating rate was set at 15 °C/min. The surface composition information of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA nanocomposites was determined using an XPS (VGESCALAB 220-IXL) with Al K α X-ray source.

2.2 Adsorption studies

Batch adsorption experiments investigated the adsorption performance and effects of experimental parameters (e.g. contact time, solution pH, temperature and initial concentrations) on the adsorption process. Here, a cationic dye (MB) was selected as the adsorbate to study the adsorption performance. The effect of contact time used 50 mL MB solution (50 mg/L) with 10 mg adsorbents at room temperature (25 °C) for 120 min. The instantaneous MB concentrations at different times t (min) were detected by an ultraviolet and visible spectrophotometer (TU-1810) instrument at 664 nm. The influence of solution pH was studied by adjusting the pH values of the MB solution (50 mg/L) to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0 using 0.1 M HCl and 0.1 M NaOH. Temperatures included 298, 303, 313, 323, 333 and 343 K. The influence of initial concentration on MB removal capability was studied by agitating different concentrations (25-250 mg/L) MB solution with the same amount of adsorbent (10 mg) for 120 min.

The adsorption capacity at equilibrium time (Q_e) and removal efficiency (R (%)) were determined by equations:

$$Q_e = \left(\frac{C_0 - C_e}{m} \right) \times V \quad R(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100$$

Where C_0 and C_e are initial and equilibrium concentrations of MB. Here, m is the amount of adsorbent (g), and V is the volume of solution (L).

The adsorption capacity at any time t , Q_t (mg/g) is calculated based on the following equation:

$$Q_t = \left(\frac{C_0 - C_t}{m} \right) \times V$$

Where C_t (mg/L) is the MB concentration at any time t (min), and C_0 (mg/L) is the initial MB concentration. V (L) is the

volume of solution in this batch experiment, and m (g) is the amount of adsorbent in the adsorption process.

3. Results and discussion

3.1. Characterization of SiO₂, SiO₂-PDA and SiO₂-PDA-PAA nanocomposites

The TEM images of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA nanoparticles are described in **Fig. 1**. The SiO₂ particles showed a spherical morphology. The diameter of raw SiO₂ particles is 100 to 200 nm (**Fig. 1A**). **Fig. 1B** presents TEM images of SiO₂-PDA, and there is little difference between the as-prepared SiO₂ nanoparticles and the SiO₂-PDA. However, some polymer films around these SiO₂ nanoparticles can be observed in the SiO₂ nanoparticles (**Fig. 1B**). These results implied that SiO₂ nanoparticles were coated with polymers through self-polymerization of DA. **Fig. 1C** and **Fig. 1D** present TEM images of SiO₂-PDA-PAA. Versus the as-prepared SiO₂ nanoparticles, some gauzy extended layers appeared on the surface of the SiO₂-PDA-PAA. Although the spherical morphology of SiO₂ nanoparticles can still be observed in SiO₂-PDA-PAA, the morphology of these SiO₂ nanoparticles became very blurry. It is difficult to find the boundary between the individual particles. Other than TEM images, the optical images of these SiO₂ powders are shown in the insets of **Fig. 1**. The color of these samples changes from white to dark brown implying that the PDA thin films were coated on the SiO₂ nanoparticles through self-polymerization.

Fig. 1 TEM images of (A) SiO₂ nanoparticles, (B) SiO₂-PDA and (C, D) SiO₂-PDA-PAA. Scale bar = 500 nm. The insets are the optical images of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA. The color change implied that the PDA thin films were covered on the surface of SiO₂ nanoparticles.

We used FT-IR analysis to further identify characteristic functional groups on the SiO₂ samples. The samples of raw SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA were analyzed and are shown in **Fig. 2 (A)**. The broad peak at 3396.5 cm⁻¹ was the

–OH stretching vibration. This originated from the surface hydroxyls of silica and PAA. This peak was easily observed in the samples of both raw SiO₂ nanoparticles and SiO₂-PDA-PAA nanocomposites. The peaks at 1110.9, 804.3 and 474.5 cm⁻¹ were associated with Si-OH stretching vibration and Si-O-Si symmetric stretching vibration peaks, respectively. The peaks at 1714.6 and 1627.9 cm⁻¹ were attributed to the C=O stretching vibration in the –COOH groups. This could be observed in the FT-IR spectrum of SiO₂-PDA-PAA. In addition, peaks from 1454.1 to 1384.8 cm⁻¹ in SiO₂-PDA-PAA can be ascribed to the C-H bending vibration from PAA. Of note, the intensity of the stretching vibration of the CH₃ and CH₂ is decreased after surface coating of SiO₂ nanoparticles with PDA. However, the intensity of these peaks increased after the SiO₂-PDA surface was coated with PAA. These changes indicated that PDA and PAA were successively immobilized on the surface of SiO₂ nanoparticles through a mussel-inspired surface coating and subsequent Michael addition.

Fig. 2 (B) shows the TGA curves of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA from 298 to 870 K. Based on the TGA data, the weight loss of original SiO₂ nanoparticles reached 9.74% when the temperature was 860 K. However, the weight loss of SiO₂-PDA increased to 12.74% in the SiO₂-PDA sample. The weight loss of SiO₂-PDA is obviously greater than that of the original SiO₂ nanoparticles. This implied that the PDA films are coated on SiO₂ nanoparticles via self-polymerization of DA. The weight loss of the SiO₂-PDA-PAA increased further to 15.91% under the same test parameters suggesting successful immobilization of PAA on SiO₂-PDA through a Michael addition. In sum, we concluded that the PAA was immobilized on the surface of the SiO₂ nanoparticles through a combination of mussel-inspired chemistry and a Michael addition reaction.

Fig. 2 (A) FT-IR spectra of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA; **(B)** TGA curves of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA.

The surface chemical information was further confirmed with XPS. **Fig. S1** shows the C1s, N1s, O1s and Si2p XPS peaks for the SiO₂ samples. The survey XPS spectra indicated that the SiO₂ samples were composed of C, N, O and Si. The detailed elemental information of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA can be further obtained from C1s, N1s, O1s and Si2p XPS spectra (**Fig. 3**). The binding energy peaks of C1s, N1s, O1s and Si2p XPS spectra in the sample of SiO₂ nanoparticles were found at 284.81, 398.43, 533.07 and 103.8 eV, respectively. However, the binding energy peaks of these XPS spectra in the sample of SiO₂-PDA shifted to 284.68, 400.03, 532.8 and 103.53 eV for C1s, N1s, O1s and Si2p, respectively. **Fig. 3A** shows the C1s

spectra of the SiO₂ samples. The C1s intensity of SiO₂-PDA and SiO₂-PDA-PAA is obviously stronger than that of the original SiO₂ nanoparticles. This indicates the successful modification of SiO₂ with PDA and PAA. In addition, a small peak at 288.68 eV was found in the C1s spectra of SiO₂-PDA-PAA. This is attributed to the C=O band of PAA. These results confirmed that PAA was truly conjugated to the SiO₂ nanoparticles via a combination of mussel-inspired chemistry and Michael addition.

More importantly, almost no N1s signal was found in the raw SiO₂ nanoparticles. However, the N1s signal was obvious in the SiO₂-PDA and SiO₂-PDA-PAA samples. This clearly implied that the PDA films were coated on the surface of the SiO₂ nanoparticles. Furthermore, versus SiO₂-PDA, the intensity of the N1s spectra decreased in the sample of SiO₂-PDA-PAA. This indicated that PAA can be conjugated to the SiO₂-PDA through a Michael addition reaction. All of these detailed XPS spectra provide firm evidence for the successful modification of SiO₂ nanoparticles via mussel-inspired chemistry and subsequent immobilization of amino-terminated PAA on the SiO₂-PDA through a Michael addition.

Fig. 3 High-resolution XPS spectra of C1s (A), N1s (B), O1s (C), and Si2p (D) for raw SiO₂, SiO₂-PDA and SiO₂-PDA-PAA.

Table 1 shows the elemental contents of SiO₂ samples based on C1s, N1s, O1s, and Si2p spectra. The elemental contents of C1s and N1s increased from 4.15% and 0.36% to 21.55% and 1.96% after SiO₂ nanoparticles were coated by PDA. The O1s and

Si2p decreased from 65.07% and 30.41% to 52.77% and 23.72, respectively. Versus SiO₂-PDA, the elemental contents of C1s and N1s in the SiO₂-PDA-PAA decreased from 21.55% and 1.96 to 18.62% and 1.31%, respectively. In contrast, the intensity of the O1s increased after the SiO₂-PDA became surface conjugated with PAA. These comparisons indicated that SiO₂ nanoparticles could be truly modified by amino-terminated polymers via mussel-inspired chemistry and a Michael addition. Furthermore, based on the XPS data, the mass ratio of SiO₂ to PDA was estimated to be 2.37:1. The weight percentage of PAA in SiO₂-PDA-PAA was 33.16%.

Table 1 Element contents (%) of SiO₂ nanoparticles, SiO₂-PDA and SiO₂-PDA-PAA based on XPS analysis.

Sample	Atom percentage (%)			
	C1s	N1s	O1s	Si2p
SiO ₂	4.15	0.36	65.07	30.41
SiO ₂ -PDA	21.55	1.96	52.77	23.72
SiO ₂ -PDA-PAA	18.62	1.31	56.09	23.97

3.2. Adsorption experiment studies

3.2.1 The effect of contact time and adsorption kinetics

The adsorption performance of synthesized adsorbents is shown in **Fig. 4 (A)**. The SiO₂-PDA-PAA showed much higher adsorption efficiency towards MB than the original SiO₂ nanoparticles. The adsorption of MB by SiO₂-PDA-PAA increased rapidly within 10 min. The adsorption equilibrium time of both SiO₂ nanoparticles and the SiO₂-PDA-PAA is about 50 min. The adsorption capability of MB by SiO₂-PDA-PAA was found to be 150.02 mg/g, while adsorption capacity of original SiO₂ nanoparticles was just 43.87 mg/g. The significant increase in adsorption capability of the modified SiO₂ nanocomposites implied that PAA was indeed immobilized on the surface of the SiO₂-PDA. This high adsorption capacity indicated that the SiO₂-PDA-PAA favored adsorption of MB.

Fig. 4 (A) The adsorption capacity of original SiO₂ nanoparticles and SiO₂-PDA-PAA towards 50 mg/L MB at room temperature,

initial pH = 7.1, and adsorbent dose 10 mg. **(B)** Kinetic curves for adsorption of MB onto SiO₂-PDA-PAA.

The adsorption kinetic models play an important role in describing adsorption mechanism, which can predict the adsorption rate and equilibrium adsorption capacity.[46] Here, three commonly used adsorption kinetic models were employed to investigate the adsorption mechanism including the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models.

The pseudo-first-order rate equation is:

$$Q_t = Q_e (1 - e^{-k_1 t})$$

Here, Q_e (mg/g) is the amount of adsorbed MB per unit mass of SiO₂-PDA-PAA at equilibrium, and Q_t (mg/g) is the amount of adsorbed MB at time t (min). Term k_1 (min⁻¹) is the rate constant of adsorption. The values of those parameters were calculated from the pseudo-first-order rate equation and listed in the following table.

The pseudo-second-order kinetic model was described by following equation[47]:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$$

$$h = k_2 Q_e^2$$

Here, k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant and h (mg/g min) represents the initial adsorption rate. The values of k_2 and h were calculated from the equation mentioned above and is listed in **Table 2**. The experimental kinetic data were fitted by a pseudo-first-order and pseudo-second-order models. The results are presented in **Fig. 4(B)**. Based on the data in **Table 2**, the calculated value of Q_e from the pseudo-second-order was 146.6 mg/g. The Q_e from the pseudo-first-order was 137.8 mg/g. The value of Q_e from the pseudo-second-order was closer to the Q_e from the adsorption experiment (150.02 mg/g), which indicated that the adsorption process of SiO₂-PDA-PAA to MB followed a pseudo-second-order. Furthermore, correlation coefficient values ($R^2 = 0.9931$) from the pseudo-second-order were found to be higher than the pseudo-first-order ($R^2 = 0.9674$). These results suggest that the adsorption procedure is better fitted as a pseudo-second-order than a pseudo-first-order.

The intra-particle diffusion model based on the Weber-Morris equation evaluated the steps of adsorption:

$$Q_t = k_p t^{0.5} + C$$

Here, k_p (mg g⁻¹ min^{-1/2}) is the rate constant of the intra-particle diffusion and is calculated from the equation listed above. The parameter C is a constant given an idea about the effect of the boundary layer.[48] **Fig. 4(B)** shows the non-linear fitting curve of intra-particle diffusion. The values of these parameters are listed in **Table 2**. The low correlation coefficient ($R^2 = 0.8207$) from intra-particle diffusion model indicated that adsorption of MB by SiO₂-PDA-PAA was not the rate limiting step. The intra-particle diffusion for the adsorption process was not significant.

Table 2 Data for pseudo-first-order, pseudo-second-order and intraparticle diffusion models parameters at 298 K.

Models	Parameters	Initial concentration (mg/L)
--------	------------	------------------------------

Pseudo-first-order equation	$Q_{e(cal)} (mg/g)$	137.80
	$k_1 (min^{-1})$	0.3058
	R^2	0.9674
Pseudo-second-order equation	$Q_{e(cal)} (mg/g)$	146.6
	$k_2 (g\ mg^{-1}\ min^{-1})$	0.003691
	$h (mg\ g^{-1}\ min^{-1})$	79.31
	R^2	0.9931
Intra-particle diffusion	$k_p (mg\ g^{-1}\ min^{-0.5})$	4.707
	C	105.8
	R^2	0.8207

3.2.2 Adsorption isotherms

Adsorption isotherms describe the adsorption behavior for a solid-solution adsorption system. The adsorption isotherm can explain the distribution of adsorbate between the solid and liquid phases when the adsorption reaction reached equilibrium.[49] In this study, the adsorption isotherm was applied to understand the adsorption mechanism. Both the Langmuir and Freundlich adsorption isotherm models fitted the equilibrium data. Of these, the Langmuir model is one of the most widely used adsorption isotherms for the solid-solution adsorption system. The adsorption constants from the Langmuir isotherm explain the adsorption mechanism. The Langmuir isotherm model is based on an assumption that adsorption occurs on the monolayer and homogeneous surface of adsorbents. This is irrelevant to the degree of surface coverage. The non-linear formation of the Langmuir isotherm model was listed as follows:

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e}$$

Here, Q_m (mg/g) is the theoretical maximum adsorption capacity of adsorbents, and K_L (L/mg) is the Langmuir adsorption constant. The Q_e (mg/g) is the equilibrium adsorption capacity per unit weight of adsorbents. Term C_e is the equilibrium MB concentration (mg/L).

This essential feature of the Langmuir isotherm model was expressed in term of a dimensionless factor:

$$R_L = \frac{1}{1 + K_L C_0}$$

Here, K_L (L/mg) is a constant of the Langmuir model. Term C_0 is the initial MB concentration (mg/L) and R_L is the dimensionless separation factor. The parameter R_L indicates that the type of Langmuir isotherm can be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$)[50]. All relative parameters from the Langmuir isotherm were calculated and listed in **Table 3** according to nonlinear analysis. **Fig. 5** shows the fitting equilibrium curve from the Langmuir isotherm model.

Fig. 5 The isotherm curves for the adsorption of MB molecules onto the functionalized SiO₂ nanocomposites.

The experimental adsorption data were also fitted with the Freundlich isotherm model. This model is based on the hypothesis that non-ideal sorption occurs on the heterogeneous surfaces. The adsorption capacity is related to the adsorbate concentration at equilibrium.[45] The non-linear form of the Freundlich isotherm model can be expressed as:

$$Q_e = K_F C_e^{\frac{1}{n}}$$

Here, K_F [(mg/g) (L/mg)^{1/n}] is the Freundlich isotherm adsorption equilibrium constant related to the adsorption capacity, and n is the heterogeneity constant related to the intensity of the adsorption interactions. Generally speaking, n negatively correlates with adsorption performance. When the value of $1/n$ is equal to 1, the adsorption is essentially homogeneous and there is no interaction among the adsorbed species. The adsorption is favorable when the value of $1/n$ is between 0 and 1. However, adsorption is unfavorable when the value of $1/n$ is over 1.[51] Terms Q_e (mg/g) and C_e (mg/L) are the amount of MB adsorbed per unit mass of adsorbents and MB concentration at equilibrium, respectively. The non-linear fitting curve of the Freundlich isotherm is shown in **Fig. 5**. The values of the Freundlich isotherm model parameters were calculated and listed in **Table 3**.

Table 3 The equilibrium parameters for the adsorption of MB molecules onto SiO₂-PDA-PAA nanocomposites.

Isotherms	Parameters	Temperatures(K)
		298
Langmuir	Q_m (mg/g)	305.9
	K_L (L/mg)	0.04469
	R_L	0.08215-0.4723
	R^2	0.9929
Freundlich	K_F [(mg/g)(L/mg) ^{1/n}]	60.80

n^{-1}	0.2978
R^2	0.9585

Table 3 shows the values of the correlation coefficient R^2 from the Langmuir isotherm model ($R^2 = 0.9929$). These were higher than the Freundlich isotherm model ($R^2 = 0.9585$) suggesting that the experimental data are better fitted via a Langmuir model. This indicated that monolayer adsorption plays a dominant role. The maximum adsorption capacity calculated from the Langmuir isotherm model was 305.9 mg/g at 298 K. The high correlation coefficient ($R^2 > 0.9$) of the Freundlich and Langmuir isotherms suggest the existence of heterogeneous active sites for adsorbents and monolayer adsorption of MB onto SiO₂-PDA-PAA. In addition, the calculated value of the dimensionless constant R_L ranged from 0.08215 to 0.4273 for different initial MB concentrations. This showed that the adsorption of MB was favorable. Moreover, the value of n was 0.2978 suggesting that the SiO₂-PDA-PAA nanocomposites were excellent at adsorbing MB.

3.2.3 The effect of pH

The pH plays an important role in the adsorption process.[52] To study the effect of initial pH on adsorption of MB by SiO₂-PDA-PAA, a batch experiment was carried out at different pH values between 2.0 and 12.0 and room temperature. **Fig. 6** shows that the pH of the MB solution had a significant effect on the adsorption of MB by the SiO₂-PDA-PAA. The value of Q_e increased from 133.5 to 214.3 mg/g with increases in solution pH. The MB removal efficiency was 87.4% at pH 11.0. This suggested that the SiO₂-PDA-PAA is highly efficient for MB removal. The pH is a crucial factor affecting the adsorption process.

The lower adsorption capacity in acidic solution can be ascribed to the competitive adsorption between H⁺ and adsorption active sites. The high concentration of H⁺ inhibited the adsorption of MB by SiO₂-PDA-PAA. At higher pH, more carboxyl groups on the SiO₂-PDA-PAA were ionized. Therefore, the SiO₂-PDA-PAA nanocomposites favor adsorption towards MB with higher adsorption efficiency. The slight change of adsorption capacity at pH 12.0 might be due to the fact that PDA in strong base was broken slightly. In conclusion, the adsorption of MB by SiO₂-PDA-PAA was pH-dependent. pH increases promoted adsorption of SiO₂-PDA-PAA nanocomposites towards MB.

Fig. 6 The effect of solution pH on the adsorption of MB by SiO₂-PDA-PAA. Experimental conditions: adsorbent dose: 10 mg, T

= room temperature.

3.2.4 The effect of temperature and adsorption thermodynamics

Temperature is generally considered an essential parameter to influence MB adsorption at the solid-liquid interfaces.[53] Batch adsorption experiments were carried out under from 295 to 343 K. **Fig. 7 (A)** shows that the adsorption capability of SiO₂-PDA-PAA towards MB decreased from 149.7 to 112.2 mg/g as temperature increased from 295 to 343 K. This indicated that the adsorption of MB onto SiO₂-PDA-PAA nanocomposites was an exothermic process. The high temperature was not beneficial for the adsorption of MB by SiO₂-PDA-PAA. This might be because the surface tension of the solution decreased with increasing temperature. This lead to low adsorption capacity. Thermodynamic studies provide further information about the adsorption process according to the inherent energetic changes.[54] Here, the related thermodynamic parameters including entropy (ΔS^0), enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) were employed to evaluate the adsorption of MB by SiO₂-PDA-PAA nanocomposites. The values of thermodynamic parameters were calculated by following equations:

$$\ln K\alpha = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T}$$

$$K\alpha = \frac{Q_e}{C_e}$$

$$\Delta G^0 = -RT \ln K\alpha$$

Here, $K\alpha$ (L·g⁻¹) is a constant in the Van't Hoff equation. The R (8.314 J·mol⁻¹·K⁻¹) represents the gas constant, and T (K) is the temperature. Terms Q_e (mg·g⁻¹) and C_e (mg·L⁻¹) are the amount of adsorbed MB at equilibrium time and the equilibrium concentration of MB solution, respectively. The thermodynamic parameters (ΔH^0 and ΔS^0) were calculated from the slope and intercept of the Van't Hoff plots of $\ln K\alpha$ versus of $1/T$ (**Fig. 7 (B)**) and are listed in **Table 4**.

Fig. 7 (A) The effect of temperature on the adsorption of MB molecules by SiO₂-PDA-PAA. Experimental conditions: $C_{MB} = 50$ mg/L, solution pH = 7.1, contact time = 60 min. **(B)** The Van't Hoff plot for the adsorption of the MB molecules onto SiO₂-PDA-PAA.

Table 4 shows that $K\alpha$ decreased with increasing temperature. This indicated that the adsorption of MB onto SiO₂-PDA-PAA nanocomposites was favored at 295 K. The values of ΔG^0 were found to be negative at different temperatures. This suggests that the adsorption was a spontaneous and favorable process. As temperature increased from 295 to 343 K, the value of ΔG^0 increased

from -5.058 to -3.984 kJ·mol⁻¹. In addition, the negative value of ΔH^0 confirmed that the adsorption process was exothermic. The negative value of ΔS^0 suggests that the randomness decreased at the solid-liquid interface during adsorption of MB on the SiO₂-PDA-PAA. Furthermore, the values of ΔH^0 and $T\Delta S^0$ verified that the adsorption of MB was an enthalpy-controlled process. These results suggested that SiO₂-PDA-PAA are very efficient adsorbents for the removal of cationic dyes at room temperature.

Table 4 Thermodynamic parameters for the adsorption of MB molecules onto SiO₂-PDA-PAA nanocomposites.

<i>T</i> (K)	<i>Ka</i> (L·g ⁻¹)	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (kJ·mol ⁻¹ ·K ⁻¹)
295	7.811	-5.058	-12.33	-0.02499
303	6.613	-4.761		
313	5.457	-4.418		
323	4.582	-4.089		
333	4.102	-3.909		
343	4.041	-3.984		

4. Conclusions

This study presented a facile method for surface modification of SiO₂ nanoparticles with PAA via a combination of mussel-inspired chemistry and Michael addition reaction. The successful preparation of SiO₂-PDA-PAA was confirmed with TEM, TGA, FT-IR and XPS. The adsorption performance of SiO₂-PDA-PAA towards MB was studied at different conditions. Versus the adsorption capacity of the original SiO₂ nanoparticles, the SiO₂-PDA-PAA exhibited an obviously higher adsorption efficiency towards MB. The data show that the adsorption process of MB onto SiO₂-PDA-PAA was pH dependent. The adsorption kinetics were pseudo-second-order and Langmuirian. The thermodynamic parameters demonstrated that the adsorption process for MB was feasible, spontaneous and exothermic. These results proved that the surface modification of SiO₂ nanoparticles with PAA could obviously enhance their adsorption efficiency towards MB. Furthermore, this strategy could also be used to fabricate many other polymer nanocomposites for strong and universal adhesion of PDA. Therefore, this strategy provides a facile and efficient route to fabricate highly efficient adsorbents for environmental adsorption applications.

Acknowledgments

This research was supported by the National Science Foundation of China (Nos. 51363016, 21474057, 21564006, 21561022), and the National 973 Project (Nos. 2011CB935700). We thank LetPub (www.letpub.com) for its linguistic assistance during the preparation of this manuscript.

References

- [1] Z. Li, J.C. Barnes, A. Bosoy, J.F. Stoddart, J.I. Zink, Mesoporous silica nanoparticles in biomedical applications, Chem. Soc. Rev., 41 (2012) 2590-2605.
- [2] D. Tang, L. Zhang, Y. Zhang, Z.-A. Qiao, Y. Liu, Q. Huo, Mesoporous silica nanoparticles immobilized salicylaldehyde cobalt complexes as high efficient catalysts for polymerization of 1, 3-butadiene, J Colloid Interf Sci, 369 (2012) 338-343.
- [3] E. Vega, C. Marzabadi, Y. Kazakevich, A.Y. Fadeev, Synthesis of chiral mesoporous silicas with oligo (saccharide) surfaces and their use in separation of stereoisomers, J Colloid Interf Sci, 359 (2011) 542-544.
- [4] Y. Su, Y. He, H. Lu, L. Sai, Q. Li, W. Li, L. Wang, P. Shen, Q. Huang, C. Fan, The cytotoxicity of cadmium based, aqueous

phase-Synthesized, quantum dots and its modulation by surface coating, *Biomaterials*, 30 (2009) 19-25.

- [5] C. Heng, M. Liu, P. Wang, K. Wang, X. Zheng, D. Fan, J. Hui, X. Zhang, Y. Wei, Preparation of silica nanoparticles based multifunctional therapeutic systems via one-step mussel inspired modification, *Chem. Eng. J.*, 296 (2016) 268-276.
- [6] Q. Qin, J. Ma, K. Liu, Adsorption of anionic dyes on ammonium-functionalized MCM-41, *J Hazard Mater*, 162 (2009) 133-139.
- [7] N. Gargiulo, F. Pepe, D. Caputo, Modeling carbon dioxide adsorption on polyethylenimine-functionalized TUD-1 mesoporous silica, *J Colloid Interf Sci*, 367 (2012) 348-354.
- [8] J. Li, X. Miao, Y. Hao, J. Zhao, X. Sun, L. Wang, Synthesis, amino-functionalization of mesoporous silica and its adsorption of Cr (VI), *J Colloid Interf Sci*, 318 (2008) 309-314.
- [9] N. Guo, Y. Liang, S. Lan, L. Liu, G. Ji, S. Gan, H. Zou, X. Xu, Uniform TiO₂-SiO₂ hollow nanospheres: Synthesis, characterization and enhanced adsorption-photodegradation of azo dyes and phenol, *Appl. Surf. Sci.*, 305 (2014) 562-574.
- [10] P. Wang, M. Cao, C. Wang, Y. Ao, J. Hou, J. Qian, Kinetics and thermodynamics of adsorption of methylene blue by a magnetic graphene-carbon nanotube composite, *Appl. Surf. Sci.*, 290 (2014) 116-124.
- [11] B. Yu, X. Zhang, J. Xie, R. Wu, X. Liu, H. Li, F. Chen, H. Yang, Z. Ming, S.-T. Yang, Magnetic graphene sponge for the removal of methylene blue, *Appl. Surf. Sci.*, 351 (2015) 765-771.
- [12] Y. Chen, E. Kang, K. Neoh, Y. Zhang, K. Tan, Oxidative graft polymerization of aniline on Si (100) surface modified by plasma polymerization of glycidyl methacrylate, *Polym Eng Sci*, 42 (2002) 1181-1196.
- [13] S.R. Whaley, D. English, E.L. Hu, P.F. Barbara, A.M. Belcher, Selection of peptides with semiconductor binding specificity for directed nanocrystal assembly, *Nature*, 405 (2000) 665-668.
- [14] M. Charbonnier, M. Alami, M. Romand, Plasma treatment process for palladium chemisorption onto polymers before electroless deposition, *J Electrochem Soc*, 143 (1996) 472-480.
- [15] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Self-assembled monolayers of thiolates on metals as a form of nanotechnology, *Chem Rev*, 105 (2005) 1103-1170.
- [16] J. Tian, H. Zhang, M. Liu, F. Deng, H. Huang, Q. Wan, Z. Li, K. Wang, X. He, X. Zhang, A bioinspired strategy for surface modification of silica nanoparticles, *Appl. Surf. Sci.*, 357 (2015) 1996-2003.
- [17] Y. Shi, M. Liu, K. Wang, H. Huang, Q. Wan, L. Tao, L. Fu, X. Zhang, Y. Wei, Direct surface PEGylation of nanodiamond via RAFT polymerization, *Appl. Surf. Sci.*, 357 (2015) 2147-2153.
- [18] J.H. Waite, T.J. Housley, M.L. Tanzer, Peptide repeats in a mussel glue protein: theme and variations, *Biochemistry*, 24 (1985) 5010-5014.
- [19] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, *Science*, 318 (2007) 426-430.
- [20] H. Lee, N.F. Scherer, P.B. Messersmith, Single-molecule mechanics of mussel adhesion, *Proc Nat Acad Sci*, 103 (2006) 12999-13003.
- [21] Q. Wan, M. Liu, J. Tian, F. Deng, G. Zeng, Z. Li, K. Wang, Q. Zhang, X. Zhang, Y. Wei, Surface modification of carbon nanotubes by combination of mussel inspired chemistry and SET-LRP, *Polym. Chem.*, 6 (2015) 1786-1792.
- [22] Q. Wan, L. Mao, M. Liu, K. Wang, G. Zeng, D. Xu, H. Huang, X. Zhang, Y. Wei, Towards development of a versatile and efficient strategy for fabrication of GO based polymer nanocomposites, *Polym. Chem.*, 6 (2015) 7211-7218.
- [23] M. Liu, J. Ji, X. Zhang, X. Zhang, B. Yang, F. Deng, Z. Li, K. Wang, Y. Yang, Y. Wei, Self-polymerization of dopamine and polyethylenimine: novel fluorescent organic nanoprobe for biological imaging applications, *J. Mater. Chem. B*, 3 (2015) 3476-3482.
- [24] X. Zhang, S. Wang, L. Xu, Y. Ji, L. Feng, L. Tao, S. Li, Y. Wei, Biocompatible Polydopamine Fluorescent Organic Nanoparticles: Facile Preparation and Cell Imaging, *Nanoscale*, 4 (2012) 5581-5584.
- [25] B. Fei, B. Qian, Z. Yang, R. Wang, W. Liu, C. Mak, J.H. Xin, Coating carbon nanotubes by spontaneous oxidative polymerization of dopamine, *Carbon*, 46 (2008) 1795-1797.
- [26] S.M. Kang, I. You, W.K. Cho, H.K. Shon, T.G. Lee, I.S. Choi, J.M. Karp, H. Lee, One - Step Modification of Superhydrophobic Surfaces by a Mussel - Inspired Polymer Coating, *Angew Chem Int Edit*, 49 (2010) 9401-9404.
- [27] S.H. Yang, S.M. Kang, K.-B. Lee, T.D. Chung, H. Lee, I.S. Choi, Mussel-inspired encapsulation and functionalization of individual yeast cells, *J Am Chem Soc*, 133 (2011) 2795-2797.
- [28] X. Zhang, J. Ji, X. Zhang, B. Yang, M. Liu, W. Liu, L. Tao, Y. Chen, Y. Wei, Mussel inspired modification of carbon

nanotubes using RAFT derived stimuli-responsive polymers, *RSC Adv*, 3 (2013) 21817-21823.

- [29] X. Zhang, M. Liu, X. Zhang, F. Deng, C. Zhou, J. Hui, W. Liu, Y. Wei, Interaction of tannic acid with carbon nanotubes: enhancement of dispersibility and biocompatibility, *Toxicol Res*, 4 (2015) 160-168.
- [30] X. Zhang, M. Liu, Y. Zhang, B. Yang, Y. Ji, L. Feng, L. Tao, S. Li, Y. Wei, Combining mussel-inspired chemistry and the Michael addition reaction to disperse carbon nanotubes, *RSC Adv*, 2 (2012) 12153-12155.
- [31] X. Zhang, G. Zeng, J. Tian, Q. Wan, Q. Huang, K. Wang, Q. Zhang, M. Liu, F. Deng, Y. Wei, PEGylation of carbon nanotubes via mussel inspired chemistry: Preparation, characterization and biocompatibility evaluation, *Appl Surf Sci*, 351 (2015) 425-432.
- [32] Q. Wan, J. Tian, M. Liu, G. Zeng, Q. Huang, K. Wang, Q. Zhang, F. Deng, X. Zhang, Y. Wei, Surface modification of carbon nanotubes via combination of mussel inspired chemistry and chain transfer free radical polymerization, *Appl. Surf. Sci.*, 346 (2015) 335-341.
- [33] X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan, F. Deng, Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu^{2+} removal, *Appl. Surf. Sci.*, 343 (2015) 19-27.
- [34] Y. Shi, M. Liu, K. Wang, F. Deng, Q. Wan, Q. Huang, L. Fu, X. Zhang, Y. Wei, Bioinspired preparation of thermo-responsive graphene oxide nanocomposites in an aqueous solution, *Polym. Chem.*, 6 (2015) 5876-5883.
- [35] X. Zhang, J. Ji, X. Zhang, B. Yang, M. Liu, W. Liu, L. Tao, Y. Chen, Y. Wei, Mussel Inspired Modification of Carbon Nanotubes Using RAFT Derived Stimuli-responsive Polymers, *RSC Adv.*, 3 (2013) 21817-21823.
- [36] X. Zhang, M. Liu, Y. Zhang, B. Yang, Y. Ji, L. Feng, L. Tao, S. Li, Y. Wei, Combining Mussel-inspired Chemistry and the Michael Addition Reaction to Disperse Carbon Nanotubes, *RSC Adv.*, 2 (2012) 12153-12155.
- [37] Q. Wan, J. Tian, M. Liu, G. Zeng, Z. Li, K. Wang, Q. Zhang, F. Deng, X. Zhang, Y. Wei, Mussel inspired preparation of highly dispersible and biocompatible carbon nanotubes, *RSC Adv.*, 5 (2015) 25329-25336.
- [38] Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, Mussel-inspired Chemistry and Michael addition Reaction for Efficient Oil/water Separation, *ACS Appl. Mater. Interf.*, 5 (2013) 4438-4442.
- [39] L. Xu, N. Liu, Y. Cao, F. Lu, Y. Chen, X. Zhang, L. Feng, Y. Wei, Mercury Ion Responsive Wettability and Oil Water Separation, *ACS Appl. Mater. Interf.*, 6 (2014) 13324-13329.
- [40] Y. Liu, K. Ai, L. Lu, Polydopamine and its Derivative Materials: Synthesis and Promising Applications in Energy, Environmental, and Biomedical fields, *Chem. Rev.*, (2014) DOI: 10.1021/cr400407a.
- [41] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *J Colloid Interf Sci*, 26 (1968) 62-69.
- [42] L. Lu, R. Capek, A. Kornowski, N. Gaponik, A. Eychmüller, Selective fabrication of ordered bimetallic nanostructures with hierarchical porosity, *Angew Chem Int Edit*, 44 (2005) 5997-6001.
- [43] W. Wang, B. Gu, L. Liang, W. Hamilton, Fabrication of two-and three-dimensional silica nanocolloidal particle arrays, *J Phys Chem B*, 107 (2003) 3400-3404.
- [44] T. Zhang, Q. Zhang, J. Ge, J. Goebel, M. Sun, Y. Yan, Y.-s. Liu, C. Chang, J. Guo, Y. Yin, A self-templated route to hollow silica microspheres, *J Phys Chem C*, 113 (2009) 3168-3175.
- [45] X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan, F. Deng, Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu^{2+} removal, *Appl Surf Sci*, 343 (2015) 19-27.
- [46] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, *Water Sa*, 30 (2004) p. 533-539.
- [47] I.A. Darwish, D.A. Blake, Development and validation of a one-step immunoassay for determination of cadmium in human serum, *Anal Chem*, 74 (2002) 52-58.
- [48] P. Sun, C. Hui, R.A. Khan, J. Du, Q. Zhang, Y.-H. Zhao, Efficient removal of crystal violet using Fe_3O_4 -coated biochar: the role of the Fe_3O_4 nanoparticles and modeling study their adsorption behavior, *Sci Rep-UK*, 5 (2015).
- [49] M. Brdar, M. Šćiban, A. Takači, T. Došenović, Comparison of two and three parameters adsorption isotherm for Cr (VI) onto Kraft lignin, *Chem Eng J*, 183 (2012) 108-111.
- [50] G. Annadurai, L.Y. Ling, J.-F. Lee, Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis, *J Hazard Mater*, 152 (2008) 337-346.

- [51] M. Rauf, S. Bukallah, F. Hamour, A. Nasir, Adsorption of dyes from aqueous solutions onto sand and their kinetic behavior, *Chem Eng J*, 137 (2008) 238-243.
- [52] W. Konicki, I. Pelech, E. Mijowska, I. Jasińska, Adsorption of anionic dye Direct Red 23 onto magnetic multi-walled carbon nanotubes-Fe₃C nanocomposite: Kinetics, equilibrium and thermodynamics, *Chem Eng J*, 210 (2012) 87-95.
- [53] L. Ai, J. Jiang, Removal of methylene blue from aqueous solution with self-assembled cylindrical graphene-carbon nanotube hybrid, *Chem Eng J*, 192 (2012) 156-163.
- [54] L. Ai, C. Zhang, Z. Chen, Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite, *J Hazard Mater*, 192 (2011) 1515-1524.