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High porosity microspheres with functional groups synthesized by thiol–yne click suspension polymerization†

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Porous polymer microspheres have been widely used in various fields, such as in ion-adsorption and drug release, and as catalyst carriers and so on. However, the facile synthesis of polymer microspheres with various available functional groups is still a challenge. Here, we firstly synthesized epoxy-functionalized porous microspheres via thiol–yne suspension polymerization of glycidyl propargyl ether and 1,3-propanedithiol, using 1,7-octadiyne as a crosslinker and polyethylene glycol (PEG) as a porogen. The epoxy groups on the microsphere surfaces were further modified to *tert*-amine, thioacetate, and carboxyl groups via thiol–epoxy click reactions. The morphologies of the porous microspheres were investigated using a scanning electron microscope (SEM). When the content of PEG was 35 wt%, porous polymer microspheres with average diameters of ~70 μm and highest porosities of 62.45% were obtained. Subsequently, diverse modified porous microspheres were used to adsorb copper ions that were dissolved in DMF. Among these as-prepared microspheres, the thioacetate-functionalized one exhibited the highest Cu^{2+} adsorption capacity (158 mg g^{-1}) at room temperature. Exploration of its adsorption behaviors illustrated that the thioacetate-functionalized microspheres followed a chemically controlled monolayer adsorption mechanism. Our work presents a brand new reliable strategy for the synthesis and functionalization of non-degradable epoxy-containing porous microspheres, which can be used for the adsorption or removal of toxic metal ions (such as copper ions).

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Introduction

Porous polymer microspheres (PPMs), with crosslinking structures that exhibit low densities and high surface areas, have been widely used as catalyst carriers and in ion-adsorption, drug release, the biological sector, and so on.^{1–7} In general, using incompatible components as porogens, PPMs can be synthesized through precipitation,^{8,9} or by microfluidic,^{10–13} dispersion^{14–16} or suspension polymerization.^{17,18} Precipitation polymerization can give rise to monodisperse products with controlled particle sizes (0.10–10 μm in

diameter).^{8,9} However, limited by the synthetic strategy, it exhibited poor production efficiency. Moreover, the large amount of crosslinker required and the low monomer concentrations (2–5%) required for this protocol lead to a high production cost.⁷ Employed in specific devices, the microfluidic polymerization technique can also afford monodisperse PPMs, as is the case for precipitation polymerization. Complicated parameters (such as the flow rate of the medium, the viscosity and surface tension of the droplet, tube distance, and so on) are involved in microfluidic polymerization,^{7,10–13} all of which are extremely difficult to control and have an important effect on the PPMs. Emulsion polymerization has been widely applied to fabricate gel-type particles with nanoscale diameters and large surface areas.^{19,20} However, such a small particle size (from 50 to 500 nm) results in hard isolation of the PPMs from the dispersion medium, which limits their applications. Compared with these aforementioned strategies, suspension polymerization is a more facile technique used in the synthesis of PPMs, due to its high efficiency and low cost and the simple isolation of PPMs from the medium.

Compared with thermoinitiated thiol–ene/–yne polymerization, UV-initiated polymerization essentially requires milder

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reaction conditions, and demonstrates a faster reaction speed and higher conversion of monomers.^{21–27} In 2012, Durham and coworkers first employed water-borne thiol-ene photopolymerization to synthesize polymer microspheres. The size of the gel-type microspheres (in the range of sub-micrometers to hundreds of micrometers) was mainly influenced by the amount of surfactant and cosolvent, the homogenization energy, and the cosolvent species.²⁸ Tan *et al.* utilized a similar protocol to synthesize PPMs using linear PMMA ($M_n = 27\,279\text{ g mol}^{-1}$, PDI = 1.89) as the porogen. When the ratio of PMMA to total monomers was 2:3, the largest porosity reached 57%.²⁹ Amine, hydroxyl and carboxyl group functionalized monodisperse PPMs (210–600 μm in diameter) were synthesized *via* a photo-initiated microfluidic technique using tetrafunctional thiol and multifunctional alkene/alkynes as the monomers, and organic molecules (such as diethyl phthalate, 1,4-dichlorobenzene, dibutylphthalate and dioctyl phthalate, *etc.*) as the porogens.³⁰ The amine and hydroxyl groups in the PPMs were present in the range of 0.23–0.69 mmol g^{-1} and 0.24–0.64 mmol g^{-1} , respectively. Undoubtedly, the properties and applications of the microspheres greatly depend on the available number of functional groups. Therefore, microspheres with a high content of useful groups on the surface are desired. In addition to the aforementioned amine and hydroxyl groups, the epoxy group is another highly reactive group which has been widely considered as a reliable molecular platform for various modifications and applications. However, the facile synthesis of epoxy-containing microspheres remains largely unexplored.

Here, we firstly reported the synthesis of epoxy-functionalized PPMs *via* thiol-yne click suspension polymerization in a one-pot method. The PPMs were further functionalized *via* thiol-epoxy addition of carboxyl-, *tert*-amino-, and thioacetic group-containing monothiol monomers and the epoxy group. Their fine structures were characterized by a combination of scanning electron microscope (SEM) analysis and Fourier transform infrared spectroscopy (FTIR). The average sizes of the resultant PPMs and their total pore areas were characterized using a particle-size analyzer and a mercury porosimeter, respectively. Furthermore, these functionalized PPMs were used to adsorb copper ions. The loading capacities and adsorption mechanisms of the modified PPMs were evaluated using UV-Vis spectroscopy. This work affords a universal strategy for the synthesis of various functional PPMs.

Experimental section

Materials

Glycidyl propargyl ether (90%, Nanjing Datang Co. Ltd), 1,3-propanedithiol (98%, Aladdin Co. Ltd), 1,7-octadiyne (97.0%, TCI Co.), 3-mercaptopropionic acid (97.0%, Aladdin Co. Ltd), thioacetic acid (97.5%, J&K Scientific Co.), 3-aminopropanethiol (97.0%, TCI Co.), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich Co. Ltd) and sodium dodecyl benzene sulfonate (SDBS, 90%, Aladdin Co. Ltd) were used as

received. Polyethylene glycol (PEG, $M_n = 10\,000\text{ g mol}^{-1}$), triethylamine (TEA), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), methanol, chloroform and cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were of analytical purity grade, and were purchased from Sinopharm Chemical Reagent Co. Ltd and used without any further purification.

Synthesis of epoxy-containing PPMs

In a typical procedure, 1,3-propanedithiol (397.1 mg, 3.7 mmol), glycidyl propargyl ether (274.5 mg, 2.5 mmol), 1,7-octadiyne (64.9 mg, 0.6 mmol), DMPA (28.2 mg, 0.1 mmol), chloroform (744.8 mg, 6.2 mmol) and PEG (257.3 mg, 0.02 mmol) were introduced into a 10 mL round bottom flask which contained a certain amount of chloroform (736.5 mg, 6 mmol) and a magnetic bar (5 mm in length). The 10 mL flask was sealed using a rubber septum and wrapped in aluminum foil. After being mixed by the magnetic stirrer, the homogeneous organic mixture was added dropwise, under stirring by a magnetic bar (8 mm in length), into a 25 mL round bottom flask which was loaded with 10 mL of aqueous 5 wt% SDBS. Finally, the 25 mL flask was immersed into an ice bath with a stirring rate of 750 rpm, and the suspension was irradiated by a continuous UV light ($\lambda = 365\text{ nm}$) for 2 h. Then, the products were washed successively with water, tetrahydrofuran (THF) and methanol three times. The resultant white powder was dried in a vacuum oven at 35 $^{\circ}\text{C}$ for 24 h, giving a yield of 76.3%.

Modification of epoxy-containing PPMs

The modification of the epoxy groups of the PPMs and the thiol was carried out in a mixture of methanol and chloroform. For example, epoxy-containing PPMs (0.40 g), ethanethioic acid (0.60 g, 7.8 mmol) and triethylamine (0.05 g, 0.5 mmol) were added into a 25 mL round bottom flask. Then, 6 mL of a mixture of methanol and chloroform ($v:v = 5:1$) was added, forming a dispersion. The flask was immersed in an oil bath at 35 $^{\circ}\text{C}$ with a stirring rate of 250 rpm for 3 d. After that, the products were washed with THF and methanol three times. The resultant pale yellow powder (Fig. S1†) was dried in a vacuum oven at 35 $^{\circ}\text{C}$ for 24 h, giving a yield of 82.8%. The modifications of the PPMs by 3-aminopropanethiol and 3-mercaptopropionic acid were also carried out according to this procedure.

Adsorption of Cu^{2+} ions using modified PPMs

The adsorption properties of the modified PPMs for Cu^{2+} ions were evaluated as follows. Firstly, equal masses (10, 20, 30 and 40 mg) of the resultant PPMs modified by ethanethioic acid, 3-aminopropanethiol and 3-mercaptopropionic, were added into glass bottles loaded with 10 mL of DMF solutions of copper sulfate (2 mM), respectively. After leaving for 72 h at room temperature, the supernatants were analysed using UV-Vis spectroscopy, and the remaining Cu^{2+} ion content in each DMF solution was calculated using eqn (1):

$$C = \frac{\text{Abs} - I}{S} \quad (1)$$

where C refers to the equilibrium concentration of Cu^{2+} ions, Abs refers to the absorbance intensity as measured by the UV-Vis spectra, and I and S are the intercept and slope of the standard work curve, respectively [Fig. S2 and S3†].

Adsorption isotherm of Cu^{2+} ions on thioacetate-containing PPMs

The isotherm adsorption experiment was conducted as follows, to explore the adsorption capacity and mechanism of the Cu^{2+} ions on the thioacetate-containing PPMs. First, 200 mg of thioacetate-containing PPMs was divided into 10 equal portions, which were then added into glass bottles. The PPMs were then immersed in DMF solutions of copper sulfate with different concentrations at 30 °C for 72 h in order to reach the adsorption equilibrium. The remaining Cu^{2+} ion content in each DMF solution was measured using ultraviolet-visible spectroscopy. The adsorption capacities (mg g^{-1}) of the modified PPMs at different Cu^{2+} ion concentrations were calculated using eqn (2):

$$\text{AC} = \left(C_0 - \frac{\text{Abs} - I}{S} \right) \times M_{\text{Cu}} / m_{\text{a}} \quad (2)$$

where AC refers to the adsorption capacity of the modified PPMs, C_0 is the initial concentration of Cu^{2+} ions, M_{Cu} is the molecular weight of copper, and m_{a} is the dosage of the used PPMs.

Adsorption kinetics of Cu^{2+} ions on thioacetate-containing PPMs

Thioacetate-containing PPMs (400 mg) and a DMF solution of Cu^{2+} (200 mL, 4 mM) were added into a 250 mL bottle. The bottle was put into a 30 °C oil bath under stirring by a magnetic bar at a rate of 400 rpm. At a given interval, 3 mL of the DMF solution of Cu^{2+} was taken out by a straw. The accurate concentrations of Cu^{2+} in the different DMF solutions were measured using UV spectroscopy.

Characterizations

SEM images were obtained on a ProX SEM system (Phenom). Firstly, the PPMs were directly spread onto a conductive adhesive. Then, the sample was put in standard sample holders. The measurements were carried out at accelerating voltages of 5, 10, or 15 kV. In order to observe their internal structures, the PPMs were cut by a razor blade. FTIR spectra were obtained on a Vector-22 IR spectrometer (Bruker) at room temperature. In all cases, the FTIR spectra were collected over 32 scans at a resolution of 4 cm^{-1} . UV-Vis spectra were measured on a Varian Cary 300 Bio UV-vis spectrometer. The particle sizes of the PPMs were measured using a particle-size analyzer (Beckman Coulter LS-230), and ethanol was used as the dispersant. Mercury porosimetry (Autopore IV 9510) was used for characterizing the microporous structures.

Results and discussion

Synthetic strategy design

The formation of pores within PPMs mainly consists of two steps: the occurrence of a phase-separation between the porogen and the crosslinked network, and removal of the porogens from the spheric gel. Generally, for PPMs, the porosities and total pore areas are the major parameters which are largely dependent on the volume fraction of porogens and the morphology of phase separation. The formation of a co-continuous phase benefits the full removal of the porogen, giving rise to interconnected channels in the crosslinked microspheres and a large enough pore area. In this work, we optimized the phase-separation conditions *via* adjusting the amount and viscosity of the porogens.

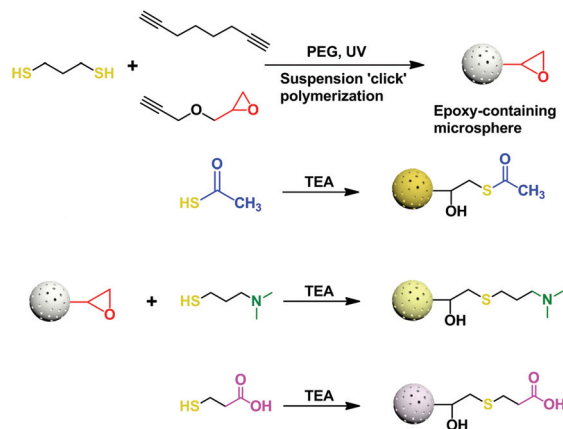
Epoxy compounds have been widely used as adhesives, coatings, composites, and so on, since the epoxy group essentially exhibits high reactivity. We designed and synthesized epoxy-containing PPMs *via* thiol-yne suspension polymerization of glycidyl propargyl ether, 1,7-octadiyne, and 1,3-propanedithiol. The photo-initiated heterogeneous polymerization was carried out at low temperature to suppress undesired thiol-epoxy addition. To expand their applications, the epoxy groups on the surfaces of the PPMs were further functionalized into various useful groups, such as *tert*-amine, thioacetate and carboxyl groups. Given that the modification of epoxy-containing PPMs is a solid-liquid interface reaction, a robust thiol-epoxy click reaction was employed to functionalize them.

Synthesis of PPMs

Compared to microspheres that are synthesized by emulsion polymerization, suspension polymerization affords microspheres with larger diameters, thus enabling facile isolation from the dispersing medium when they are used as catalyst carriers or in ion-adsorption, *etc.* Moreover, suspension polymerization can incorporate soluble porogens into the microspheres to form porous structures, whereas emulsion polymerization cannot achieve porous microspheres *via* this strategy, as it is confined by its specific mechanism.

In suspended droplets, the thiol-yne click polymerization of 1,3-propanedithiol, glycidyl propargyl ether and 1,7-octadiyne with a feeding mole ratio of 4 : 2 : 1 was triggered by thiyl radicals (Scheme 1). At low temperature, the thiol-epoxy addition could be efficiently restrained,³¹ so that epoxy-containing PPMs were facilely and efficiently synthesized by suspension “click” polymerization. According to the feeding ratios of the monomers, the amounts of introduced epoxy groups within the resultant PPMs were calculated to be in the range of 2.33–3.39 mmol g^{-1} . Furthermore, in this work, the calculated yield was 76.3% which was in good agreement with the results of Zhang *et al.*²⁹

In addition, the linear polythioether that is synthesized by thiol-yne polymerization generally possesses a glass transition temperature (T_g) of about $-50 \text{ }^\circ\text{C}$.³¹ Such a low T_g made the linear polythioether take the form of a very viscous, honey-like



Scheme 1 Synthesis and modification of epoxy-functionalized PPMs.

liquid at room temperature. Therefore, to achieve shape-stable PPMs, it was required that the molar ratio of 1,7-octadiyne to glycidyl propargyl ether was kept at a greater value (e.g., 2 : 1). As evidenced by DSC tests (Fig. S4†), the T_g values of the resultant epoxy-containing PPMs were increased from about -47.4 to -23.7 °C, which were slightly higher than those of their linear analogues because of cross-linking. Moreover, the gelation that occurred during polymerization effectively avoided the collapse and refusion of the formed PPMs. Incidentally, we explored the effect of porogen content on the particle size. Different from the results of Zhang and coworkers,²⁹ the addition of PEG had no obvious influence on the resultant PPM size (in the range of 60–90 μm , see Fig. 1).

Influence of PEG on pores

To access PPMs, a porogen was added and utilized as the template of the pores. In general, both high boiling organic solvents and linear polymers were used as porogens,^{32–39} as both are relatively chemically stable and can be easily removed from the system. Furthermore, porogens commonly have poor com-

patibility with the matrix, which means phase-separation can occur smoothly prior to gelation. In this work, PEG ($M_n = 10\,000\text{ g mol}^{-1}$) was selected as the porogen, due to its low cost, narrow molecular weight distribution, and nontoxic and accessible features. Moreover, PEG is insoluble in the resultant polythioether and can be easily removed through simple water washing. Compared to small molecule solvents (such as toluene, *n*-heptane, and so on), the molecular weight and solution viscosity of PEG are relatively high, which is beneficial in the phase separation and formation of large size pores.

The formation of pores in PPMs corresponds to the procedure of phase-separation.^{40–42} As thiol-yne photo-polymerization proceeded, phase separation behavior gradually took place in the droplets, driven by the decrease of the mixing entropy (ΔS_{mix}). Similar to the mechanism of reaction-induced phase separation, the photo-triggered crosslinking reaction reduced the ΔS_{mix} of the reactive system, which resulted in enhancement of the Gibbs free energy of mixing (ΔG_{mix}). Because the porogen was excluded from the crosslinked epoxy group-containing polythioether, the original homogeneous structure gradually turned into the heterogeneous one. After removing the excluded PEG, the inception space occupied by the separated porogen *in situ* was converted into the same volume of pores.

In addition to the effect of the type of porogen, the amount of it had an important effect on the polymerization viscosity which dominated the phase separation behaviors and morphologies of the cross-linked microspheres. As shown in Fig. 2, the morphologies of the obtained PPMs obviously changed upon increasing the amount of PEG. When the amount of porogen was <35 wt% (e.g. 10 and 20 wt%), the volume fraction of PEG was much less than that of the polythioether network. Therefore, PEG was dispersed in the formed spheres as numerous isolated areas. Removing the excluded PEG afforded PPMs with discrete small pores (<3 μm) (Fig. 2a–c).

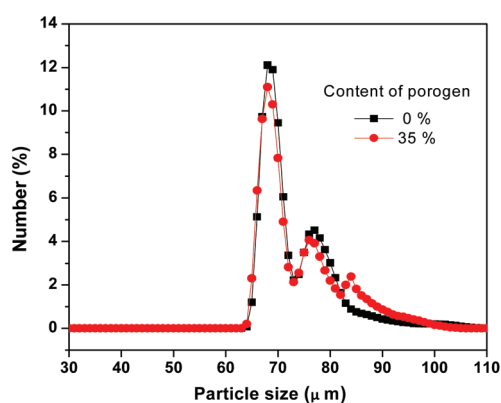


Fig. 1 Particle size distribution of microspheres with 0 and 35% PEG content.

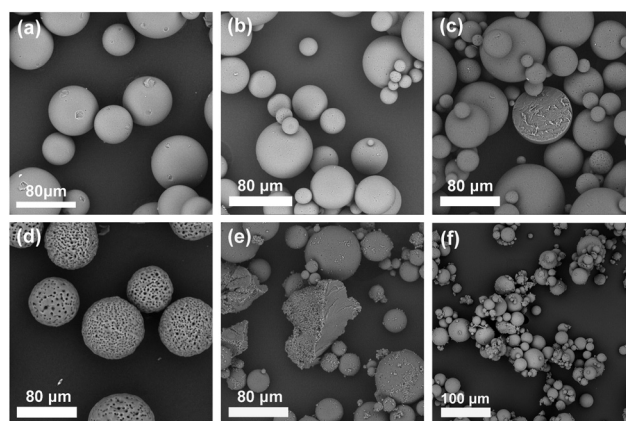


Fig. 2 SEM images of epoxy-containing PPMs made with different PEG mass fractions relative to the monomer mass. (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 35 wt%, (e) 40 wt% and (f) 50 wt%.

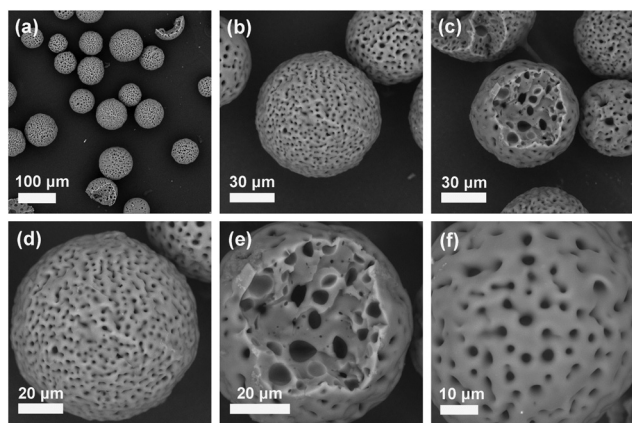


Fig. 3 SEM images of PPMs, made by 35 wt% PEG, with different magnifications.

Upon increasing the amount of PEG to 35 wt%, the volume fraction of PEG increased within the polythioether network, leading to a large scale separated phase (Fig. 2d). Hence, the resultant PPMs exhibited relatively large pore sizes (in the range of 5–10 μm) with a total pore area of $\sim 7.77 \text{ m}^2 \text{ g}^{-1}$ and a porosity of 62.45% (Table S1†). Detailed SEM images are shown in Fig. 3. After removal of PEG, a macroporous structure was formed both on the surface and on the inside of the PPMs as shown in Fig. 3a–c. As evidenced by Fig. 3c and e, some pores were discontinuous, which may influence the expected porosity of the PPMs by decreasing the pore areas and volumes. Additionally, trace amounts of PEG would be trapped in the PPMs, owing to the presence of blind holes.

When the content of PEG was over 35 wt% (e.g. 40 and 50 wt%), lots of small nonporous spheres and irregular polymeric debris were generated, owing to the phase inversion process (Fig. 2e and f). Therefore, in our work, the suitable content was 35 wt%, which gave rise to a suitable viscosity and an appropriate level of phase-separation.

Functionalization of PPMs

The epoxy groups introduced in the polythioether *via* thiol-yn polymerization can be modified to various groups, such as amino, hydroxyl, carbonyl, thiol, thioacetate, *etc.* It was inferred reasonably that the epoxy groups on the surfaces of the PPMs could be functionalized to other available groups. Yet, the modification between the epoxy-functionalized PPMs and the modifier was essentially an interface reaction. Therefore, in order to functionalize every available epoxy group, a robust synthetic strategy (such as the epoxy-thiol click reaction) was needed. FTIR spectra of the PPMs, modified by thioacetic acid, 3-mercaptopropionic acid and 3-amino-propanethiol, are shown in Fig. 4.

The chemical structures of the epoxy-containing PPMs were characterized *via* FTIR spectra (Fig. 4a). Two obvious absorption peaks at 846 and 909 cm^{-1} were attributed to the epoxy groups, implying the presence of epoxy groups in the PPMs. The peaks located at 2120 and 2550 cm^{-1} were ascribed to the

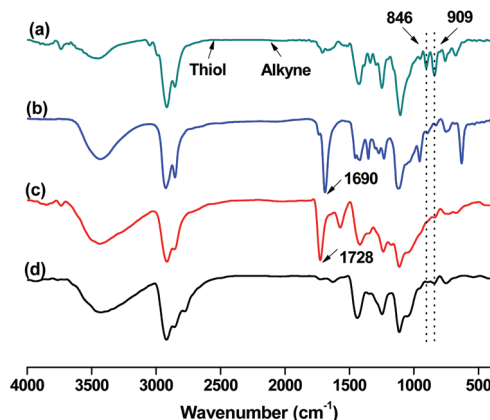


Fig. 4 FTIR spectra of functionalized PPMs: (a) epoxy-containing PPMs, (b) thioacetate-functionalized PPMs, (c) carboxyl-functionalized PPMs, and (d) tertiary amine-functionalized PPMs.

alkyne and thiol groups, respectively. Meanwhile, all of these groups were fully unobservable in Fig. 4a, illustrating that the alkyne and thiol groups were consumed. Based on our previous work, all thiols were employed to carry out thiol-yn click suspension polymerization, since possible thiol-epoxy addition had been effectively suppressed at the same reaction conditions.³¹ Hence, the absorption band at $\sim 3500 \text{ cm}^{-1}$ should be ascribed to the $-\text{OH}$ groups of residual PEG or trace amounts of water in the PPMs. After modification, the intensities of the epoxy absorption peaks obviously became weak, due to the consumed epoxy groups on the surface.

The characteristic peaks at 1690 and 1728 cm^{-1} were ascribed to thioacetate and carboxyl, respectively (Fig. 4b and c). Compared with Fig. 4a, no apparent change took place in Fig. 4d except for the obviously reduced intensities of the epoxy peaks, because the tertiary amine group has no specific characteristic peak in FTIR spectra. All these results indicated that the epoxy groups were successfully functionalized by the epoxy-thiol reaction. Additionally, taking the thioacetate-functionalized PPMs as an example, the morphology of the PPMs before and after modification was similar (Fig. 5). That is, the modification process did not destroy or change their microstructures. Some hollow PPMs are shown in Fig. 5c and d; these specific structures were formed during the previous suspension polymerization process. When the cross-linked polythioether precipitated in droplets, they were trapped near the interface, which was attributed to surface coagulation.⁴³

Application of PPMs for Cu^{2+} adsorption

Modified polythioether PPMs with abundant bonding sites and unique non-degradable properties are promising candidates for adsorption of metal ions. Among numerous metal ions, copper ions have been widely used as catalysts for organic reactions, but need to be isolated from the products because of their undesirable colors and biotoxicities. Here, the copper ion was selected as a prototype to investigate the adsorption behaviors of PPMs.

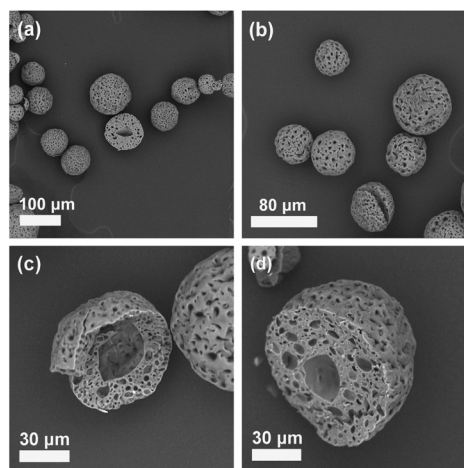


Fig. 5 SEM images of thioacetate-functionalized PPMs.

Modified PPMs with various functional groups (*e.g.* carbonyl, *tert*-amine and thioacetate groups) derived from epoxy groups were employed for copper ion adsorption (Fig. 6). Upon increasing the dosage of PPMs, the number of remaining Cu^{2+} ions in DMF gradually reduced. For the thioacetate- and *tert*-amine-functionalized PPMs, the concentration of Cu^{2+} ions reached the lowest value, as the added amounts were 20 and 30 mg, respectively. In contrast, the amount of carboxyl-functionalized PPM added was 40 mg, and the remaining Cu^{2+} content was still higher than its lowest value. At the same dosage of PPMs, the thioacetate-functionalized PPMs exhibited the largest adsorption capacity, therefore, they were selected to adsorb copper ions and to investigate its adsorption behavior.

Langmuir and Freundlich adsorption isotherm models are commonly used to describe the largest adsorption capacity and to explore adsorption mechanisms.^{44–46} Fig. 7 shows the fitting results of the adsorption data according to the equations below (eqn (3)–(6)).

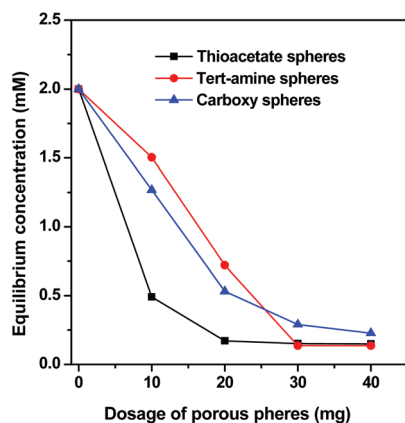


Fig. 6 Adsorption of copper ions on various modified PPMs in DMF solution (10 mL, 2 mM).

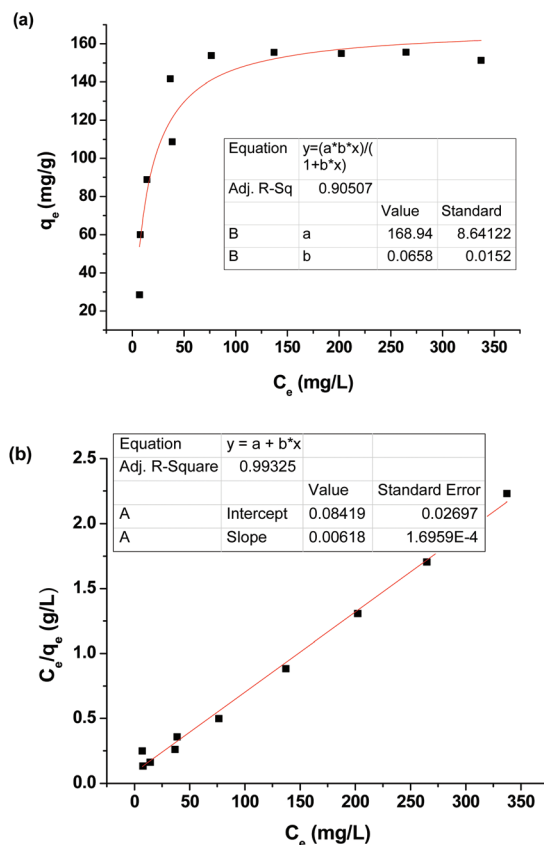


Fig. 7 Langmuir adsorption isotherm models for the adsorption of copper ions on the thioacetate-functionalized PPMs.

$$q_e = bq_m C_e / (1 + bC_e) \quad (3)$$

$$C_e/q_e = (1/bq_m) + (1/q_m)C_e \quad (4)$$

$$q_e = K_F C_e^n \quad (5)$$

$$\log q_e = \log K_F + n \log C_e \quad (6)$$

Here, C_e (mg L^{-1}) is the equilibrium concentration of copper ions in solution, q_e (mg g^{-1}) is the amount of copper ions adsorbed at equilibrium, q_m is the quantity of copper ions adsorbed on the adsorbent at saturation or monolayer capacity (mg g^{-1}), b is a constant relating to the intensity of adsorption, K_F (L g^{-1}) is the Freundlich constant and n is the Freundlich coefficient.

In general, the Langmuir adsorption isotherm model is based on monolayer adsorption, while the Freundlich isotherm model is inclined towards multilayer adsorption. As shown in Fig. 7 and S5,[†] the Langmuir isotherm model has a higher correlation coefficient (0.993) than the Freundlich isotherm model (0.673). Therefore, the Langmuir isotherm model is more suitable to describe the adsorption behavior of Cu^{2+} on the modified PPMs, which implies that the adsorption of Cu^{2+} ions is a monolayer adsorption, and that the largest adsorption capacity is about 158 mg g^{-1} at room temperature.

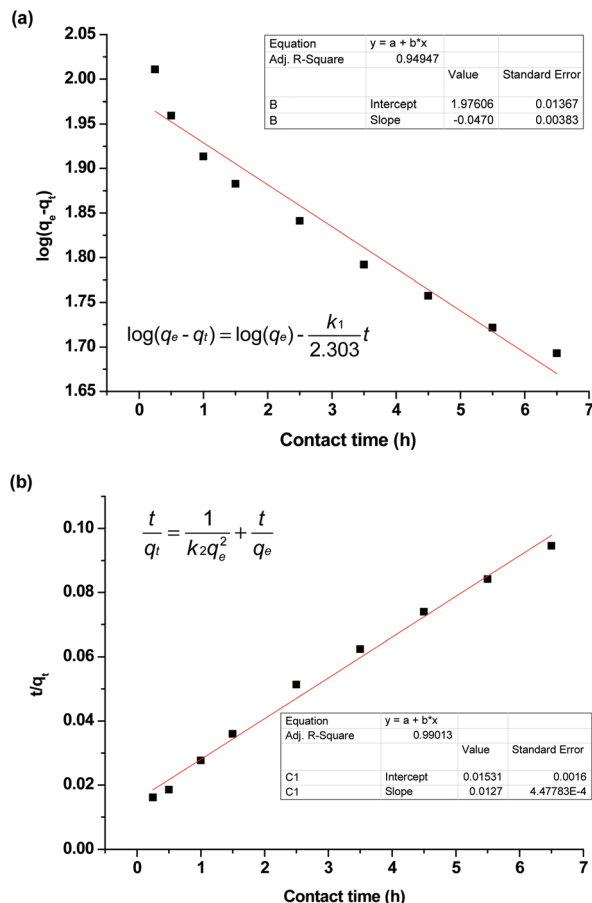


Fig. 8 Kinetic models of Cu^{2+} ion adsorption on thioacetate-functionalized PPMs.

Pseudo-first order (eqn (7)) and pseudo-second order (eqn (8)) models were applied to illustrate the kinetics of Cu^{2+} ions adsorption on the modified PPMs. Fig. 8 shows the fitting results of two different kinetics models. It was found that the pseudo-second order kinetics equation had a higher correlation coefficient ($R = 0.99$) than the pseudo-first order kinetics equation ($R = 0.95$), indicating that chemical adsorption was the rate-limiting step in the aforementioned adsorption process.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Here, t (h) is the contact time, q_t (mg g^{-1}) is the amount of copper ions adsorbed at time t , k_1 is the pseudo-first-order rate constant and k_2 is the pseudo-second-order rate constant.

Conclusions

In summary, we employed a combination of thiol-yne click polymerization and suspension polymerization for the synthesis

of porous epoxy-functionalized polymeric microspheres. Subsequently, the microspheres were used as modified platforms, affording products with various desired functionalities (hydroxyl, amino, and thioacetate groups) *via* robust thiol-epoxy click chemistry. As evidenced by FTIR, the modifications of the epoxy-functionalized PPMs were successful. Their morphologies were characterized by SEM, and the ideal PPMs were achieved with 35 wt% PEG. After modifications, the average sizes of the epoxy-containing PPMs exhibited no obvious change (about 70 μm), while the total pore area was $\sim 7.77 \text{ m}^2 \text{ g}^{-1}$ and the porosity reached 62.45%. Accordingly, the loading capacity of copper ions of the thioacetate-functionalized PPMs reached 158 mg g^{-1} at room temperature. Based on the coordination of sulphur atoms and copper ions, in DMF solution, the PPMs exhibited chemically controlled monolayer adsorption behavior.

Acknowledgements

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