Preparation and Adsorption Performances of Novel Negatively Charged Hybrid Materials

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ABSTRACT: A series of novel negatively charged hybrid materials were prepared via sol–gel process and a subsequent epoxide ring-opening reaction. The coupling reaction was conducted between 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS), which was confirmed by FTIR spectra. TGA, and DrTGA analyses showed that their thermal stabilities were higher and the optimal molar ratio of GPTMS and TEOS was equal to 1 : 1. The ion-exchange capacities (IECs) exhibited that they were related to the amount of anionic groups in the hybrid materials, indicating that the negatively charged properties of the hybrid materials could be artificially controlled via the adjustment of silica in these charged hybrid materials. The adsorption properties for Pb^{2+} and Cu^{2+} ions revealed that these hybrid materials were able to absorb heavy metal ions, suggesting that they have potential applications in the separation and recovery of environmentally hazardous substances. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2179–2184, 2009

Key words: negatively charged hybrid materials; adsorption; sol–gel process; heavy metal ions; GPTMS

INTRODUCTION

Environmental pollution, especially the contamination derives from heavy metal ions in industry, has become a severe problem. To remove these toxic pollutants from waste water, various kinds of methods are explored and some fruitful results are obtained in the past.[1–3] Among them, the removal of metal ions by adsorption is considered as one of the important issues; because the metal ions can be chemically bonded on the organic polymer/inorganic hybrid particles.[4] Some researchers have synthesized inorganic/polymer hybrid particles that contain suitable groups for such purpose.[5–7]

As one type of inorganic–organic hybrid materials, charged hybrid materials including positively or negatively charged ones have attracted escalating interests. This is because they not only combine the advantages of pure organic and inorganic ones but also exhibit excellent performances, such as structural flexibility, thermal, and mechanical stability.[8–10] In particular, this type of charged hybrid materials has the ability to absorb hazardous substance via electrostatic interactions due to their electrical properties. Consequently, they are expected to separate and recover valuable metals from industrial waste chemicals and contaminated water.[11,12]

Currently, various innovative approaches are utilized to fabricate charged hybrid materials.[13–15] Since sol–gel process provides a convenient, versatile, and low temperature-demanding route, it is regarded as one of the most effective methods to prepare the charged hybrids. For preparing such hybrid materials, inorganic ingredients such as silane coupling agents are usually directly used as hybrid precursors for sol–gel reaction.[13,14] With the increasing demand for ion-exchange hybrid membranes to treat environmentally harmful substances, the investigation of charged hybrid materials and the related membranes is therefore significantly important.

Recently, some attempts have been made to develop ion-exchange hybrid materials and membranes in our research group.[16–19] Our continuing interest in such charged hybrids stimulates us to make further efforts. Herein, we will present a novel approach for synthesizing a series of new negatively charged hybrid materials. The formation of anionic groups is mainly carried out between the epoxy ring and sodium bisulfite. Their adsorption behaviors for heavy metal ions will be also investigated. For this study, we chose Pb^{2+} and Cu^{2+} ions as typical adsorbed species due to their dangerous natures to human health. Compared with our previous

TABLE I
Compositions of the Synthesized Negatively Charged Hybrid Materials

Sample	GPTMS (mol)	TEOS (mol)	NaHSO$_3$ (mol)
(a)	1	0	2
(b)	1	0.5	2
(c)	1	1	2
(d)	1	2	2
(e)	1	1	0

studies,[16–19] special attention will be paid to the novel route for the preparation of negatively charged hybrid materials and their potential applications in the separation and recovery of environmentally hazardous substances.

EXPERIMENTAL

Materials

3-Glycidoxypropyltrimethoxysilane (GPTMS, purity: >95.0%) was purchased from Wuhan University Silicone New Material Co. (Wuhan City, Hebei Province, China). Tetraethoxysilane (TEOS, purity: >28.0%) was purchased from Shanghai Chemical Reagent Co. (Shanghai City, China). Sodium bisulfite (NaHSO$_3$) and other reagents were of analytical grade and used as received.

The preparation of negatively charged hybrid materials

The synthesis of negatively charged hybrid materials was conducted by a coupling reaction between GPTMS and TEOS via sol–gel process and a subsequent epoxide ring-opening reaction. The preparation procedure was described briefly as follows:

Firstly, 0.1 mol GPTMS and stoichiometric ratio TEOS were dissolved in proper ethanol, respectively. And then, they were mixed together and stirred vigorously for additional 12 h to form the homogeneous solution through sol–gel process. After the completion of the sol–gel reaction, the product was dried at 60°C, cleaning with deionized water to obtain the xerogel. Finally the above-prepared xerogel was immersed in sodium bisulfite solution to produce the anionic groups in the molecular chain via epoxide ring-opening reaction. The negatively charged hybrid materials can thus be obtained. The chemical composition for these hybrid materials was listed in Table I and the possible reactions were shown in Scheme 1.

FTIR, TGA, and DrTGA characterizations

FTIR spectra of the step products were obtained using a Bruker Vector-22 Fourier transform infrared spectrometer in the region of 4000-400 cm^{-1}.

The degradation process and thermal stability of these negatively charged hybrid materials were investigated via TGA and DrTGA analyses using a Shimadzu TGA-50H thermogravimetry analyzer, under an argon flow 20 mL min^{-1} at a heating rate of 10°C min^{-1} in a temperature range from 30 to 700°C.

Ion exchange capacity

The ion-exchange capacity (IEC) of these hybrid materials were determined by titration method as reported by Zhang et al.[20] About 0.5 g xerogel was immersed in large amount of deionized water for 24 h and purged several times so as to remove the impurity. Then, it was immersed in an aqueous Na$_2$SO$_4$ solution (0.1 mol dm^{-3}) for 24 h to replace H$^+$ by Na$^+$ ions; then back titrated with an aqueous NaOH solution (0.01 mol dm^{-3}). The IEC can thus be calculated based on the amount of H$^+$ ions exchanged by Na$^+$ ions in the sulfonic acid groups.

Adsorption behavior for heavy metal ions

The adsorption for heavy metal ions was determined using conductometric analysis. About 0.5 g of the above-prepared charged hybrid materials was immersed in 50 mL (0.05 mol dm^{-3}) lead nitrate, Pb(NO$_3$)$_2$ or copper chloride, CuCl$_2$ for 24 h, respectively; and then the sample was took out and purged by deionized water. In the collected remained solution, the conductivity was measured. The adsorption performance of the prepared charged hybrid materials can be obtained based on the standard curve-fitting of different concentrations of Pb(NO$_3$)$_2$ or CuCl$_2$ solution.
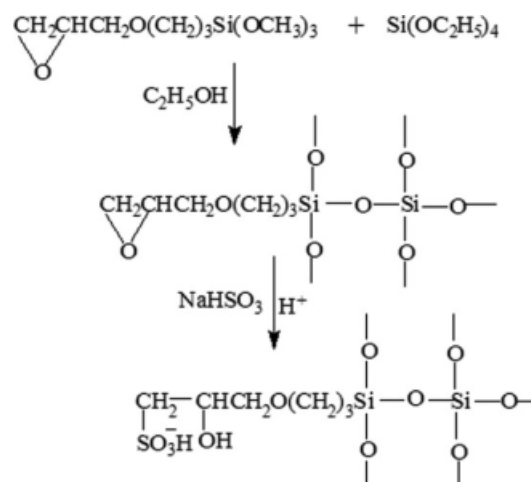
Scheme 1 The preparing route of negatively charged hybrid materials, Step 1 was the sol–gel process and Step 2 was the epoxide ring-opening reaction.
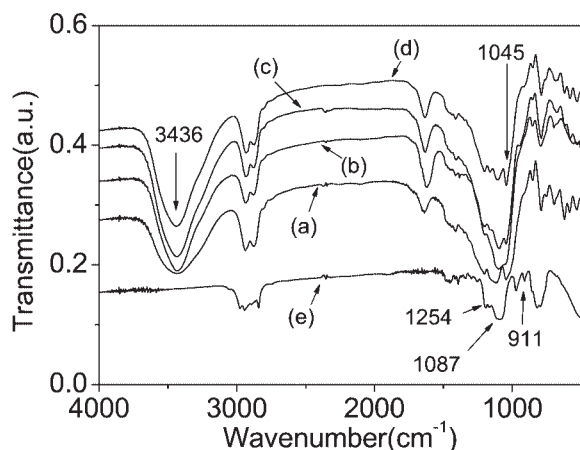
Figure 1 The FTIR spectra of samples (a)–(e).

RESULTS AND DISCUSSION

FTIR spectra

To confirm the reactions described in Scheme 1, FTIR spectra of the step products were carried out and shown in Figure 1(a–d). For the convenience of comparison, the spectrum of the product containing epoxide groups was also presented in the same plot as Figure 1(e).

As shown in Figure 1(a–d), the broad strong peak in the range of 2500–3000 cm^{-1} can be ascribed to the stretching vibration of CH_3— and —CH_2— groups of GPTMS.[16,18] The strong absorption peak at around 1087 cm^{-1} is the overlapping of asymmetric stretching vibration of Si—O—Si and Si—O—C bands from the trimethoxysilane groups of GPTMS.[21–23] In Figure 1(e), it can be noted that the peak at near 1254 cm^{-1} is the symmetric axial in-phase deformation of the epoxide ring (ring breathing). Meanwhile, the asymmetric deformation is observed at about 909 and 821 cm^{-1}. By comparison with Figure 1(e), it is interesting to find in Figure 1(a–d) that a new strong peak located at 3436 cm^{-1} appeared when the sodium bisulfite was added; such new peak can be ascribed to the O—H stretching due to the formation of —SO_3H. The stretching vibration of S=O connected with —SO_3H group can be observed in the range of 1100–1200 cm^{-1}, which is overlapped with the stretching vibration of Si—O—Si and Si—O—C bands.[24,25] Moreover, by comparison with that in Figure 1(e), it can also be seen that the intensity of peak at 1116 cm^{-1} in Figure 1(c) increases a little. These changes in the adsorption peak suggest that the epoxide ring-opening reaction has occurred, corroborating the step reactions described in Scheme 1.

TGA and DrTGA analyses

To investigate the degradation process and thermal stability of the hybrid materials, TGA and DrTGA analyses were conducted.
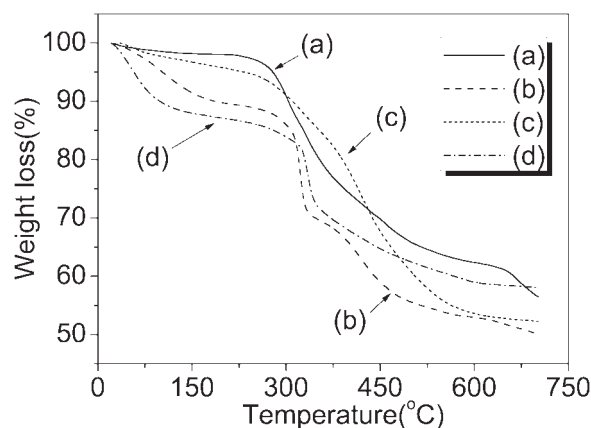

Figure 2 The TGA curves of samples (a)–(d).

As shown in Figure 2, it can be noted that for different charged hybrid materials, the degradation process is different. For samples (a) and (b), three main degradation steps can be clearly observed; meanwhile for samples (c) and (d), only two degradation steps are found. Corresponding to these degradation processes, several markedly endothermic peaks can be discovered in DrTGA curves as presented in Figure 3, hereinafter.

For samples (a) and (b), a noticeable weight loss below 215°C is primarily caused by the decomposition of organic —CH_2 bonds in the polymer chains in that longer —CH_2 spacers are always disadvantageous to heat stability of the hybrids. A gradually decline of weight loss around 330°C can be ascribed to the decomposition of organic ingredients. Whereas the slight weight loss beyond 400°C is assigned to the breaking of —C—Si— and —Si—O— bonds and the further degradation of organic residues into the crystallized silica. With regard to samples (c) and (d), the weight loss below 230°C is primarily caused by the decomposition of organic —CH_2 bonds in the polymer chains. Meanwhile, the weight loss beyond 330°C can be ascribed to the
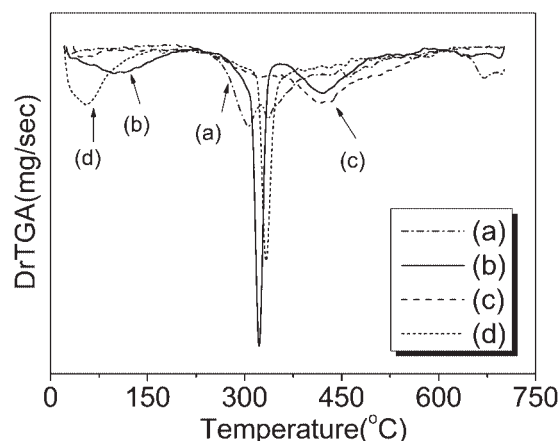

Figure 3 The DrTGA curves of samples (a)–(d).

further degradation of organic groups and the production of crystallized silica.

The theoretical explanation to such trends can be attributed to an increase of inorganic components in the produced samples (a) to (d) and the consolidation of silica network.[26] Their thermal stabilities are improved due to the increase of inorganic ingredients; the weight loss of the produced charged hybrid materials is thus reduced accordingly.

Furthermore, considering the TGA curves for samples (b), (c), and (d) in Figure 2, it is interesting to find that the weight loss exhibited different change trends, suggesting the existence of lower incompatibility between the inorganic and organic ingredients in the produced hybrid materials. By comparing the three TGA curves, it can be noted that sample (c), which has the molar ratio of GPTMS and TEOS = 1 : 1, exhibits the highest thermal stability among them, suggesting that this sample demonstrate a relatively higher compatibility between the inorganic and organic ingredients. However, when the molar ratio of GPTMS and TEOS is larger or below the molar ratio of 1 : 1, the amount of weight loss peak increases (as exhibited in Fig. 3, hereinafter). This result conflicts with the fact that the thermal stability of the hybrid material increases with an increase in the inorganic silica content.[25] The reason might be related to the incompletion of inorganic and organic network in the hybrid materials,[21] leading to the relatively lower compatibility between the inorganic and organic ingredients.

Figure 3 presents the DrTGA curves of the investigated samples. It can be noted that for different samples, the DrTGA curves indicate different amount of endothermic peaks. For samples (a) and (d), two endothermic peaks around 306 and 335°C as well as 55 and 330°C are observed, respectively. For sample (b), three endothermic peaks near 103, 322, and 420°C are found. However, for sample (c), only one endothermic peak around 415°C is discovered, demonstrating the highest stability among these samples. As explained above, the first endothermic peak is mainly related to the decomposition of organic —CH$_2$ bonds in the polymer chains. The second one is attributed to the decomposition of organic groups and the further polymerization of silanol groups, whereas the third one is primarily ascribed to the fabrication of silica. In addition, by comparison the intensity of the main endothermic peaks, it can be found that samples (b) and (d) have stronger main endothermic peak than the others; meanwhile, these degradation temperatures have the similar position at about 325°C as that of observed in sample (a).

To explain the above phenomena, special attention will be paid to the unequal molar ratio of GPTMS and TEOS in the prepared hybrid materials, which will affect the formation of hybrid network struc-

ture.[21,26] As listed in Table I, for samples (a)–(d), the inorganic ingredients of TEOS increases proportionally; their main degradation temperatures also increase slightly. An exception is the sample (c), which reveals the highest thermal degradation temperature among them. Both the completion of hybrid network and the increased connectivity of organic network might be responsible for such tendency.[21,26] It is well accepted that the incorporation of inorganic composition will increase the thermal stability of hybrid materials. Meanwhile, the introduction of TEOS can also conduce to the formation of silica network and the promotion of cross-linking degree of Si—O—Si bond, leading to the creation of intimate structure of inorganic and organic hybrid network.[26,27] As a result, the intensity of the main endothermic peak increases distinctly as revealed in Figure 3.

Moreover, from the TGA and DrTGA curves of the probed hybrid materials, it can be deduced that proper incorporation of inorganic composition will favor the formation of hybrid network and the increase of thermal stability of hybrid materials. However, excessive or deficient amount of TEOS will not be beneficial to an increase in the hybrid silica network, resulting in negligible contribution to the increase of their thermal stabilities. Furthermore, it can be noted that the production of sulfonic acid group in the hybrid materials only increases their hydrophilicity, leading to the first endothermic peak shift to lower temperature (as illustrated in Fig. 3). Meanwhile, no noticeable evidence can be spotted that the creation of sulfonic acid group has damaged the thermal stability of the charged hybrid materials, suggesting that the implementation of charge on hybrid materials do not give rise to disadvantageous impact on their performances. This finding means that the characteristics of hybrid materials can be regulated by the accomplishment of charge on organic functional groups. In addition, based on the data of TGA and DrTGA, it can also be deduced that sample (c) has the optimal molar ratio of GPTMS and TEOS as well as relatively higher thermal stability.

Ion-exchange capacity

Ion-exchange capacity (IEC) is able to characterize the ion-exchange ability of charged hybrid materials. To examine the electrical characteristics of these charged ones, the measurement of IEC was performed and the related results were shown in Table II.

It can be seen in Table II that the IEC values decrease with the increasing content of TEOS, suggesting the decreasing trends in the ion-exchange ability of these hybrid materials. To interpret such

TABLE II
Ion-Exchange Capacity (IEC) of the Negatively
Charged Hybrid Materials

Sample	(a)	(b)	(c)	(d)
IEC(m mol g^{-1})	1.643	1.054	0.528	0.496

trend, special attention can be given to the change of sulfonic acid group produced in the hybrid materials. As exhibited in Scheme 1, GPTMS has the epoxy ring and TEOS doesn't contain any charged group. The coupling reaction between GPTMS and TEOS is mainly carried out via Si—O—Si bond during the sol–gel reaction; therefore, the anionic group (sulfonic acid group) primarily comes from GPTMS by the epoxide ring-opening reaction. The increasing content of TEOS is thus unable to increase the amount of anionic group. As a result, the IEC is not improved further. The increase of TEOS (inorganic composition) in the hybrid materials mainly favors an increase in their thermal stabilities and the production of hybrid network (cf. Figs. 2 and 3). Such result has been approved by other investigations.[26,27] This finding reveals that the IEC of hybrid materials can be artificially adjusted via the incorporation of inorganic ingredients.

Adsorption behavior for heavy metal ions

To have an insight into the adsorption behavior of the negatively charged hybrid materials for heavy metal ions, the adsorption experiments were conducted via measure the conductivity of the remained salt solution; which was adsorbed firstly by the prepared charged hybrid materials. In this case, Pb^{2+} and Cu^{2+} ions were selected as typical adsorbed species. The testing results were summarized in Table III. For comparison, the conductivity of original salt solution, which was not absorbed by those hybrid materials, was also determined and shown in Figure 4.
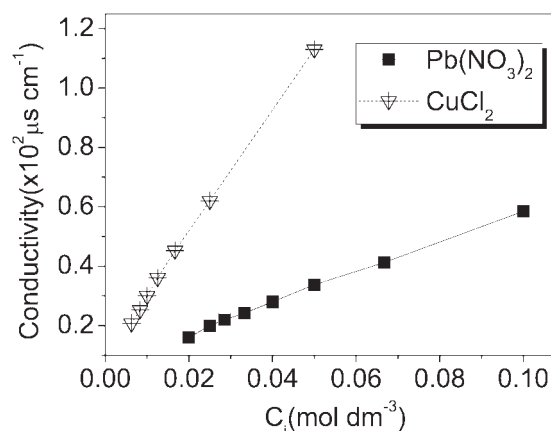
Figure 4 presents the dependency of salt concentration (unabsorbed by the hybrid materials) of both

TABLE III
The Conductivity of the Remained Solution

Sample	(a)	(b)	(c)	(d)
$K_{Pb}{}^{2+}$ (µs cm^{-1})[a]	44.3	39.0	31.6	31.2
$K_{Cu}{}^{2+}$ ($\times 10^2$µs cm^{-1})[b]	1.425	1.19	1.10	1.125

[a] Denotes the conductivity of the remained lead nitrate solution after it was adsorbed by the explored negatively charged hybrid materials.
[b] Is the conductivity of the remained copper chloride solution after it was adsorbed by the explored negatively charged hybrid materials. The original salt concentration (unabsorbed by the hybrid materials) was 0.05 mol dm^{-3}.

Figure 4 The dependency of original salt concentration (unabsorbed by the negatively charged hybrid materials) on its conductivity; the regression ratio $R = 0.999$.

lead nitrate and copper chloride on their conductivities. It can be found that at lower concentration, the relationship between the conductivity and salt solution concentration is linear (regression ratio $R = 0.999$). Therefore, the adsorption behavior of the negatively charged hybrid materials for Pb^{2+} and Cu^{2+} ions can be investigated via conductometric analysis.

As shown in Table III, it can be seen that when the negatively charged hybrid materials were dipped into the salt solution for stipulated time 24 h, the conductivity of remained solution decreases with an increase content of TEOS; suggesting that the amount of free ions in the remained solution decreases after the adsorption has occurred. This result reveals that the charged hybrid materials are able to adsorb heavy metal ions.

To explain such trend, special attention will be paid to the static interaction between the charged hybrid materials and the heavy metal ions. Because of this type of charged hybrid materials containing sulfonic acid group, it can adsorb counter-ion. Meanwhile, both Pb^{2+} and Cu^{2+} ions all process positive charge, they can be chemically adsorbed by sulfonic acid group via static interaction. As a result, the conductivity of the remained solution decreases when the free ions are adsorbed by the charged hybrid materials.

Based on the above findings, it can be concluded that that these hybrid materials are able to absorb Pb^{2+} and Cu^{2+} ions, demonstrating that they can be potentially applied to separate and recover environmentally hazardous heavy metal ions.

CONCLUSIONS

A series of novel negatively charged hybrid materials containing sulfonic acid group were synthesized via sol–gel process and epoxide ring-opening reaction. FTIR spectra proved the occurrence of the

coupling reaction between 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS). TGA and DrTGA analyses displayed that their thermal stabilities could arrive at near 300°C and the optimal molar ratio of GPTMS and TEOS is 1 : 1. The measurements of ion-exchange capacities (IECs) revealed that these IECs were related to the content of ionic groups in the charged hybrid materials produced. The adsorption behavior for Pb^{2+} and Cu^{2+} ions demonstrated that these hybrid materials can be used to absorb and separate heavy metal ions. Consequently, they are expected to prepare ion-exchange hybrid membrane for the separation and recovery of environmentally hazardous substances, demonstrating their potential applications in environmental protection aspects. Further studies on the adsorption kinetics of these hybrid materials are under way.

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