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Preparation of FeBTC/silica aerogels by a co-sol-gel process for organic pollutant adsorption

Hongli Liu\textsuperscript{1,2} \textsuperscript{1}, Chengfeng Jiang\textsuperscript{1}, Hongyan Li\textsuperscript{3} and Zhong Chen\textsuperscript{2}

\textsuperscript{1} School of Materials Science and Engineering, Tianjin Chengjian University, Tianjin 300384, People’s Republic of China
\textsuperscript{2} School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
\textsuperscript{3} Author to whom any correspondence should be addressed.

E-mail: liuhongli@tcu.edu.cn, jcf85200@163.com, lihongyan@tcu.edu.cn and aszchen@ntu.edu.sg

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Abstract

In this paper, a series of FeBTC/silica hybrid aerogels (FeBTC-SA) have been successfully prepared by a facile method. Specifically, Fe (III) metal salts were added to a silica (SiO\textsubscript{2}) sol containing trimesic acid (H\textsubscript{3}BTC) at room temperature for co-sol gelation and then CO\textsubscript{2} supercritical drying was introduced to obtain FeBTC/SiO\textsubscript{2} hybrid aerogels. The composites have been completely characterized by FT-IR, SEM, elemental analysis and HR-TEM analysis techniques. Meanwhile, adsorption properties of hybrid aerogels have also been systematically investigated through a typical organic dye methyl blue (MB). The results show that all the as-synthesized FeBTC-SA composites have a three-dimensional porous network structure. The TEM analysis further shows that the composite is a semi-crystal, while the FeBTC particles are crystalline of MIL-100(Fe). Furthermore, with the increase of FeBTC content, MB adsorption performance of composites is increasingly improved. By the elaborately manipulating the π–π interactions between MB and the benzene rings of FeBTC/SiO\textsubscript{2} hybrid aerogels, the static adsorption efficiency of FeBTC-SA (3:50) (molar ratio of Fe:Si = 3:50) can be quickly reached at 99.1%, which is increased by 11% compared to the pure SiO\textsubscript{2} aerogels. Therefore, It provides a new avenue for the important applications of hybrid aerogels as highly efficient adsorbents in water purification.

1. Introduction

Recently, water pollution disposal has become one of the most urgent global problems [1–3]. Organic dyes, as main contaminants of water pollution, have seriously done harm to human health, water environment and the ecological environment due to the continuous waste emission from industrial production [4–7]. The removal methods of dyes from aqueous solution typically include chemical precipitation [8], evaporation [9], solvent extraction [10], ion exchange [11], electrochemical treatment [12], membrane filtration and adsorbent adsorption technologies [13–15]. Thereinto, adsorbent adsorption has attracted extensive research interest due to its incomparable advantages, e.g., easy to operate and highly effective in the removal of water pollutants even at low concentrations. In the presence of adsorbents, adsorption process could take place, which mainly involves separation of a substance from one phase and then accumulation at another surface [16]. As a promising adsorbent candidate, SiO\textsubscript{2} aerogels, characteristic of low density, high porosity and high specific surface area [17], have brought about the broad application prospect in the field of environmental purification owing to their high adsorption efficiency and high adsorption stability [18, 19].

Given the high adsorbability of SiO\textsubscript{2} aerogels, a wide array of pure SiO\textsubscript{2} and SiO\textsubscript{2}-based composite aerogels have been successfully developed thus far [20, 21]. It is well known that the adsorption process is basically divided into physical adsorption and chemical adsorption [22]. Therefore, these two aspects should be comprehensively taken into consideration to improve the adsorption performance of SiO\textsubscript{2}-based aerogels. On the one hand, the higher the porosity of the SiO\textsubscript{2}-based aerogels, the better the physical adsorption performance. Supercritical drying process has been applied in the preparation of SiO\textsubscript{2}-based aerogels so as to obtain a porous
structure. For example, early in 2002, it has been reported that FeCo–SiO2 nanocomposite aerogels could be prepared by high temperature supercritical drying of alcogels and different supercritical drying process could give rise to different porous structures [23]. It is noteworthy that since silica aerogels have a certain strength, they are suitable as the skeleton materials of composite aerogels [24–26]. On the other hand, TiO2–SiO2 composite aerogels with higher adsorption efficiency of rhodamine B have been successfully prepared using ambient pressure drying by sol-gel and surface modification with HMDSO/TMCS [27] in the view of chemical adsorption. Recently, higher adsorption capacity of 17.10 mg g\(^{-1}\) and better reusability have been demonstrated in the Ag2O–SiO2–50 aerogel, whose adsorption mechanism is mainly attributed to the π-complexation between thiophene and adsorbents [28].

Moreover, metal–organic frameworks (MOFs) as a new class of porous materials have been extensively studied. They are commonly synthesized via a metal coordination approach between organic linkers and metal nodes [29, 30]. Similar to SiO2-based aerogels, MOFs can also be good adsorbents because of their high specific surface area and diverse functionality, of which can be made full use to achieve stronger or more selective binding affinity to target adsorbates [31]. Due to Fe's low toxicity and high biocompatibility, Fe-based MOFs are particularly desirable in environmental applications [32, 33]. In 2010 hung et al firstly reported the use of MOFs in dye adsorption. They systematically studied the methyl orange (MO) adsorption on chromium MIL-101 and MIL-53. It has been demonstrated that the adsorption capacity and adsorption kinetic constant of MIL-101 were apparently greater than those of chromium MIL-53 due to the larger pore size and surface area of MIL-101 [34]. Wang et al prepared a magnetic porous carbon composite with high surface area using a Fe-based metal–organic gel as a template. The adsorption capacity and adsorption kinetics of the composites for MO were 182.82 mg g\(^{-1}\), 8.13 \times 10^{-3} g mg\(^{-1}\) min\(^{-1}\), respectively [35]. Therefore, it is attractive to develop a SiO2 composite aerogel combined with Fe-based MOFs by a facile method.

In fact, hybrid materials related MOFs with SiO2-based aerogels have received extensive attention, such as HKUST-1@silica aerogel composites and silica aerogel–ZIF-8 hybrid materials [36, 37]. So far, various synthesis approaches of MOF@silica-based aerogels have been proposed. For instance, Sachse et al reported that the as-prepared silica aerogel monolith was immersed in CuBTC precursors and then subjected to hydrothermal treatment to acquire composites [38]. Tanaka and Yan developed hybrid aerogels through a sol–gel process in which the as-synthesized MOFs or commercially produced MOFs were directly incorporated in TEOS precursors in advance [39, 40]. However, these approaches all present a same shortcoming, namely, the fabrication process of MOF@Silica composite aerogels is quite time-consuming. It is worthy to emphasize that sol-gel including a co-sol-gel process is indeed a widely applied method for preparation of homogeneous materials [41]. In the co-sol-gel process, several precursors are used to form a homogenous mixture.

In this study, Fe (III) metal salts were added to a SiO2 sol containing H3BTC at room temperature for co-sol gelation to prepare FeBTC/SiO2 composite aerogels. Subsequently, the morphologies of the composite aerogels were systematically investigated by finely manipulating the Fe/Si molar ratios. The hybrid aerogels can retain porous structures without deterioration of their individual properties. Finally, these as-prepared composite aerogels were exploited to act as dye adsorbents for MB adsorption, which would play an important role in water pollution disposal.

2. Experimental section

2.1. Reagents

Tetraethyl orthosilicate (TEOS) was obtained from Tianjin jindongtianzheng Precision Chemical Regent Factory. Trimesic acid (H3BTC) and ferric nitrate nonahydrate (Fe(NO3)3·9H2O) were obtained from Shanghai Macklin Biochemical Co. Ltd Anhydrous ethanol and aqueous ammonia (NH3·H2O, 25%) were provided by Tianjin Baiaotai Chemical Technology Co. Ltd The solution of ammonia used in this study was prepared with ammonia and anhydrous ethanol with a 1:2 ratio.

2.2. Method

FeBTC-SA composites were synthesized by a facile co-sol-gel method. As shown in figure 1, (H3BTC 0.105 g 0.5 mmol) was dissolved in 5 ml ethanol (denoted as solution A) and [Fe(NO3)3·9H2O 0.303 g 0.75 mmol] was dissolved in another 5 ml ethanol (denoted as solution B), which are all sonicated for 15 min in an ultrasonic bath. The solution A and 5.2 g tetraethyl orthosilicate (TEOS) solution (mass ratio of TEOS/EtOH = 0.65) were mixed with magnetic stirring for 30 min at room temperature (denoted as solution A1), then solution B was slowly poured into solution A1 under continuous stirring at room temperature. Following this step, the as-prepared solution of ammonium was appropriately added into the mixture until the solution became viscous, followed by the transfer to a cylindrical plastic mold for gelation about 2–3 h. Subsequently, the wet gels were immersed in ethanol for further aging at room temperature for 2 days, which was performed to remove residual
impurities or water remaining in the gel pores. The ethanol solution was refreshed every 12 h. These wet gels were subjected to supercritical CO2 drying to obtain hybrid aerogels named FeBTC-SA(x:y), in which the molar ratios of Fe and Si are denoted as x and y, respectively. It is noteworthy that with the increase of FeBTC content, the gel monolith couldn’t be formed under the same experimental conditions. Therefore, we just study the morphologies and performances of pure SiO2 aerogel, FeBTC-SA(3:400), FeBTC-SA(3:100), and FeBTC-SA(3:50).

2.3. Characterization
The molecular structure of the sample was characterized using Fourier Transform Infrared (FT-IR) spectra recorded on a Nicolet 380 FTIR Spectrometer with KBr pellets in the wave number range of 4000–400 cm$^{-1}$. The morphologies of the samples were obtained using Scanning Electron microscope (SEM, JSM-7800F) equipped with an EDS detector and a Transmission Electron microscope (TEM, JEM-2100F) operated at an accelerating voltage of 200 kV.

2.4. Dye adsorption experiment
Typically, the cationic dye methyl blue (MB) acts as a guest molecule of a adsorption study, while the as-prepared FeBTC-SA composites act as adsorbents. The adsorption experiment was systematically investigated at room temperature and pH $\approx 7$. The aqueous stock solutions of MB with initial concentrations of 10 mg l$^{-1}$ were prepared by dissolving MB in deionized water. These stock solutions were stored in dark box and kept in dark place before use to keep them from decoloration by direct sunlight.

Adsorption abilities of the FeBTC-SA composites toward MB were characterized by UV–vis spectroscopy (TU-1900) at the maximum wavelength of 664 nm. Typically, 10 mg FeBTC-SA composites were added into 15 ml MB solution at the concentration of 10 mg l$^{-1}$ and the mixture solutions were kept static during the adsorption experiments. At regular time intervals, the suspension was extracted to determine the MB concentration. The adsorption capacity of MB at equilibrium ($Q_e$) as a factor for evaluation of dye adsorption properties. The removal efficiency of MB was calculated according to the following Eq (Bhaumik et al 2013) [42]:

$$R(\%) = \frac{(C_0 - C_1)}{C_0} = \frac{(A_0 - A_t)}{A_0}$$

where $C_0$ and $C_1$ represent the initial and final MB concentration (mg l$^{-1}$), respectively, while $A_0$ and $A_t$ represent the initial and final absorbance of MB aqueous solution, respectively.

3. Results and discussion

3.1. Structure and morphology of as-prepared FeBTC-SA composites
Figure 2 shows the FT-IR spectra of pure SiO2 aerogel, pure FeBTC and FeBTC-SA composites with different molar ratios of Fe/Si prepared by a co-sol-gel method. Specifically, figure 2(a) exhibits the typical characteristic peaks of the pure amorphous SiO2. For example, a broad peak at 3455 cm$^{-1}$ is apparently attributed to the asymmetric stretching vibration of –OH; bands at 1080, 800, 470 cm$^{-1}$ belong to asymmetric and symmetric stretching vibration, bending vibration of Si–O–Si bonds, respectively; In addition, the stretching vibration band of Si–OH could be found at 965 cm$^{-1}$. For pure FeBTC, bands at 1626/1577 cm$^{-1}$ and 1447/1337 cm$^{-1}$ correspond to –C=O asymmetric and symmetric stretching vibration of organic ligands, while the vibration of –
COOH is around at 1710 cm$^{-1}$ (figure 2(e)). In figures 2(b)–(d), not only peaks of SiO$_2$ but also FeBTC could be observed apparently, suggesting the successful preparation of FeBTC-SA composites. Furthermore, with the increase of FeBTC content, e.g., the molar ratios of Fe/Si ranging from 3:400 to 3:50, the FTIR characteristic peaks of FeBTC become more obvious.

Additionally, the influence of FeBTC content on the morphologies of FeBTC-SA composites is systematically investigated (figure 3). As displayed in figure 3, either pure SiO$_2$ aerogels or FeBTC-SA composites all possess a porous homogeneous structure. The pure SiO$_2$ aerogels are inclined to be typical sponge-like porous structure (figure 3(a)) [20], while the skeletal framework of FeBTC-SA composites reveals more slender chain linked networks (figures 3(b)–(e)). As a result, pure SiO$_2$ aerogels look more compact than FeBTC-SA composites. Moreover, the morphologies of FeBTC-SA composites obviously differ with the FeBTC contents. FeBTC-SA (3:400) and FeBTC-SA (3:100) composites present relatively obvious chain liked structure due to the fine FeBTC particles induced to easily form dual-phase networks (figures 3(b), (c)). However, FeBTC-SA (3:50) composites show more agglomeration of FeBTC nanoparticles so that some pores in network structures are blocked (figure 3(d)). This leads to the looser structure in FeBTC-SA (3:50) composites in contrast to FeBTC-SA (3:400) and FeBTC-SA (3:100) composites. It can be seen that adding different amount of FeBTC would directly alter the morphologies of the composites. Subsequently, the chemical composition of a representative hybrid aerogel has been studied by EDS (figure 3(e)), which provides the key element information on dual phases of hybrid aerogels. There into Fe element colored purple and Si element colored blue distribute homogeneously in the element mapping, demonstrating a homogeneous distribution of FeBTC in the entire SiO$_2$ aerogel monolith at a molecular level.

To further illustrate the structure of the materials. We then applied nitrogen adsorption–desorption isotherms to assess the porosity parameter of the prepared — samples obtained by super critical CO$_2$ dry which can be important for organic dye adsorption applications. N$_2$ adsorption/desorption isotherms (figure 4(a) and the corresponding pore size distribution (figure 4(b)) of SiO$_2$ aerogel and composite aerogels at 77 K is shown in figure 4. The textual properties of the typical aerogels are shown in table 1. In N$_2$ adsorption–desorption isotherms, all samples exhibit type-IV behavior with H$_4$ hysteresis loop according to the IUPAC classification, indicating their mesoporous nature. The BET surface area of SiO$_2$ aerogel, FeBTC-SA (3:400), FeBTC-SA (3:100) and FeBTC-SA (3:50) are 871, 784, 728, 640 m$^2$ g$^{-1}$ respectively. The BET surface area and microporosity of hybrid aerogels are reduced and increased respectively with the increasing amount of FeBTC, compared to pure silica aerogel. The reducing specific area of composite aerogels might be due to some fraction of micropores of the MOF occupy mesopores of silica aerogel. Further, we can see in table 1, at low FeBTC content, the total pore volume and micro pore volume of FeBTC-SA (3:400) are slightly higher than SiO$_2$ aerogel, might due to the content is less and promotes the formation of micropores; at high FeBTC content, the pore volume gradually increased, but the total pore volume gradually decreased, indicating that as the content of FeBTC content increases, it will block the pore structure of a part of silica to form a larger pore while promoting the formation of micropores of composites. In addition, the micropore surface area are directly proportional to the MOF weight percent in the composite indicating the availability of MOF’s micropore in the silica network.
Figure 3 SEM images of pure SiO$_2$ aerogel (a), hybrid aerogels of FeBTC-SA (3:400) (b), FeBTC-SA (3:100) (c), FeBTC-SA (3:50) (d), and EDS mapping of FeBTC-SA (3:50) composite (e).

Figure 4. N$_2$ adsorption-desorption isotherms (a) and pore size distribution curves (b) of SiO$_2$ aerogel, FeBTC-SA(3:400), FeBTC-SA (3:100), FeBTC-SA(3:50).
Therefore, the content of FeBTC content is vital influence factor for the structure of hybrid aerogels. FeBTC-SA (3:50) possesses wide pore-size distribution (figure 4(b)) which is favorable for adsorbing MB dyes. TEM image further confirms that FeBTC-SA composites possess uniform well-distributed porous microstructures and the agglomerated FeBTC nanoparticles are irregularly interconnected in hybrid aerogels (figure 5(a)). What’s more, the high-resolution magnification TEM image in figure 4(b) is an enlarged view of the red circle part in figure 4(a). It can be seen that there is a distinct interface between the amorphous SiO2 and the FeBTC crystal. Meanwhile, an interplanar crystal spacing with 0.28 nm is acquired, which confirm the formation of MIL-100 (Fe) nanocrystals and the successful incorporation of them into SiO2.

3.2. Dye adsorption capacities of as-obtained FeBTC-SA composites

Adsorption properties of the as-prepared SiO2-based aerogels as adsorbents have been systematically investigated in MB solutions (15 ml, 10 mg l−1) as a model organic dye polluting water. Figures 6(a)–(d) display the UV–vis spectra of MB solutions collected in 72 h during the adsorption process corresponding to FeBTC-SA (3:400), FeBTC-SA (3:100), FeBTC-SA (3:50) composites and pure SiO2 aerogel, respectively. The insets in figures 5(a)–(d) are the representative photographs of MB solutions before (left) and after (right) adsorption with the aerogels. After adsorption with FeBTC-SA (3:100) and FeBTC-SA (3:50) composites for 3 days, the supernatants are apparently close to colorless compared with pure SiO2 aerogel and FeBTC-SA (3:400) composites. As exhibited in figure 5(e), adsorption abilities of SiO2-based aerogels under investigation in removal of MB within 120 min are found in the following order: FeBTC-SA (3:50) > FeBTC-SA (3:100) > FeBTC-SA (3:400) ≈ pure SiO2 aerogel. Finally, static adsorption efficiencies of as-prepared aerogels to MB dye after 3 days are shown in figure 6(f). Specifically, with the increase of the content of FeBTC, the adsorption efficiencies of the hybrid aerogels are gradually increased. Pure SiO2 aerogel is the lowest (89.3%), while the FeBTC-SA (3:50) composites exhibit the highest (99.1%) and the Qe is 14.9 mg g−1. These results might be attributed to two aspects: one is the pore structures of aerogels, the other is the FeBTC content in aerogels. When increasing the FeBTC contents, the FeBTC particles in SiO2 matrix provide more active reaction sites to guide the diffusion and loading of MB molecule. Therefore, these findings indicate that the removal of MB is mainly dominated by the FeBTC content of the composite and the flexible structure of FeBTC, which can achieve high adsorption capacities of the hybrid aerogels. The adsorption mechanism may be explained by the π–π interaction between the benzene rings of FeBTC and MB [7]. In addition, it should be pointed out that the hybrid aerogels exhibit the improved MB removal efficiency compared to pure SiO2 aerogel, proving the necessity of preparation of FeBTC-SA composites again.

The morphologies of pure SiO2 aerogel and FeBTC-SA composites after adsorption of MB are clearly displayed in figure 7. The pure SiO2 aerogel has a relatively smooth surface covered by MB dyes and the pores are blocked by adsorbed MB dyes as well. However, the morphology of FeBTC-SA (3:50) composite has an obvious

| Sample          | \( S_{\text{BET}} \) m² g⁻¹ | \( S_{\text{BET micro}} \) m² g⁻¹ | Pore volume (cm³ g⁻¹) | Pore micro volume (cm³ g⁻¹) |
|-----------------|-------------------------------|-----------------------------------|-----------------------|----------------------------|
| SiO2 Aerogel    | 871                           | 117                               | 2.62                  | 0.0496                     |
| FeBTC-SA (3:400)| 784                           | 120                               | 2.68                  | 0.0529                     |
| FeBTC-SA (3:100)| 728                           | 141                               | 1.99                  | 0.0648                     |
| FeBTC-SA (3:50) | 640                           | 257                               | 1.39                  | 0.1265                     |

Figure 5. TEM image of FeBTC-SA (3:50) composite (a) and the high-resolution magnification TEM image of red circle part (b).
Figure 6. UV–vis spectra of MB solution treated by SiO$_2$-based aerogels with different time: (a) pure SiO$_2$ aerogel, (b) FeBTC-SA (3:400) composite, (c) FeBTC-SA (3:100) composite, and (d) FeBTC-SA (3:50) composite; (e) variation of C$_0$/C$_t$ with the time of SiO$_2$-based aerogels in MB solutions; (f) MB removal efficiency of different SiO$_2$-based aerogels.

Figure 7 SEM micrographs of SiO$_2$ aerogel (a) and FeBTC-SA (3:50) composite (b) after adsorption of MB.
difference with pure SiO₂ aerogel. The surface of hybrid aerogel is cauliflower-like and many extra micropores appear on it, which can considerably increase the contact area with MB dyes. As a result, a large amount of MB dyes are also found to aggregate in the larger micropores, as observed in inset image of figure 7(b). On the other hand, the larger the amount of FeBTC in hybrid aerogels, the more obvious the chemical adsorption between aerogels and MB dyes. Under this dual influence, the adsorption amount of hybrid aerogels to MB greatly increases as the FeBTC amount increases. For example, the adsorption efficiency of FeBTC-SA (3:50) composite to MB dyes is as high as 99.1%.

4. Conclusion

In summary, the FeBTC-SA composites have been innovatively prepared by a co-sol-gel synthesis process and then their adsorption performance for organic dyes is systematically investigated. The results indicate the FeBTC-SA composites have the same well-distributed porous structures as the pure SiO₂ aerogel and a fraction of FeBTC nanoparticles still remain a typical crystal structure in the composites. Meanwhile, with the increase of FeBTC content, the adsorption performance of the hybrid aerogels to MB dyes is improved. For instance, the adsorption efficiency of FeBTC-SA (3:50) composite is finally as high as 99.1%. Certainly, adsorption capacities of the FeBTC-SA composites are markedly higher than that of the pure SiO₂ aerogel, which reveal the necessity of preparation of hybrid aerogels again. It is strongly believed that these novel results not only benefit the understanding of synthesis and morphologies of hybrid aerogels, but also provide a new avenue for the important applications of hybrid aerogels as highly efficient adsorbents in water purification.

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Conflict of interest

The authors declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

ORCID iDs

Hongli Liu @ https://orcid.org/0000-0002-9401-474X

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