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# Preparation of ordered mesoporous silica materials templated by ionic liquids in alkaline condition

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## Abstract

A serial of mesoporous silica materials (including highly ordered and worm-like mesoporous structure) have been successfully prepared using ionic liquids as templates in alkaline conditions. The combined characterizations of XRD, $N_2$ isotherms, and TEM techniques exhibit that samples templated by ionic liquids produced from long-chain alkyl bromide (**I**-16 and **I**-14) show highly ordered mesoporous structure with uniform pore size and high surface area in the presence of NaOH or ammonia. Additionally, worm-like mesoporous silica materials have been also prepared using ionic liquids produced from short-chain alkyl bromide (**I**-12, **I**-10 and **I**-8) as templates in the presence of NaOH, tetramethylammonium hydroxide or ammonia. Our present work is of importance because it provides a new methodology to synthesize mesoporous materials for various applications.

**Keywords** Mesoporous silica · Ionic liquid · Alkaline

## 1 Introduction

Since the first reported in 1990s, mesoporous silica materials have attracted considerable attention due to their excellent properties of high surface area, uniform pore size distribution, and tunable mesoporous structure [1–3]. These unique properties ensure their wide applications in various fields of adsorption, separation, catalysis, biosensing, chemical sensing, and so on [4–6]. It is well known that the structure direct agents (such as organic templates) play an important role in mesoporous structures of mesoporous silica materials. Up to now, numerous organic templates have been developed for preparation of mesoporous silica materials. Among them, cationic surfactants, such as cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC) and nonionic surfactants, such as P123 (triblock copolymer, $EO_{20}PO_{70}EO_{20}$) and F127 (triblock copolymer, $EO_{106}PO_{70}EO_{106}$) have been widely used to synthesize mesoporous silica materials with various structures [7–9]. Later, anionic surfactants have also been developed for preparation of chiral mesoporous silica materials with the aid of co-structure-directing agents (such as, aminosilane and quaternized aminosilane) [10]. Additionally, a series of non-surfactant molecules, such as sugar, citric acid, cyclodextrins, hyperbranched polyglycerol, and organic supermolecules have also been developed to fabricate mesoporous silica materials [11–13]. However, it is still a big challenge to synthesize ordered mesoporous silica materials by these templates.

On the other hand, ionic liquids, typical organic salts with low melting point, have received much interest in numerous fields of chemistry and industry [14]. Morres and co-authors have reported the preparation of zeolite analogues using ionic liquids as both solvent and template [15]. Additionally, ionic liquids have also been used as templates for preparation of mesoporous materials, providing a new strategy for preparation of mesoporous materials [16–20]. It is found that the ionic liquids also exhibit obvious advantages for preparation of mesoporous silica as templates. For example, ordered mesoporous silica could be synthesized under different conditions, such as both acidic and alkaline conditions; Additionally, the pore size of the mesoporous silica is distributed from super-micropore to mesopores. Finally, the micropores could be introduced into the mesoporous silica materials. Although ionic liquids have been used to

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prepare mesoporous silica, a relative high-cost tetramethylorthosilicate (TMOS) was used as silica source [16, 19]. In this work, low-cost tetraethylorthosilicate (TEOS) was used as silica source for preparation of mesoporous silica. However, the effect of synthesis condition on mesostructure of mesoporous silica materials templated by ionic liquids is still highly required.

Herein, we have demonstrated the preparation of mesoporous silica materials with various structures using ionic liquids as templates in alkaline condition. The effect of length in linear alkyl chain on the mesoporous structure for mesoporous silica materials has also been examined in detail. As shown in the previous publications, NaOH, ammonia and TMAOH are usually used as alkaline sources for preparation of mesoporous silica [21–23]. Thus, the effect of these alkaline sources on mesoporous structure has been examined in this work. It is found that both highly ordered mesoporous silica materials and worm-like mesoporous silica materials have been successfully synthesized in the present work.

## 2 Experimental

### 2.1 Materials

1-Hexadecyl bromide, 1-tetradecyl bromide, 1-dodecyl bromide, 1-decyl bromide, and 1-octyl bromide were purchased from Aldrich. 1-Methylimidazole, tetramethylammonium hydroxide (TMAOH), ammonia, NaOH, tetrahydrofuran (THF) and TEOS were purchased from Beijing Chemical Corp (Beijing, China). All chemicals were used without any further purification. The water used throughout all experiments was purified through a Millipore system.

### 2.2 Preparation of ionic liquids

Ionic liquids were prepared using 1-methylimidazole and alkyl bromide as precursors, according to the previous publication [16]. The ionic liquids thus obtained were designated as **I**-16, **I**-14, **I**-12, **I**-10 and **I**-8, when 1-hexadecyl bromide, 1-tetradecyl bromide, 1-dodecyl bromide, 1-decyl bromide, and 1-octyl bromide were used as precursor. In a typical synthesis of **I**-16, 3.05 g of 1-hexadecyl bromide and 0.82 g of 1-methylimidazole were added into a 200-mL flask, followed by refluxing at 90 °C for 24 h. After cooling to room temperature, a white waxy solid was obtained. The product was dispersed into 200 mL of THF, from which I-16 recrystallized. After washing several times with THF, the crystalline I-16 powder was collected by centrifugation and dried in a vacuum at room temperature.

The preparation of the other **I**-*n* ionic liquids was achieved by repeating the above procedure with substitution of the corresponding alkyl bromide by 1-tetradecyl bromide, 1-dodecyl bromide, 1-decyl bromide, and 1-octyl bromide.

### 2.3 Preparation of mesoporous silica materials

Mesoporous silica materials were prepared using ionic liquids as templates in the presence of NaOH. In a typical run, 0.51 g of **I**-16 was added into 26.5 mL of water, followed by addition of 0.17 g of NaOH. After dissolution of **I**-16, 2.25 mL of TEOS was added into the above mixture, followed by stirring at room temperature for 24 h. Then, the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave and then heated at 180 °C for 12 h. After that, the products were collected by centrifugation, washing by water, and dryness at room temperature. After calcination at 550 °C for 3 h, mesoporous silica materials were obtained, which is designated as MS-S-I-16 (Mesoporous Silica prepared in Sodium hydroxide). Other mesoporous silica materials were also prepared by using other ionic liquids as templates, including **I**-14 (0.47 g), **I**-12 (0.44 g), **I**-10 (0.40 g) and **I**-8 (0.36 g), which are designated as MS-S-I-16, MS-S-I-14, MS-S-I-12, MS-S-I-10 and MS-S-I-8.

Mesoporous silica materials were also prepared using TMAOH as alkaline by the similar method, where the amount of **I**-16, water, TMAOH and TEOS are 1.35 g, 8.5 mL, 0.73 g and 2.25 mL, respectively. Other mesoporous silica materials were also prepared using **I**-14 (1.23 g), **I**-12 (1.16 g), **I**-10 (1.06 g) and **I**-8 (0.96 g) as templates. These samples are designated as MS-T-I-16, MS-T-I-14, MS-T-I-12, MS-T-I-10 and MS-T-I-8 (Mesoporous Silica prepared in TMAOH).

Mesoporous silica materials were also prepared using ammonia as alkaline source by the similar method, where the amount of **I**-16, water, ammonia and TEOS are 1.17 g, 30, 6 and 4.5 mL, respectively. Other mesoporous silica materials were also prepared using **I**-14 (1.06 g), **I**-12 (1.0 g), **I**-10 (0.92 g) and **I**-8 (0.83 g) as templates These samples are designated as MS-A-I-16, MS-A-I-14, MS-A-I-12, MS-A-I-10 and MS-A-I-8 (Mesoporous Silica prepared in Ammonia).

### 2.4 Characterizations

Powder X-ray diffraction (XRD) data were recorded on a Siemens D5005 (40 kV, 30 mA) using nickel-filtered Cu Kα radiation with wavelength of $\lambda = 1.5406$ Å. Diffraction patterns were collected under ambient conditions in the 2θ range of 1°–7° at a scanning rate of 1.0° $min^{-1}$. $N_2$ isotherms were obtained at − 196 °C on a Micromeritics Tri-star. Samples were normally prepared for measurements by treating at 150 °C under $N_2$ atmosphere for 12 h. Pore size distribution was calculated using Barrett–Joyner–Halenda (BJH) method from the adsorption branch. The BET surface area were calculated at $P/P_0 = 0.2$. Transmission electron micrograph

(TEM) images were obtained on Philips CM 200 LaB6 operating at an accelerating voltage of 200 kV.

## 3 Results and discussion

In this paper, mesoporous silica materials were firstly prepared using ionic liquids as templates and NaOH as alkaline source. Figure 1 shows the XRD patterns of mesoporous silica materials (MS-S-I-*n* samples) thus obtained. It is clearly seen that MS-S-I-16 sample exhibits a strong diffraction peak at 2θ of 2.23° and two weak diffraction peak at 2θ of 3.86° and 4.46°, which are associated with characteristic reflections (100), (110), and (200) of hexagonal mesoporous silica with space group *p*6*mm* [24]. By decreasing the length of alkyl chain in ionic liquids, MS-S-I-14 sample also exhibits three diffraction peaks attributed to reflections (100), (110), and (200) of hexagonal mesoporous silica, indicating formation of ordered mesoporous silica. Notably, the (100) peak in MS-S-I-14 shifts to high degree at 2θ of 2.40 with enhanced intensity, compared to MS-S-I-16, suggesting the formation of ordered mesoporous silica materials with small pore size. By further decreasing the length of alkyl chains, the intensity of diffraction peaks attributed to (100) reflection tremendously decreased and the other peaks centered at high degree gradually disappear, indicating that the mesoporous structure of mesoporous silica materials changed from highly ordered structure to worm-like structure [25]. Additionally, the position of diffraction peaks shifts to high degree, indicating the formation of mesopores with small pore size, which is attributed to the decrease of length of organic templates (ionic liquids). For example, the diffraction peaks of MS-S-I-12, MS-S-I-10 MS-S-I-8 are centered at 2θ of 2.47°, 2.76° and 2.87°, respectively. All these observations indicate that ordered mesoporous silica materials have been successfully prepared using **I**-16 and **I**-14 as templates in the presence of NaOH. Although no ordered mesostructure is observed for the samples templated by **I**-12, **I**-10, and **I**-8, all the MS-S-I-12, MS-S-I-10, and MS-S-I-8 samples exhibit tunable and relatively small pore size distribution, which is also of importance for selective catalysis and separation.

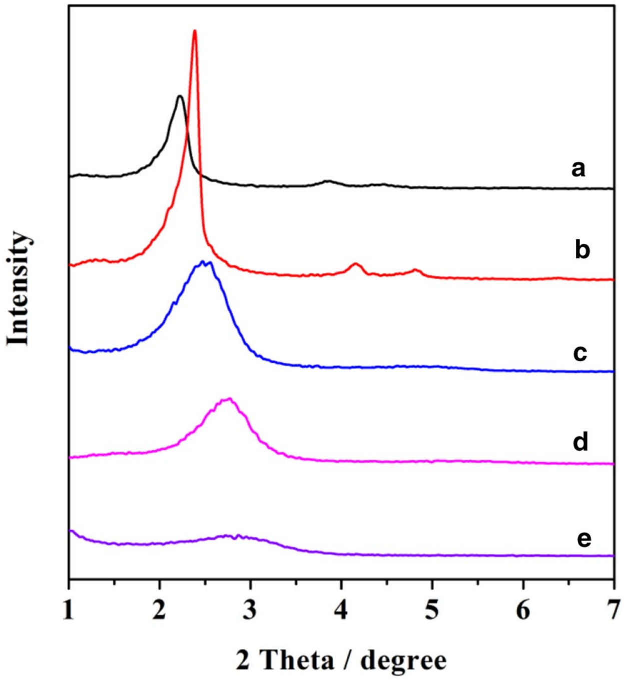

**Fig. 1** XRD patterns of *a* MS-S-I-16, *b* MS-S-I-14, *c* MS-S-I-12, *d* MS-S-I-10, and *e* MS-S-I-8

To further examine the mesoporous structure of the samples templated by ionic liquids in the presence of NaOH, MS-S-I-16, and MS-S-I-8 samples were characterized by $N_2$ isotherms. Figure 2a shows the $N_2$ adsorption/desorption isotherms of MS-S-I-16, and MS-S-I-8. It is seen that a typical IV-type adsorption isotherm is observed for MS-S-I-16 sample, and obvious $N_2$ uptakes at relative pressure of 0.3–0.5 is also observed, further indicating the formation of mesoporous structure. Clearly, MS-S-I-8 exhibits relatively low $N_2$ uptake, indicating formation of poor mesostructure, which is agreement with the results of XRD pattern. The corresponding pore size distribution curves and texture parameters are shown in Fig. 2b and Table 1. The pore size of MS-S-I-16 is about 2.4 nm with high intensity, further confirming the formation of mesostructure. As shown in Table 1, MS-S-I-16 has a BET surface area of 974 $m^2\ g^{-1}$ along with microporous surface area of 379 $m^2\ g^{-1}$. Additionally, the pore volume of MS-S-I-16 is 0.81 $cm^3\ g^{-1}$, indicating the formation of mesopores in MS-S-I-16. This property is different from the conventional mesoporous silica materials MCM-41 templated by CTAB [26], and the presence of micropores ensures that MS-S-I-16 could be used as hard template for preparation of other ordered mesoporous materials by nanocasting method. It is also found that the MS-S-I-8 exhibits low BET surface area (144 $m^2\ g^{-1}$), and low pore volume (0.12 $cm^3\ g^{-1}$).

The mesoporous structure of MS-S-I-16 sample was further examined by TEM technique. Figure 3 shows the TEM images of MS-S-I-16 sample viewed from (1 1 0) and (1 0 0) direction, which are very similar to the previously reported highly ordered hexagonal mesoporous silica materials [27]. The pore size based on TEM image (Fig. 3a) is about 2–3 nm, which is the same to $N_2$ isotherm results. Additionally, Fig. 4 shows the TEM image of MS-S-I-8 sample, revealing the formation of worm-like mesoporous structure.

It is well known that the alkaline sources play an important role in tuning the mesoporous structure for mesoporous silica materials. Thus, mesoporous silica materials were also prepared using TMAOH and ammonia as alkaline sources.

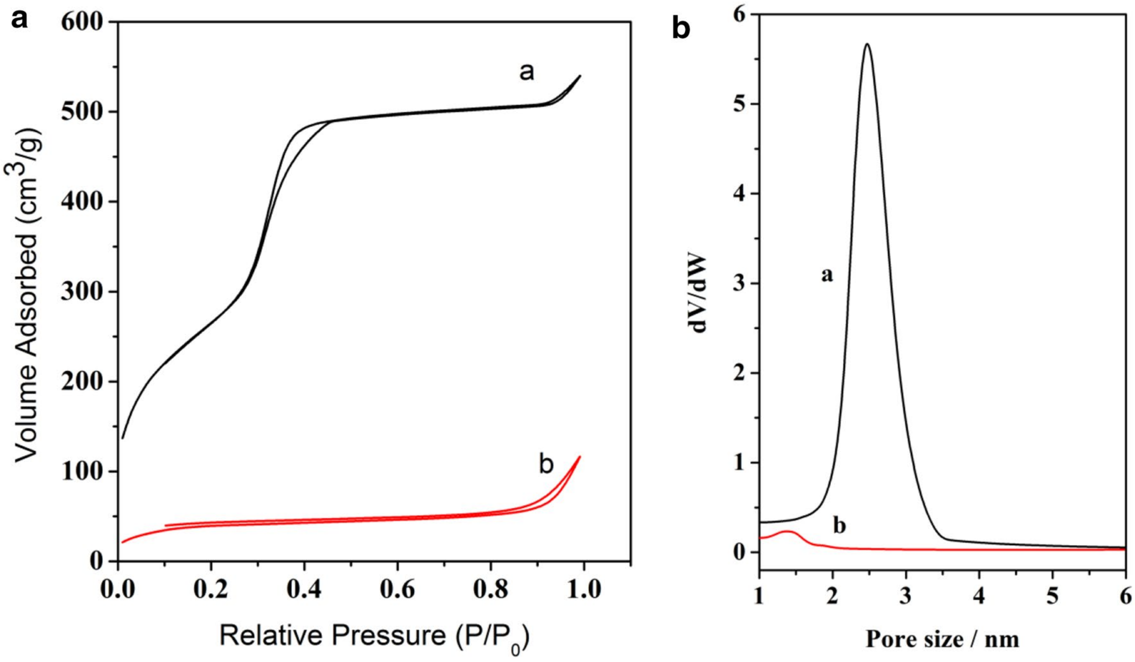

**Fig. 2** **A** $N_2$ adsorption/desorption isotherms and **B** pore sizes distribution curves of *a* MS-S-I-16, and *b* MS-S-I-8

**Table 1** Textural parameters of MS-S-I-*n* samples

| Sample | *d* (nm) | $S_{BET}$ ($m^2\ g^{-1}$) | $S_{micro}$ ($m^2\ g^{-1}$) | $V_{meso}$ ($cm^3\ g^{-1}$) | D (nm) | Wall (nm) |
|---|---|---|---|---|---|---|
| MS-S-I-16 | 3.9 | 974 | 379 | 0.81 | 2.4 | 2.2 |
| MS-S-I-8 | 3.1 | 144 | 56 | 0.12 | – | – |

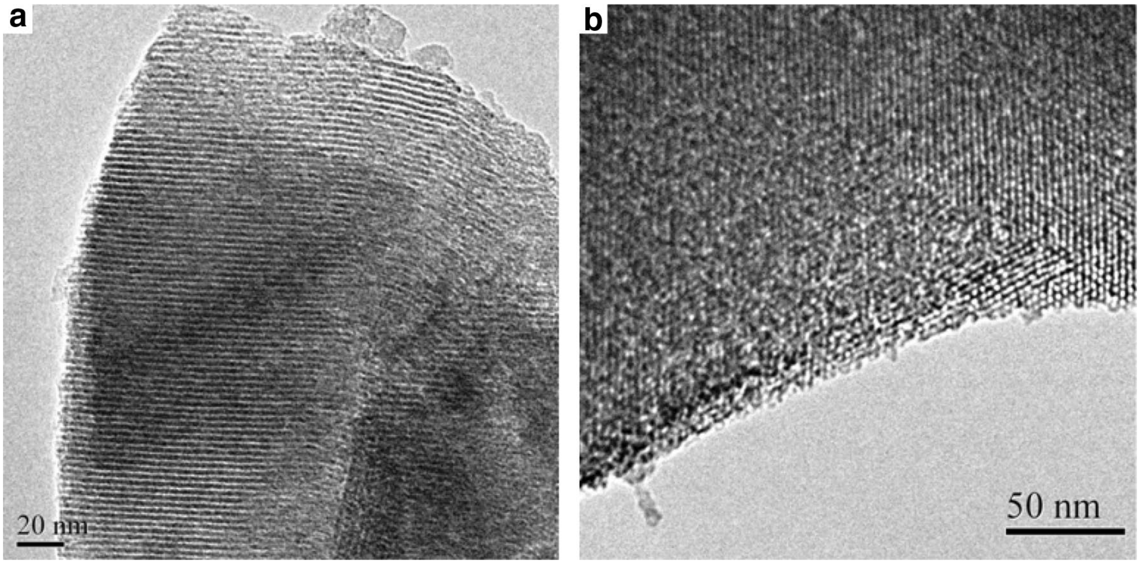

**Fig. 3** TEM images of MS-S-I-16 taken **a** in the (110) and **b** (100) directions

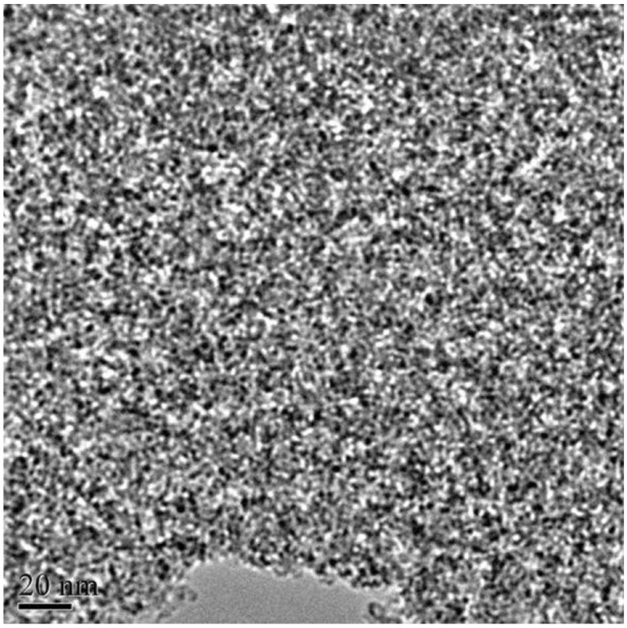

**Fig. 4** TEM image of MS-S-I-8 sample

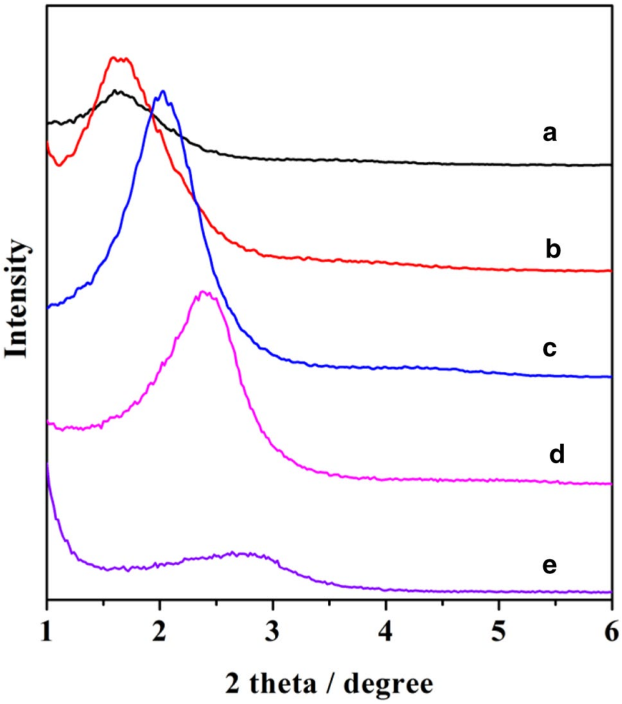

**Fig. 5** XRD patterns of *a* MS-T-I-16, *b* MS-T-I-14, *c* MS-T-I-12, *d* MS-T-I-10, and *e* MS-T-I-8

Figure 5 shows the XRD patterns of MS-T-I-*n* sample in the presence of TMAOH. It is seen that all these MS-T-I-*n* samples exhibit only a broad diffraction peak, indicating the formation of worm-like mesoporous silica materials [25]. Additionally, the diffraction peaks shift to high degree with decreasing the length of alkyl chain in ionic liquids, suggesting formation smaller mesopores.

Furthermore, the mesoporous silica materials were also prepared using ammonia as alkaline source. Figure 6 shows the XRD patterns of MS-A-I-*n* samples in the presence of ammonia. It is seen that highly ordered mesoporous silica materials with hexagonal structure were obtained using **I**-16 and **I**-14 as templates. Similar to the results of MS-S-I-*n* samples, worm-like mesoporous silica materials were observed with decreasing the length of alkyl chains in ionic liquids.

## 4 Conclusion

A series of mesoporous silica materials have been successfully prepared using ionic liquids as templates in the presence of various alkaline sources, such as NaOH, TMAOH and ammonia. It is found that highly ordered mesoporous silica with hexagonal structure were synthesized using **I**-16 and **I**-14 as templates in the presence of NaOH or ammonia. Worm-like mesoporous silica materials with small pore size were also prepared by decreasing the length of alkyl chains in ionic liquids. Most importantly, this work opens a new methodology for preparation of mesoporous materials for various applications.

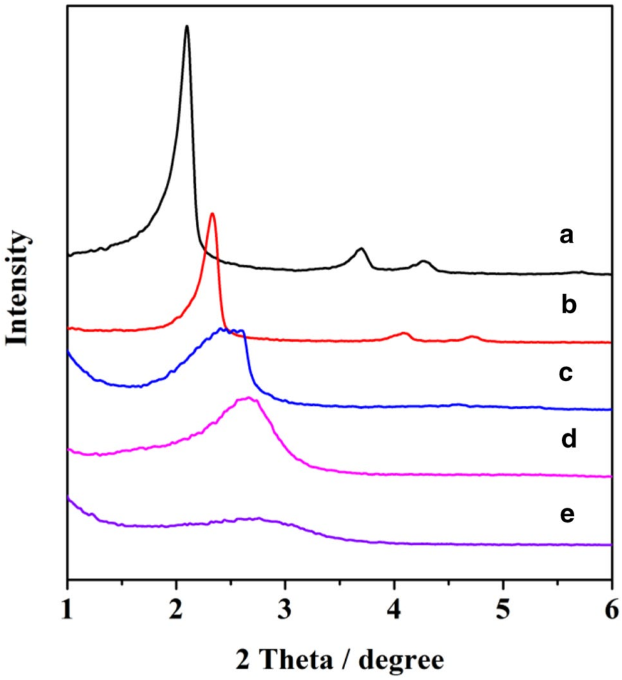

**Fig. 6** XRD patterns of *a* MS-A-I-16, *b* MS-A-I-14, *c* MS-A-I-12, *d* MS-A-I-10, and *e* MS-A-I-8

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