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Synthesis and Morphological Control of Mesoporous SiO_2 with Cotton as Bio-Template†

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Mesoporous SiO_2 with special short open axis-like morphology was successfully fabricated by using cotton fibers as bio-templates. Mesostructure and morphology of the samples were systematically studied by changing the cotton/SiO_2 weight ratio and hydrothermal treating temperature. Textural property and morphology of the obtained mesoporous SiO_2 were characterized by the combination of X-ray diffraction, N_2 adsorption-desorption experiments and scanning electron microscope. Finally, batch adsorption of methylene blue was performed to detect the adsorption capacity of the cotton co-templated materials.

Keywords: Cotton, SBA-15, Morphology control, Bio-template.

INTRODUCTION

Recent studies show that one of the major factors influence mesoporous silicate materials' practical applications was the external morphology[1]. Simple morphologies with short, unhindered path lengths such as short axial like particles as well as short, straight rods are beneficial for applications processes such as catalysis and adsorption, *etc.*[2]. Thus, not surprisingly, extensive work was devoted to the morphological control of mesoporous SiO_2. Most approaches were based on changes in synthesis conditions, which including temperature, acidity, stirring speed, salt, co-solvent, co-surfactant, silica source, *etc.*[3-6]. However, to the best of our knowledge, there is no report on the use biotemplate to control morphology of mesoporous SiO_2 until now. Hence, in this work, we use cotton as bio-template to control the morphology of mesoporous SBA-15 and those samples with special morphologies were used to remove the organic pollutant in aqueous solution.

EXPERIMENTAL

SBA-15 was synthesized according to the reported method[7]. In a typical synthesis, 2 g of Pluronic P123 was dissolved in 75 g of aqueous hydrochloric acid (HCl) solution (1.6 M), then 4.25 g of tetraethylorthosilicate (TEOS) was added at 313 K. The resulting mixture was stirred for 24 h and then hydrothermal treated at 373 K for another 24 h under static conditions. The as-synthesized sample was filtered, washed, dried and calcined at 823 K for 5 h to remove the template.

The cotton co-templated mesoporous SiO_2 materials were synthesized by a similar method to the synthesis of SBA-15 with the addition of some cotton into the reaction mixture at the first step. The cotton/SiO_2 ratio was varied from 0.5, 0.9 to 1.4 and the hydrothermal treatment temperature was changed from 353, 373-397 K. The finally obtained materials were named as PC-x-Y, where x was denoted as the cotton/SiO_2 weight ratio and Y was labeled as the aging temperature, respectively.

XRD patterns were recorded on a Bruker D8 Advance diffractometer with CuK_α radiation. N_2 physisorption isotherms at 77 K were measured using a Belsorp II system. SEM was performed on a HITACHI S-4800 electron microscope. The methylene blue concentration was determined using an UV-2450 spectrophotometer at maximum wavelength around 665 nm.

RESULTS AND DISCUSSION

Fig. 1 displays the low-angle XRD patterns of the cotton co-templated PC-x-Y samples synthesized with different cotton/SiO_2 weight ratio. The long-range highly ordered meso-structure of SBA-15 is retained after the introduction of cotton into the synthetic solutions. All the PC-x-Y samples possess three well-resolved diffraction peaks with *d*-spacing ratios of $1:3^{1/2}:2$ at 2θ of 0.5-2.0°, which can be indexed as (100), (110) and (200) reflections of typical 2-D hexagonal meso-

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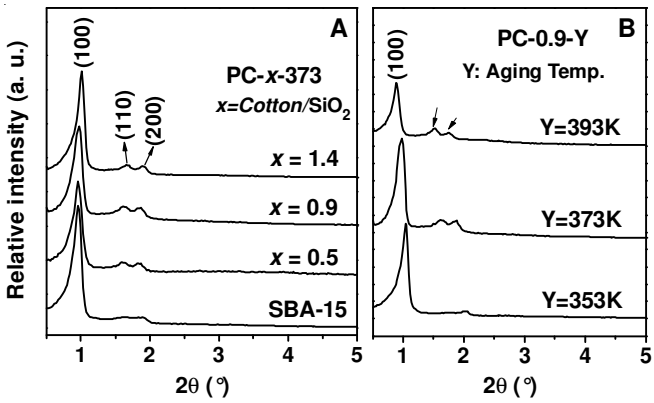

Fig. 1. Low angle XRD patterns of the samples synthesized with different cotton/SiO_2 (w/w) ratio (A) and aging temperature (B)

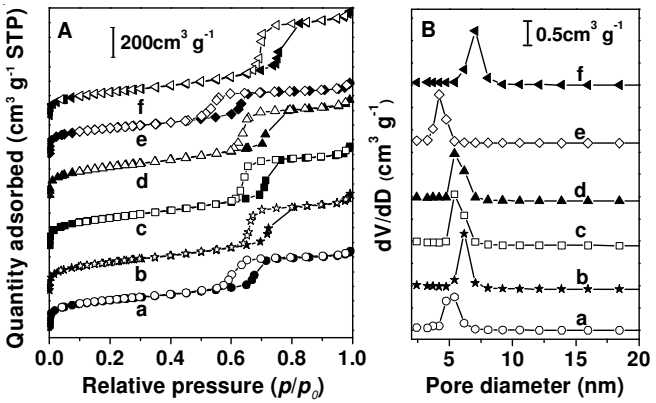

Fig. 2. N_2 adsorption-desorption isotherms (A) and pore size distributions (B) of SBA-15 (a) and cotton co-templated samples: PC-0.5-373 (b), PC-0.9-373 (c), PC-1.4-373 (d), PC-0.9-353 (e) and PC-0.9-393 (f) samples. Curves are offset for clarity

structure (space group P6mm). The lattice parameters of SBA-15 and PC-0.5-373 calculated from the (100) diffraction peaks are the same (10.6 nm), whereas those of PC-0.9-373 and PC-1.4-373 samples shift toward lower values (10.4 and 10.0 nm, respectively), indicating an improved condensation of siliceous species after the addition of cotton into the reaction system.

The XRD patterns of the materials synthesized with cotton/SiO_2 weight ratio of 0.9 at different hydrothermal treating temperatures are shown in Fig. 1B. The lattice parameters of the PC-0.9-Y samples are enlarged according to the increase of the aging temperature (Table-1). This is a common phenomenon occurs in the synthesis of SBA-15 related materials and is due to the micelle dehydration upon higher temperature, which then causes larger pore size for the sample synthesized at high temperature than at low temperature[8].

TABLE-1
PHYSICAL AND ADSORPTION PROPERTIES OF THE MESOPOROUS SiO_2 MATERIALS

Sample	a_0 (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_P (nm)	h_w (nm)	Removal of methylene blue (%)
SBA-15	10.6	729	0.83	5.4	5.2	79.4
PC-0.5-373	10.6	762	1.03	6.2	4.4	83.5
PC-0.9-373	10.4	789	1.07	5.4	5.0	97.9
PC-1.4-373	10.0	774	1.04	5.4	4.6	86.5
PC-0.9-353	9.4	692	0.77	4.2	5.2	86.8
PC-0.9-393	11.6	646	1.12	7.1	4.5	78.5

a_0: Lattice parameter calculated from $a_0 = d_{100}*2/3^{1/2}$; S_{BET}: BET specific surface area; V_p: total pore volume; D_p: pore diameter; h_w: wall thickness calculated from $h_w = a_0-D_p$.

Fig. 2 presents N_2 adsorption–desorption isotherms and pore size distributions of SBA-15 and the cotton co-templated PC-*x*-Y samples. Corresponding surface areas, pore volumes, pore diameters are listed in Table-1. The isotherm shapes of all the PC-x-Y samples are similar to that of parent SBA-15, *i.e.*, type IV with an H1 hysteresis loop. This is characteristic of materials with uniform cylindrical mesopores. For the samples synthesized with different amount of cotton additives, PC-x-373, show sharp capillary condensation and evaporation steps in a higher p/p_0 range. Further, the pore size distribution curves of PC-x-373 samples are narrower than that of SBA-15, suggesting that the pore ordering of SBA-15 is improved by using cotton as co-template. It is noticeable that pore diameters of PC-0.9-373 and PC-1.4-373 samples are identical to SBA-15 (5.4 nm), while that of PC- 0.5-373 is a bit higher (6.2 nm). Pore sizes of the PC-0.9-Y samples change dramatically according to the hydrothermal treating temperature (Table-1). The pore size of PC-0.9-393 sample is 7.1 nm, which is much larger than 4.2 nm of PC-0.9-353 sample and 5.4 nm of PC-0.9-373 sample. BET surface areas of all the cotton co-templated PC-x-Y samples are larger than that of SBA-15 with two exceptions, PC-0.9-353 and PC-0.9-393 (Table-1).

Fig. 3 shows the SEM images of SBA-15 and cotton co-templated PC-x-Y samples. SBA-15 has a ropelike morphology and a long "rope" is formed by many short "sticks". Those short "sticks" link together then form a straight "rope" (Fig. 4A,B). Interestingly, morphology of SBA-15 is changed seriously with the introduction of cotton during the synthesis. Long "ropes" alter to short "axis" when cotton fiber was added into the reaction mixture. When the introduced cotton amount varies from cotton/SiO_2 weight ratio of 0.5-0.9, all the PC-x-373 materials possess open pore structure with apparently neat, smooth surface (Fig. 4C-E), which is different from that of normal SBA-15. When the introduced cotton increases to cotton/SiO_2 (w/w) ratio of 1.4, the surface of PC-1.4-373 sample is doped with some small particles (Fig. 3F). Morphology of the PC-0.9-Y samples which were synthesized with the fixed cotton/SiO_2(w/w) ratio alters according to the hydrothermal temperature. The short "axis" becomes more and thicker when the hydrothermal temperature rises from 353 to 393 K.

The adsorption property of the cotton co-templated PC-x-Y samples is displayed in Table-1 and Fig. 4. Mesoporous PC-x-Y samples exhibit better adsorptive capacity in methylene blue dye purification than traditional SBA-15. Among those, PC-0.9-373 is the most efficient one for the adsorption of methylene blue and the methylene blue decoloring rate could reach 98 % after 0.5 h on PC-0.9-373 sample. The removal percent of methylene blue on PC-1.4-373 and PC-0.9-353 is near 87 %, which is a bit higher than that on SBA-15. This is probably due to the short "axis" morphology of the cotton co-templated samples, which supply more open pores and provide more contact sites than traditional SBA-15.

Conclusion

In this study, we use cotton as bio-template to synthesize mesoporous SiO_2 materials. XRD and N_2 physisorption results

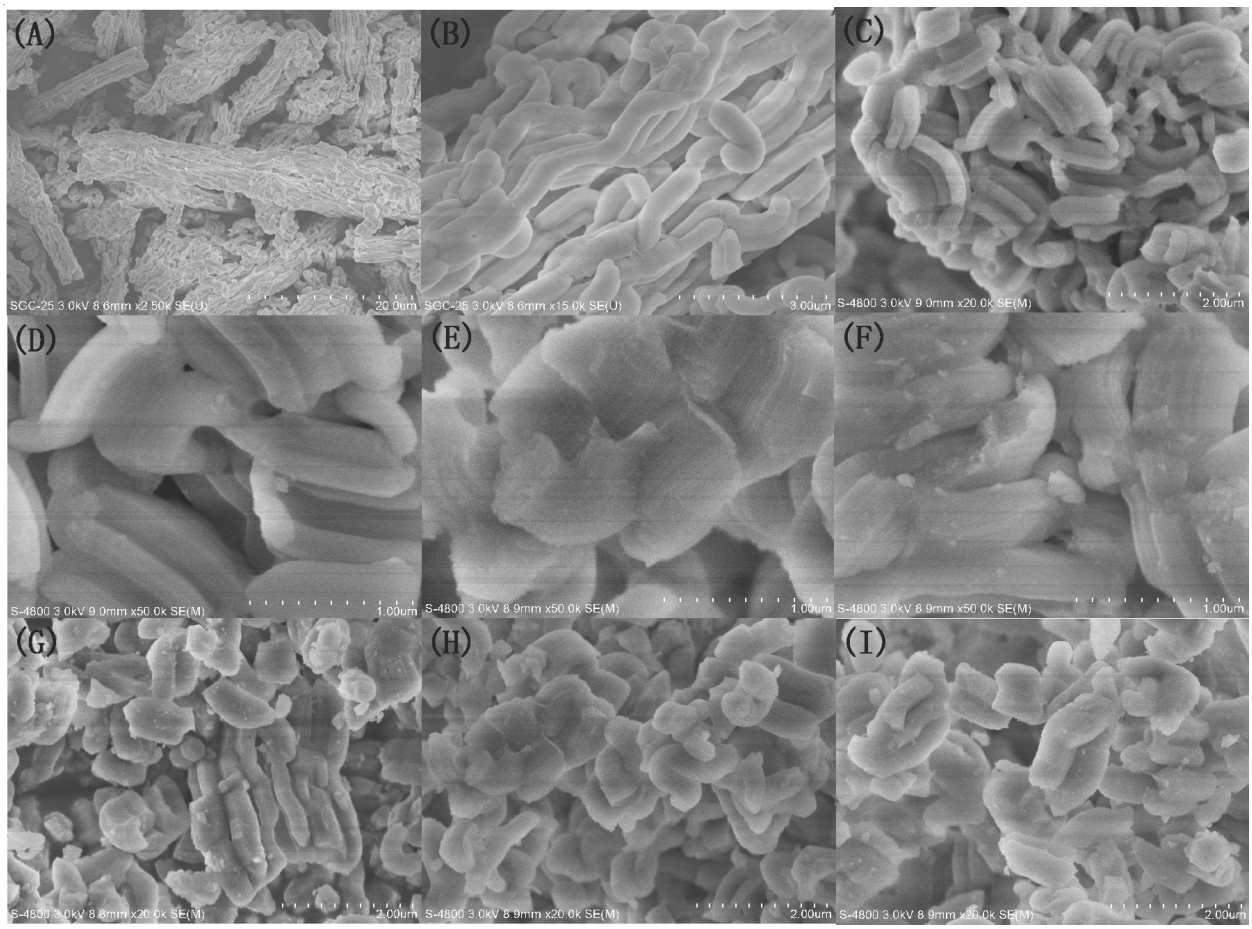

Fig. 3. SEM images of SBA-15(A, B) and cotton co-templated samples: PC-0.5-373 (C, D), PC-0.9-373 (E, H), PC-1.4-373 (F), PC-0.9-353 (G) and PC-0.9-393 (I) samples

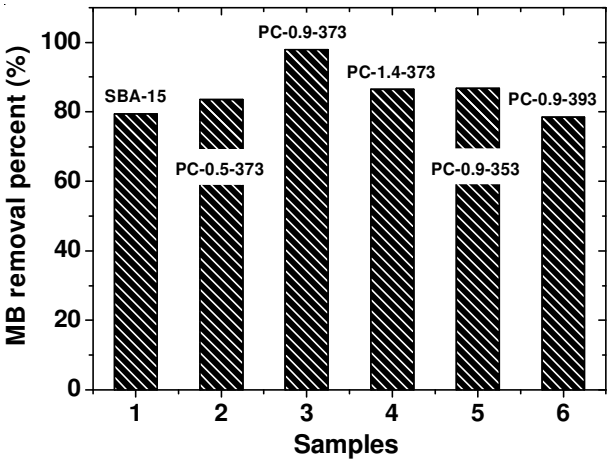

Fig. 4. Methylene blue (MB) adsorption results on different PC-x-Y samples. (Initial methylene blue concentration: 20 mg/L, adsorbent dose: 1 g/L and contact time: 2 h)

illuminate that all the cotton co-templated PC-x-Y samples have ordered mesostructure like SBA-15. However, morphology of PC-x-Y is different from that of tradition SBA-15. PC-x-Y samples have short "axis" morphologies and many open pores, which make those samples display higher adsorption capacities to methylene blue than SBA-15.

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