A Fast Way for Preparing Crack-Free Mesostructured Silica Monolith

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Large-sized, crack-free silica monoliths with highly ordered mesostructure are prepared by a fast and easy way via liquid-paraffin-medium protected solvent evaporation. By employing the inert liquid paraffin as the morphology “protector”, cracks of the materials can be successfully avoided and the processing time can be reduced to 8 h. The block copolymer−silica composite monoliths are transparent and crack-free with a large size. The mesoporous silica monoliths have been characterized by small-angle powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and nitrogen adsorption, which show that the materials have a highly ordered hexagonal mesostructure of space group *p*6*mm* and narrow pore size distribution, with a mean pore diameter of 5.65 nm. In addition, metal ions can be easily doped into the monoliths, indicating potential optical, electronic, magnetic, and catalytic properties. This fast synthetic method is valuable for the applications of mesostructured silica monoliths in optics and separation.

Introduction

Ordered mesoporous silica materials synthesized through self-assembling of amphiphilic block copolymers[1−12] are of great interest because of their variety in both pore structure and macroscopical morphology. Using different amphiphilic block copolymers as the structure-directing agents, two-dimensional (2D) hexagonal and 3D cubic mesoporous structures can be obtained, such as SBA-15 (*p*6*mm*)[1] and SBA-16 (*Im*3*m*).[2] Moreover, the morphologies of this kind of materials can be controlled by adding inorganic salts or small molecular organic species. Mesoporous silica thin films,[3] single crystals,[4] spheres,[5a] rods,[5a] fibers,[5b,5c] and monoliths[6−12] have been synthesized, and they show potential applications in catalysis, separation, optics, electronics, and so on. Among all these morphologies, transparent mesostructured silica monolith with bulk size is an ideal host material for optical devices, such as lenses, chromophores, laser devices, and nonlinear optical media.[13] In addition, the mesoporous monoliths can be used as the promising substrates for macromolecular separations because of their lack of external surface area. Monolithic mesoporous silica has been prepared through the complete removal of the residue solvent of mesostructured silica gel templated by amphiphilic block copolymers[6−10,12] or microemulsion liquid crystal.[11] However, the primary problem that has to be overcome is the occurrence of macrocracks through drying due to the large shrinkage that occurs when solvent is removed from the gels; this severely impedes the preparation of crack-free monoliths with large size and limits their practical applications. So far, although some synthetic methods proposed on the basis of the understanding of sol−gel process,[14,15] such as critical point extraction,[8] sealed-vessel evaporation,[9,10] and vacuum-drying,[11] partly solved the problem, the reaction conditions are too demanding and the processing period is too long (at least 6 weeks[10]), which limits the practical application of monolithic mesostructured silica.

In this paper, we report a fast and easy way of liquid-paraffin-medium protected solvent evaporation to prepare large-sized, crack-free silica monoliths with highly

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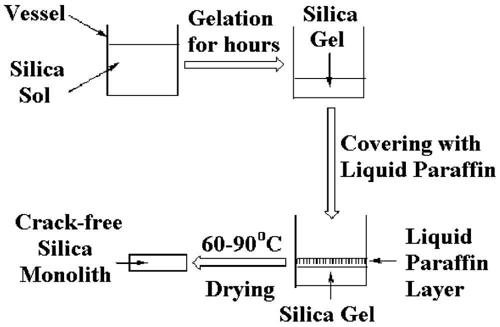
Scheme 1. Preparation Process for Transparent and Crack-Free Silica Monolith with Highly Ordered Mesostructure



ordered mesostructure. Employing the liquid paraffin is critically important to protect the macromorphology of the monolith without cracking and reduces the processing time to 8 h. In addition, metal ions can be easily doped into the monoliths, indicating potential optical, electronic, magnetic, and catalytic properties. This fast synthetic method is valuable for the application of mesostructured silica monoliths in optics and separation.

Experimental Section

The mesostructured silica monoliths were synthesized through solvent evaporation from the silica gel prepared by using tetraethoxysiliane (TEOS) as silica source and poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) amphiphilic block copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) as structure-directing agent. As Scheme 1 shows, by covering a layer of inert medium liquid paraffin (ρ = 0.835−0.855 g/mL at 20 °C, bp = 298−302 °C), the residue solvents in the silica gel were removed at relatively high temperature ranges (60−90 °C) in a mild way, which reduces the processing period to 8 h and preserves the macromorphology of the monolith from cracking.

Preparation of Mesostructured Silica Monolith. For a typical synthesis, 1 g of P123 (MW = 5800, Aldrich) was dissolved in a mixture with 5 g of ethanol and 0.2 g of aqueous HCl (1 mol/L), and stirred until a homogeneous solution formed. While the mixture was still stirring, 2.08 g of TEOS was added to the solution, and the mixture was further stirred for 10 min. The solution derived above was then transferred into a ceramic vessel with different shapes and aged at room temperature (15 °C for our experiments) for 36 h in air. Herein, sufficient aging time (20−48 h, based on temperature, humidity, ventilation, and so on) is necessary because insufficient aging time yields a weak network that does not possess the dimensional stability to withstand the increasing compressive stress during the evaporation process,[14,15] and causes macrocracks in the early drying stage at relative high temperature. Also, the rigid silica network formed after enough aging time is favorable to keep the highly ordered mesostructure, and too short an aging time would result in disordered mesostructure. Then the silica gel was covered with a layer of liquid paraffin in 2−3-mm thickness and heated at 60 °C for 18 h to remove the ethanol completely. After the heating treatment, the liquid paraffin was collected and used again. The residue liquid paraffin on the surface of the products was removed and cleared by using filter paper. For the removal of the block copolymer, calcination was carried out in an oven at 550 °C in air for 6 h. The process started from room temperature and the heating rate was 30 °C/hr to retain the macromophorlogy.

Preparation of Doped Mesostructured Silica Monolith. The metal-ion-doped silica monoliths were prepared with a procedure similar to that described above. The corresponding metal salts were initially dissolved in the P123/HCl/ethanol mixture and stirred for 0.5 h before the addition of TEOS. The mass ratio of the metal salt to P123 was varied between 0 and 0.1.

Figure 1. (a) Photograph of ordered transparent mesostructured block copolymer−silica composite prepared by liquid-paraffin-medium protected solvent evaporation. The given sample is 4.8 cm long, 2.1 cm wide, and 0.2 cm thick, crack-free, and optically transparent. (b) Photograph of mesoporous silica monolith after calcination, which is opaque perhaps due to microcracks inside.

Characterizaion. Small-angle powder X-ray diffraction (XRD) patterns were recorded with a Bruker D4 powder X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. Nitrogen adsorption−desorption isotherms were measured with a Micromeritics Tristar 3000 analyzer at 77 K. The Barrett−Emmett−Teller (BET) method was utilized to calculate the surface areas. The pore volume and pore-size distributions were derived from the adsorption branchs of the isotherms using the Barrett−Joyner−Halanda (BJH) method. FT-IR curves were obtained with an AUATAR 360 FT-IR (Nicolet) analyzer.

Results and Discussion

A normal photograph (Figure 1a) shows a typical rectangular mesostructured silica monolith, which has fully copied the shape of the reaction vessel. Using vessels with different shapes and changing the quantities of reactants, the shapes (such as dish, peg-top column) and sizes of the monoliths can be varied (Figure 2). To take the monolithic dish as an example, the diameter and thickness are tunable in the ranges of 0.9−6.5 cm and of 0.1−0.7 cm, respectively. All samples derived by this method are crack-free and optically

Figure 2. Photographs of ordered transparent mesostructured block copolymer–silica composites doped with transition metal ions of the peg-top column shape prepared by liquid-paraffin-medium protected solvent evaporation. Given samples are shown in (a) vertical view and (b) side view. The typical size of given samples is 0.9 cm high and 0.8 cm in diameter of the cross section. These monoliths show various colors in accordance with the corresponding slovation metal ions doped within them, which is colorless for pure silica sample, pink for Co^{2+}, yellow for Fe^{3+}, and green for Cu^{2+} (from left to right).

transparent. Mesoporous materials are obtained by calcination at 550 °C for 6 h. After calcination, macroscopical shapes are retained with relative large size (Figure 1b), and the volumes of the materials shrink 15–20%. The calcined mesoporous silica monoliths become white and lose their previous transparency, perhaps due to internal micro-cracks which resulted from the decomposition of the template surfactant.[3d,10,11]

Small angle powder X-ray diffraction (XRD) patterns of the as-synthesized and calcined mesoporous silica monolith by using block copolymer P123 as a structure-directing agent are shown in Figure 3. Both of the samples show three well-resolved XRD peaks. Combined with TEM analysis (see below), the diffraction peaks can be indexed to (100), (110), and (200) reflections of 2D-hexagonal mesostructure for space group $p6mm$, which is the same with mesoporous silica powder SBA-15 templated by P123.[1] After calcination, the first diffraction peak is shifted to higher angle ($2\theta = 1.03°$, and $2\theta = 0.84°$ before calcination) and the values of the d spacing of the (100) peak are calculated to be 10.48 and 8.54 nm for as-synthesized and calcined mesoporous silica monolith, respectively. This fact shows that the calcination of those samples at 550 °C causes obvious shrinkage, however the mesostructure regularity does not decline, which is further proved by TEM characterization.

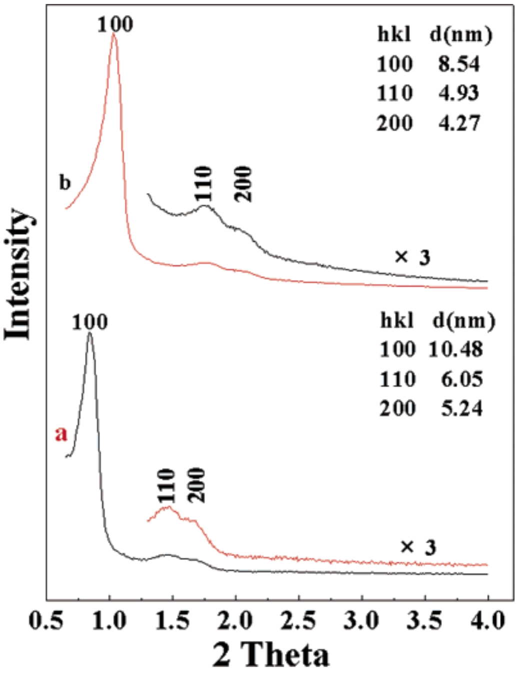


Figure 3. Powder-XRD patterns of (a) as-synthesized and (b) calcined mesoporous silica monolith prepared by liquid-paraffin-medium protected solvent evaporation. XRD patterns were recorded with a Bruker D4 powder X-ray diffractometer using Cu Kα radiation.

TEM images for calcined mesoporous silica monolith prepared by liquid-paraffin-medium protected solvent evaporation method show large ordering domains with highly ordered hexagonal (Figure 4a) and strut-like arrays (Figure 4b). The unit cell parameter (a value) of the sample is calculated to be 9.9 nm, in good agreement with the value determined from the XRD data. Moreover, the results combined with the XRD and TEM measurements reveal that the calcined monolith has a high-quality hexagonal mesostructure, indicating that the liquid-paraffin-medium protected solvent evaporation at relatively high temperature does not destroy the mesostructure of the materials.

Calcined mesoporous silica monolith synthesized from the liquid-paraffin-medium protected solvent evaporation method yields a type IV isotherm with a H_1 hysteresis loop (Figure 5), which is typical of adsorption for mesoporous materials with 2D-hexagonal structures.[1] A well-defined step occurs at approximately $p/p_0 = 0.50–0.75$, which is associated with the filling of the mesopores due to capillary condensation. A narrow pore-size distribution (inset of Figure 5) is calculated from the adsorption branch based on the BJH model, indicating that the monolith has uniform pore structures. The mean pore diameter is calculated to be 5.65 nm. The BET surface area and the total pore volume are 641 m^2/g and 0.93 cm^3/g, respectively.

Compared with previously reported preparation processes of mesostructured silica monoliths, the innovation of our work is to introduce liquid paraffin as the morphology “protector” to overcome cracking during removal of the solvent and processing at relatively high temperature to accelerate the drying process, which results in preparing large-sized crack-free silica monoliths in a short time.

According to the theory of sol–gel process, the stress that causes cracking is mainly attributed to the internal

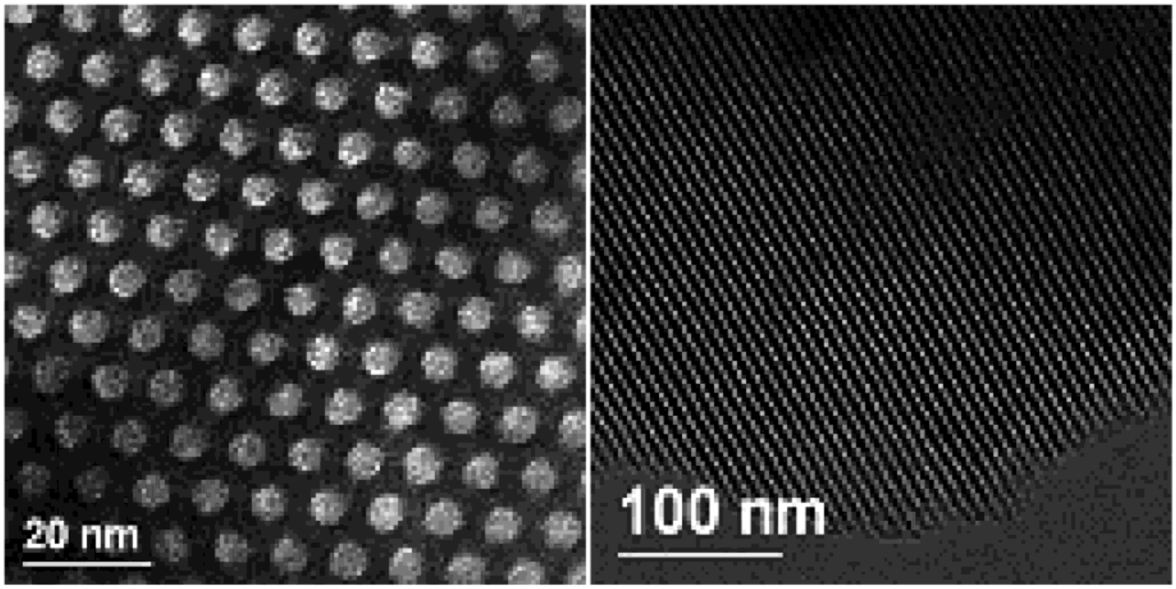


Figure 4. TEM images of calcined mesoporous silica monolith synthesized by liquid-paraffin-medium protected solvent evaporation: along the (a) [110] and (b) [100] directions. TEM photographs were obtained with a JEOL JEM2011 microscope operated at 200 kV.

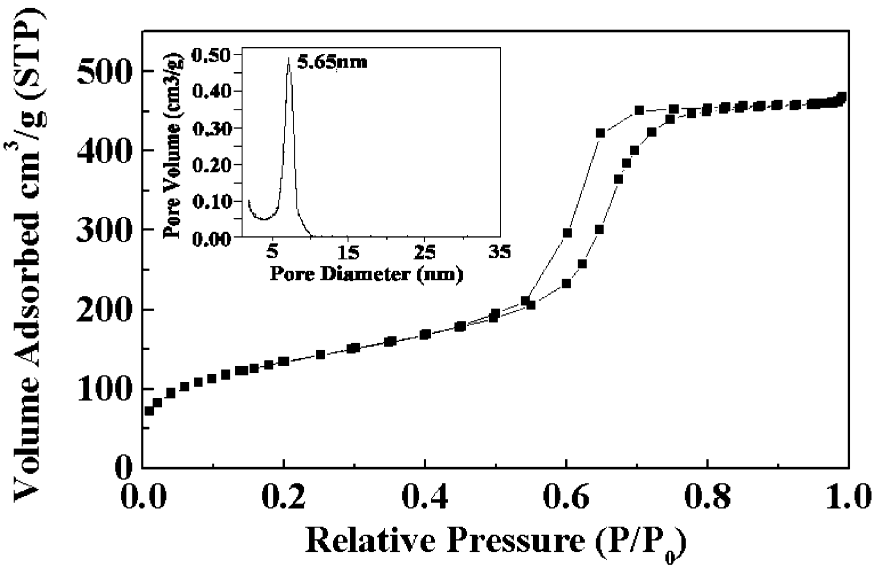


Figure 5. Nitrogen adsorption/desorption isotherm plots and pore size distribution curve (inset) of calcined mesoporous silica monolith. N_2 adsorption measurements were performed at 77 K using a Micromeritics Tristar 3000 analyzer utilizing Barrett−Emmett−Teller (BET) calculations for surface area and Barrett−Joyner−Halanda (BJH) calculations for pore volume and pore size distributions for the adsorption branch of the isotherm.

pressure gradient.[14−25] As evaporation proceeds, vapor phase and liquid phase exist simultaneously in the pores of the silica gel (the pores mentioned in this mechanism discussion section are the holes formed between the partially polymerized silica network but not those templated by surfactants). If the evaporation rate is relatively high and the gel loses its permeability, an internal pressure gradient will form inside the silica gel and cracking will start from the flaws at the gel surface to reduce this pressure gradient. In addition, during drying, pores of different diameters evaporate with different rates, and larger pores that empty first will passively shrink under the capillary pressure of nearby pores that are saturated with liquid. The flaws at the surface that lead to cracks may be created by such inhomogeneous capillary forces (on the order of 100 MPa). As a result, cracking should be prevented based on both macroscopic and microscopic perspectives.

The liquid paraffin is an inert medium with high boiling point (298−302 °C) and has no, or weak, chemical interaction with silica or the copolymers. When covered onto the silica gel to conduct thermal treatment,

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the liquid paraffin is able to seep into the interface between the monolith and the vessel when the monolith shrinks and therefore fully separates the gel from the atmosphere. By this means, damage caused by the internal pressure gradient is obviously reduced in three ways. First, while heating, the evaporation rate is accelerated in a mild way and the viscosity of the liquid (alcohol) is decreased so that the permeability of the gel is increased. As a result, the internal gradient is reduced. Second, the flaws at the surface of the gel are filled with paraffin, and the initial alcohol−vapor interface is replaced by alcohol−paraffin interface. Consequently, the internal pressure net force that pulls the flaws open is reduced. Third, the thermal treatment makes the silica species in the gel highly polymerized, which strengthens the silica framework and increases its tolerance of the internal pressure and the tension that the expansion of the liquid puts on the network during heating. Moreover, the flaws caused by imbalanced capillary pressure is also reduced with the presence of liquid paraffin. Evaporation rates in the pores of all sizes are restrained by paraffin as compared with those without paraffin covering under the heating condition, which makes the pores tend to be empty at the same time. So the capillary pressure imbalance resulting from nonuniform pore sizes can be reduced. In addition, higher temperature accompanies lower liquid surface energy and capillary pressure, which also leads to lower local stresses. Therefore, uniform shrinkage is attained and cracks are prevented.

The above detailed analysis clearly shows the advantages of this liquid-paraffin-medium protected solvent evaporation method in preparing large-sized mesoporous silica monoliths. Because of the existence of paraffin, the morphology protector, the silica gel can be heated at a relatively high temperature to accelerate the evaporation process, while the layer of paraffin restrains the evaporation to some extent and provides a controlling effect. Combined with all these factors, the evaporation process is much faster than it is in ambient conditions without paraffin protection. Thus, the processing time is sharply reduced, but the process occurs in a mild way, helping to preserve the well-defined macromorphology.

To confirm the effectiveness of the liquid paraffin, a series of parallel experiments have been carried out via heating silica gels with identical compositions in open vessels and sealed vessels (a number of pinholes on the top of the vessels) at different temperatures (40−70 °C) to examine their macromorphology. At last, catastrophic cracks happened to the gels, and the causes of the cracking have been mentioned above. These results indicate the importance of liquid paraffin to the process.

One question that remains is whether the paraffin penetrates into the silica framework and stays inside the gel after the thermal treatment. For this consideration, an FTIR spectrum was measured for the as-synthesized mesostructured silica monolith prepared by the liquid-paraffin-medium protected solvent evaporation method. The residual liquid paraffin on the surface of the products was removed and cleared by using filter paper. The characteristic groups of paraffin, $-(CH_2)_x-$, possess a rocking adsorption at 720 cm^{-1}.[26] However, this peak is not detected in the spectrum (Figure 6), indicating that there is little paraffin in the material. The reason may be attributed to the thermal treatment that makes the silica gel highly polymerized to make the pores well cross-linked. As a result, the paraffin used in this method acts only a macromorphology protector, and does not change the chemical composition of the final mesostructured silica monolith.

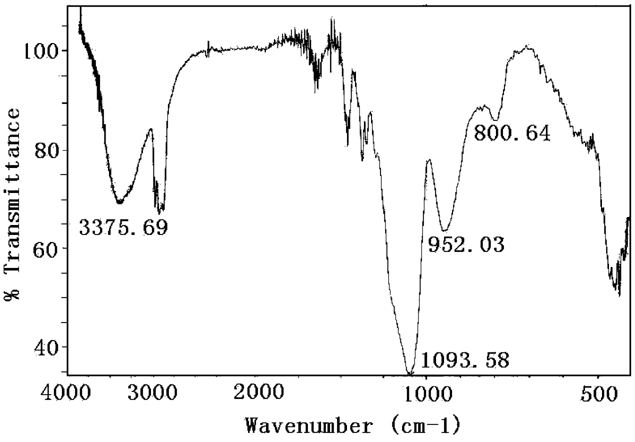

Figure 6. FT-IR spectrum of the as-synthesized mesostructured silica monolith prepared by liquid-paraffin-medium protected solvent evaporation method.

The processing time to obtain a crack-free mesostructured silica monolith depends much on the volume of liquid paraffin (in our experiment, 2−3 mm is appropriate) and the heating temperature (for example, 18 h for 60 °C and 8 h for 90 °C with a 2−3-mm-thick layer of paraffin), with the purpose of complete removal of solvent. Heating temperature higher than 90 °C is not recommended because the high temperature (>90 °C) results in damage of both the mesostructure and the macromorphology. Using an appropriate volume of liquid paraffin is also important to the preparation process. Insufficient liquid paraffin cannot operate as the “protector”, whereas too much liquid paraffin prolongs the processing time due to more difficulty of solvent evaporation without obviously increasing the integrity of the monolith and regularity of the mesostructure.

The mesostructured silica monoliths can be prepared at a wide range of copositions of 1 P123/5 C_2H_5OH/1.16−3.47 TEOS/0.05−0.8 H_2O/0.007−0.056 HCl (mass ratio). Among these changeable compositions, the mass ratio of TEOS to P123 is the most important factor to the ultimate mesostructured regularity of monoliths. Highly ordered mesostructure can be formed only in the range of 1.88−2.32/1.

Colored mesostructured silica monoliths doped with metal ions can be synthesized by simply adding metal salts (such as ferric nitrate, cupric nitrate, and cobaltous nitrate) into the initial reaction mixture. As-synthesized block copolymer−silica monoliths show various colors in accordance with the corresponding slovation metal ions doped within them, for example yellow for Fe^{3+}, green for Cu^{2+}, and pink for Co^{2+} (Figure 2). XRD patterns (Figure 7) confirm that the doping monoliths still have a highly ordered mesostructure. TEM and XRD measurements all show that the mesostructured

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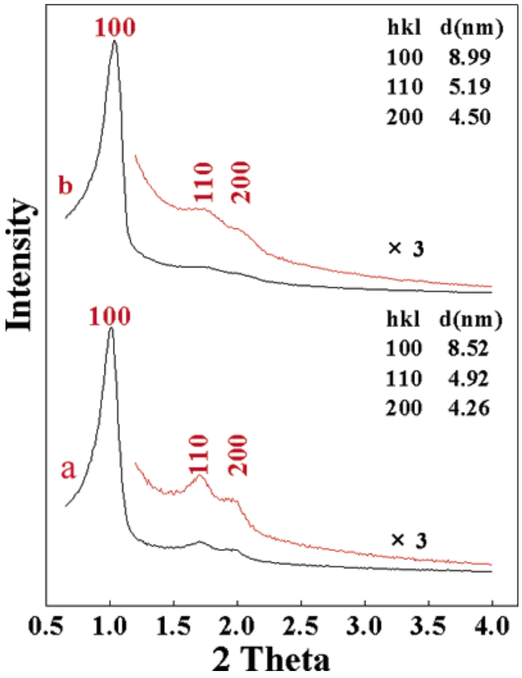

Figure 7. Powder-XRD patterns of calcined mesoporous silica monoliths doped with (a) Cu^{2+} and (b) Co^{2+}. For the initial reaction mixture, the mass ratio of P123 to $Cu(NO_3)_2{\cdot}3H_2O$ or $Co(NO_3)_2{\cdot}6H_2O$ are both 1:0.06.

ordering regularity can be a little improved by the doping of a small amount of transition metal ions. It is not strange and can be easily explained from an assisted assembly by the transition metal complexes formed by the interaction of metal ions with the —O— groups of the copolymers, as previously reported.[27,28]

Conclusions

We demonstrated a liquid-paraffin-medium protected solvent evaporation method to yield a transparent, crack-free macroscopical morphology, and highly ordered mesostructured silica monolith. By accelerating the evaporation process of silica gel with inert medium liquid paraffin under heating conditions, the processing period is shortened to within 8 h. In addition, metal ions can be easily doped into pure silica monoliths. Monolithic materials prepared based on this liquid-paraffin-medium protected solvent evaporation method are excepted to have positive implications for their applications in optics and separations.

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