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Preparation and Characterization of (SBA-15)-(*p*-Methyldibromoarsenazo) Composite Material

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Mesoporous SBA-15 molecular sieve was prepared under a strong acidic condition by using triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol) as template. The composite material (SBA-15)-(*p*-methyldibromoarsenazo) was prepared by embedding *p*-methyldibromo-arsenazo into the pores of the SBA-15 by liquid grafting method. By means of chemical analysis, powder X-ray diffraction, Fourier transform infrared spectroscopy, low-temperature nitrogen adsorption-desorption technique, UV-Vis solid state diffuse reflectance absorption spectroscopy and luminescence studies, the composite material was characterized. The results showed that the guest was sucessfully encapsulated in the channels of the SBA-15.

Key Words: Composite material, Mesoporous SBA-15 molecular sieve, *p*-Methyldibromo-arsenazo, Characterization.

INTRODUCTION

The molecular sieve is a class of materials which have nanometer scale porous channels. It has been widely used in catalysis, adsorption and host-guest chemistry field[1,2], *etc*. The mesoporous molecular sieve is special suitable as nano templates to construct nanostructures due to its large nanometer scale porous channels. The study where the porous channels of molecular sieves were used as host to incorporate guest materials caused scientists great interest recently[2-6]. The non-ionic surfactant poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) triblock copolymer was used as template to synthesize mesopore material SBA-15 under the acidic condition, which is different from MCM-41. It is a great breakthrough in the research of synthesis of host silica mesopore material[7,8]. SBA-15 has a high order of plane hexagonal phase and a porous material is obtained after calcination at 550 ºC in air. The organic template can also be removed by extraction method. Pore size ranges from 4.6 to 30 nm and pore wall thickness of the molecular sieve is 3.1-6.0 nm. The thermal stability of SBA-15 is higher than 900 ºC and there are a large number of silanol groups on its inner surface. It has a higher thermal

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stability (high temperature resistance) and water stability (cold water or hot water) after removing the template. The different size of SBA-15 can be prepared by a change of template and preparation conditions. It followed the outstanding characteristics. The synthesis is easy. The channels present high order of hexagonal phase. The pore size distribution is very narrow. It has large specific surface area and rich surface chemical properties, *etc*. SBA-15 has obvious advantages compared to other mesopore molecular sieve. For example, it has higher thermal stability and hydrothermal stability, larger pore size, thicker pore wall and much irregular small pore penetrating pore wall. Due to the above advantages, the mesoporous silica material SBA-15 was synthesized by triblock copolymer as directing agent becomes a research focus recently. *p*-Methyldibromoarsenazo (DBM-ASA) {2-[(2-arsenoxylphenylazo)-7-(2,6-dibromo-4-methylphenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid]} is an asymmetric arsenazo type derivatives of chromotropic acid, belonging to a high sensitive reagent which has been used in the determination of rare earth elements in acid medium[9]. Its structural formula is shown as Fig. 1.

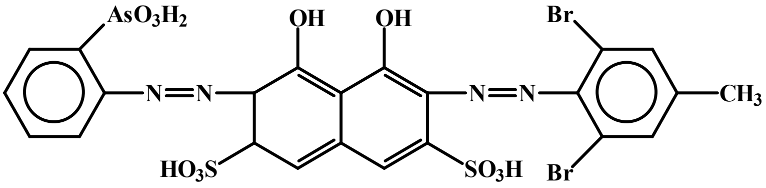

Fig.1. Structure of *p*-methyldibromoarsenazo

Dye molecules have agglomeration tendency. In solution, the agglomeration of dye molecules can occur even under the condition of very small concentration. After agglomeration, the excitation energy of a dye molecule is easy to release by thermal relaxation. Therefore, the optical active performance can not be incarnated. If dye molecules can be dispersed into the channels of a molecular sieve, this can avoid the agglomeration of dye molecules and thus the dye molecules exhibit a good optical active performance such as laser. In this study, SBA-15 molecular sieve was used as host to prepare (SBA-15)-(DBM-ASA) composite material by means of liquid grafting method[6]. The prepared material was characterized by chemical analysis, powder XRD, Fourier transform infrared spectroscopy, N_2 adsorption-desorption, ultraviolet-visible (UV-Vis) solid diffusion reflectance absorption spectra. In addition, luminescence phenomenon of the material was observed.

EXPERIMENTAL

Triblock copolymer, ploy(ethyleneglycol)-block-poly (propyleneglycol)-block-ploy(ethyleneglycol) (average molecular weight 5800, Fluka); Tetraethyl orthosilicate (TEOS, Shanghai Lingfeng Chemical Co., Ltd., China, A.R.); *p*-methyldibromoarsenazo (DBM-ASA, East China Normal University, China, A.R.), hydrochloric acid (Beijing Chemical Plant, China, A. R.), deionized water.

Preparation of (SBA-15)-(DBM-ASA) composite material: 2 g of Amphiphilic triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was dispersed in 15 g of water and 60 g of 2 mol/L hydrochloric acid solution while stirring, followed by the addition of 4.25 g of tetraethyl orthosilicate to the homogeneous solution under stirring. The initial optimum molar ratio was (Template: TEOS:HCl:H_2O=1:59:348:2417).This gel mixture was continuously stirred at 400 ºC for 24 h and crystallized in a Teflon-lined autoclave at 100 ºC for 2 d. The solid product was flitered, washed with deionized water and dried in air at room temperature, The material was calcined in static air at 550 ºC for 24 h to decompose the triblock copolymer. The white powder, mesoporous silica SBA-15 molecular sieve was obtained. Before SBA-15 was used for the preparation of composite material, SBA-15 was dehydrated at 400 ºC for 3 h. Then, SBA-15 was placed into 60 mL of 1.0×10^{-4} mol/L *p*-methyldibromoarsenazo solution with stirring for 48 h at room temperature. The resulting solid was recovered by filtration, extensively washed with deionized water and dried at 60 ºC for 6 h. The composite material prepared was disigned as (SBA-15)-(DBM-ASA).

Sample characterization: Determination of silicon in molecular sieve was determined by molybdosilicate bule photometry[10] on a 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd, China). Power X-ray diffraction (XRD) measurement was carried out on a D5005 diffractometer (German Siemens Company) with Cu-Kα radiation operating at 30 kV and 20 mA for small angle from 0.4° to 10° (2θ) with 0.02 step size. Physical adsorption of nitrogen was performed on a Micromeritics ASAP2010M volumetric adsorption analyzer (American Mike Company) at 77 K. A sample was degassed in vacuum at 573 K for 12 h before measurement. The data was calculated according to BdB (Broekhoff and de Boer) model[11]. The surface area was determined by the BET method[12] and the pore size distribution was determined using the BJH method[13]. The infrared spectra were recorded on a Nicolet 5DX-FTIR spectrometer (American Mike Company) using KBr pellet technique. The UV-Vis absorption spectra were measured using a Hitachi UV-4100 spectrometer (Japan). The luminescence measurements were performed on a SPEX-FL-2T-2 (American SPEX Company) double grafting fluorometer at a room temperature of 25 ºC.

RESULTS AND DISCUSSION

Elemental analysis: The content of SBA-15 in the (SBA-15)-(DBM-ASA) composite material was 96.8 % (in mass), which was determined by molybdosilicate blue photometry. The content of *p*-methyldibromoarsenazo in the prepared nanocomposites material was 3.11 % (in mass) determined by difference subtraction method.

Powder XRD analysis: Fig. 2 shows the XRD pattern of SBA-15. There are four diffraction peaks over the small angle range of 0.5°-2.5°. The sample exhibits a prominent diffraction peak at 0.88°, corresponding to the (100) peak of the SBA-15. The other three peaks are relatively weak but clear for (110), (200) and (210) diffraction peaks. This is consistent with the XRD characteristic pattern[5] of the SBA-15. It shows that the preparation of SBA-15 was very successful and has a very high order. Three diffraction peaks appear in curve B of the figure, which correspond to the (100), (110) and (200) diffraction peaks of the SBA-15 sample. However, its intensity reduces to some extent. At the same time, the (210) diffraction peak has disappeared. This indicates that the crystallinity and order degree of the composite material decreased but the structure of the SBA-15 molecular sieve is still remained after the incorporation of *p*-methyldibromoarsenazo into SBA-15.

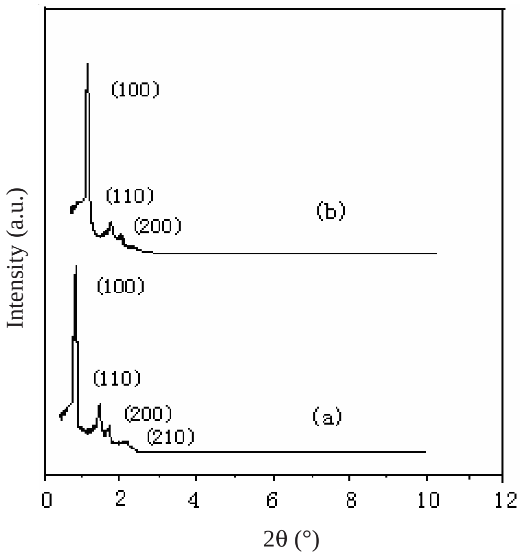

Fig. 2. XRD pattern of the samples: (a) SBA-15; (b) (SBA-15)-(DBM-ASA)

Fourier transform infrared spectra: Fig. 3 shows the Fourier transform infrared spectra of the samples for comparison of the infrared spectra among SBA-15, (SBA-15)-(DBM-ASA) and DBM-ASA over the region of 1400-400 cm^{-1}. In Fig. 3a, the IR spectrum of the pure SBA-15 exhibits a Si-O-Si bending vibration peak at 466 cm^{-1}, a symmetrical stretching vibration peak of the tetrahedral SiO_4 at 802 cm^{-1}, a bending vibration band at 962 cm^{-1} and an asymmetric stretching vibration of Si-O-Si at 1090 cm^{-1}. The IR spectrum of the (SBA-15)- (DBM-ASA) (Fig. 3b) shows the similar absorption bands to those of the SBA-15, but the characteristics band of DBM-ASA is not observed. This indicates that the framework of the (SBA-15)-(DBM-ASA) is still remained intact and DBM-ASA has already been dispersed in the pores of the SBA-15 and no collected DBM-ASA existed. For (SBA-15)-La_2O_3[6], the similar phenomenon was also observed. The SBA-15 provided ordered pore channels and is suitable for the confinement of quantum dots in the channels. Therefore, the DBM-ASA existed as the quantum dot in the channels of SBA-15 and it did not exist in the form of congeries or nanocrystalline.

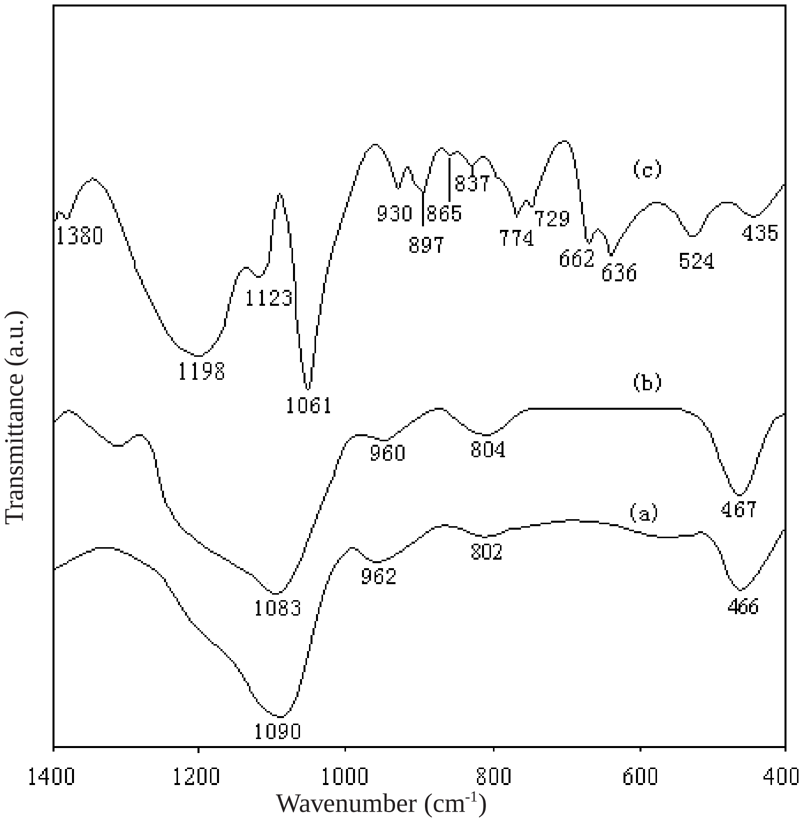

Fig. 3. Infrared spectra of the samples: (a) SBA-15; (b) (SBA-15)-(DBM-ASA); (c) DBM-ASA

Low-temperature nitrogen adsorption-desorption isotherms: The low temperature nitrogen adsorption-desorption isotherms and pore size distribution patterns of the samples are shown in Figs. 4 and 5, respectively. It can be seen that all the nitrogen adsorption/desorption isotherms are of type IV in nature as IUPAC classification and exhibiting a H1-type broad hysteresis loop which is characteristic of mesoporous materials with narrow pore size distribution. The adsorption branch of each isotherm showed a steep increase in the relative pressure (P/P_0) range of 0-0.6, the molecules of nitrogen adsorb on the inner surface of mesoporous pores as nonolayer. A sharp inflection in the relative pressure (P/P_0) range of 0.6-0.8 showed and the increase suggests the characteristic of capillary condensation within uniform pores and the ordered mesoporous channels are still retained. When the relative pressure (P/P_0) is higher than 0.8, the capacity of absorption changes little from the relative pressure. This is because the absorption gradually reached saturation. The relative pressure of the (SBA-15)-(DBM-ASA), at which a break took place, is smaller compared to the SBA-15. This implies that part of the pore space has been occupied by the DBM-ASA and the pore size reduced.

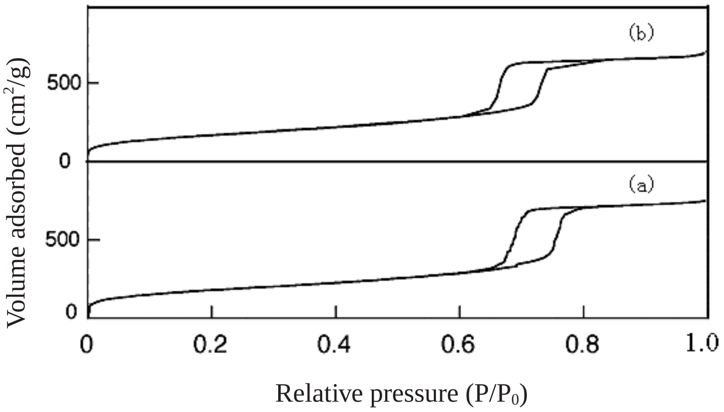

Fig. 4. Low temperature nitrogen adsorption-desorption isotherms of the samples: (a)SBA-15; (b)(SBA-15)-(DBM-ASA)

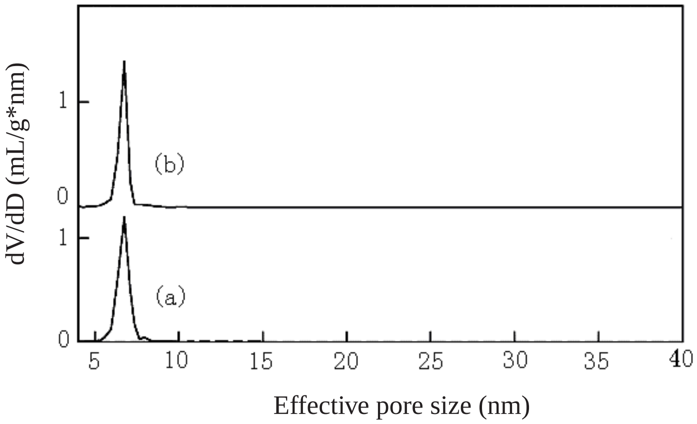

Fig. 5. Pore size distribution patterns of the samples: (a)SBA-15; (b) (SBA-15)-DBM-ASA)

Fig. 5 shows the porous size distribution patterns of the samples. It can be seen that SBA-15 and (SBA-15)- (DBM-ASA) have regular, well-defined one-dimensional pore channel systems. It indicates that the samples possess one-dimensional array of uniform mesopore with narrow pore size distribution.

The pore stucture parameters of samples are shown in Table-1. The unit cell parameter, crystal face spacing and the wall thickness increase a little due to the DBM-ASA adhering to the inner surface of the SBA-15. However, the pore volume, the pore diameter and the BET specific surface area decreased, showing that the DBM-ASA has been incorporated into the channels of the molecular sieve and occupied the space of the channels.

TABLE-1
PORE STRUCTURE PARAMETERS OF THE SAMPLES

Sample	Crystal face spacing/ $d_{(100)}$ (nm)	Unit cell parameter/ a_0^a(nm)	BET surface area ($m^2\ g^{-1}$)	Specific pore volume[b] ($cm^3\ g^{-1}$)	Pore size[c] (nm)	Wall thickness[d] (nm)
SBA-15	9.56	11.04	662	1.14	6.77	4.27
(SBA-15)-(DBM-ASA)	10.27	11.86	634	1.08	6.35	5.51

[a] $a_0 = \frac{2}{\sqrt{3}} d_{100}$; [b] Pore volume is BJH adsorption cumulative volume of pores; [c] Pore size is calculated from the adsorption branch; [d] Wall thickness is calculated by (a_0 - pore size).

UV-Vis solid state diffuse reflectance spectra: The UV-Vis diffuse reflectance spectra of the samples are shown in Fig. 6. There is no absorption from SBA-15 molecular sieve in the range of the wavelength studied. However, the absorption of (SBA-15)-(DBM-ASA) composite material displayed. The onsets of absorption appeared at 225 and 574 nm, respectively, which presented a blue-shift compared to the onsets of absorption 346 and 692 nm of *p*-methyldibromoarsenazo due to the increase in the energy of the forbidden band of DBM-ASA. This phenomenon can be attributed to the result from a stereoconfinement effect of the channels of the SBA-15. This further showed that *p*-methyldibromoarsenazo has located in the channels of the SBA-15 molecular sieve. Since the SBA-15 has a huge inner surface area, it provides the dye molecules encapsulated in the channels of SBA-15. This makes dye molecules maintain certain distance, making them easily be adsorbed on the SBA-15 pore wall in the form of monomer. The solid state diffuse reflectance absorption spectra illustrated that *p*-methyldibromoarsenazo was encapsulated and confined in the channels of the SBA-15 and presented in a highly dispersed state. The Si-OH in SBA-15 channels and the hydroxyl of DBM-ASA interact in a way of hydrogen bond.

Luminescence spectra: Fig. 7 is excitation and emission spectra of (SBA-15)-(DBM-ASA) composite. SBA-15 itself does not have luminescence character, but the (SBA-15)-(DBM-ASA) has luminescence character due to the assembly of DBM-ASA. In solution, dye molecules agglomerate even under the condition of very small concentration. After agglomeration, the excitation energy of dye molecules is very easy to release by thermal relaxation. Therefore, the optically active performance can not be showed. The distance of dye molecules are far in mesoporous

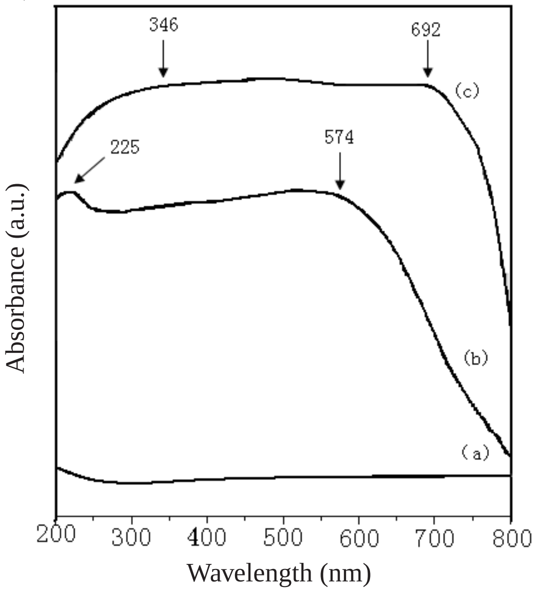

Fig. 6. Solid state diffuse reflectance absorption spectra of the samples:(a) SBA-15; (b) (SBA-15)-(DBM-ASA); (c) DBM-ASA

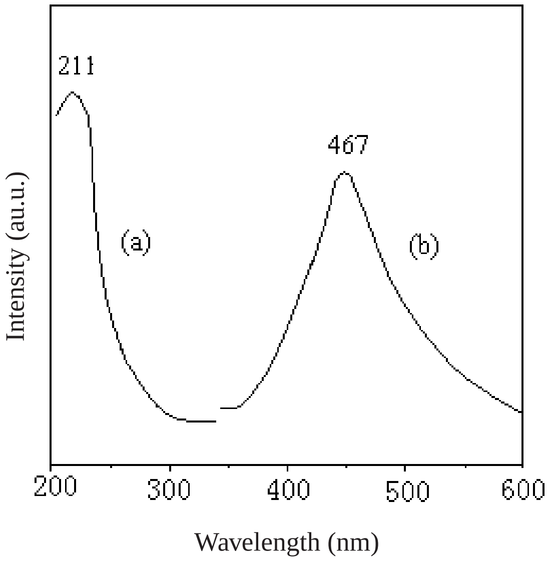

Fig. 7. Luminescence spectra of the (SBA-15)-(DBM-ASA) sample: (a) excitation spectrum; (b) emission spectrum

SBA-15 and interaction is weaker. The contribution of fluorescence quenching is relatively small. As porous silica has a huge specific surface area to provide enough space for the dye molecules enchased in it, this makes dye molecules keep a certain distance among them and makes DBM-ASA be adsorbed on the channels of mesoporous SBA-15 as a monomeric form. The nanometer scale channels of SBA-15 limited the interaction between dye molecules and this interaction often occurs in a solution or powder. The result suggests that the interaction between the dye molecules filled in the SBA-15 is very weak and the molecules are difficult to aggregate and form oligomer. Thus, the material exhibits the luminescence properties similar to those of single molecules. In porous silica, dye molecules basically exist in a monomeric form. The dye molecules transits from ground states to different energy level when irradiated by exciting light. The activity of molecules is limited by pore size and the rotational energy weakened greatly. Because the non-radiation compound resulted from rotational relaxation decreases, at last the dye molecule from different vibrational level of excited states transits to the different vibration levels of ground state and emits fluorescence. Thus, SBA-15 may be a good carrier and has a potential application prospect in development of solid-state dye laser. The (SBA-15)-(DBM-ASA) composite material may be hopefully applied as laser material.

In conclusion, in this article SBA-15 was prepared by a hydrothermal method and the (SBA-15)-(*p*-methyldibromoarsenazo) composite material was prepared by means of liquid grafting method. The effectiveness of the preparative method was characterized by powder XRD, infrared spectroscopy, low temperature N_2 adsorption-desorption technique, proving that the guest molecules were successfully encapsulated in the channels of the SBA-15 molecular sieve.

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