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Self-assembly directed synthesis of tubular conducting polymer inside the channels of MCM-41

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Abstract : Diphenyl amine (DPA) was polymerized inside the channels of the mesoporous silica (MCM-41). MCM-41 (C) and MCM-41 (D) were prepared with cetyltrimethyl ammonium bromide (CTAB) and dodecyltrimethyl ammonium bromide (DTAB), respectively and used as hosts. Initially, the self assembly of DPA inside the pores of MCM-41 was made in β-naphthalene sulfonic acid (NSA) medium and subsequently poly (diphenylamine), PDPA was formed by oxidative polymerization. N_2 adsorption-desorption measurements of PDPA loaded MCM-41 (C) and MCM-41 (D) show variations in pore volume and surface area between them. A tubular form of poly (diphenylamine), PDPA was envisaged to form in the pores of MCM-41 and supported by high resolution transmission microscopy. The presence of PDPA inside the channel of MCM-41 was further confirmed by FTIR spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction.

Key words : Mesoporous silica (MCM-41), poly (diphenylamine), self-assembly

1. Introduction

Studies have been recently focused on the possibility of alignment of the encapsulated molecules into the host channels for making nanostructured organic-inorganic composites. Mesoporous materials can accommodate polymer chains with larger backbones. Mesoporous molecular sieves of MCM-41 type with a hexagonal packed array of channels and a narrow pore size distribution[1,2] offer unique opportunities for the preparation of new nanostructured composite materials. The interesting physical properties like high specific surface area (1000 $m^2\ g^{-1}$), specific pore volume (0.5 $cm^3\ g^{-1}$) and a high thermal stability are well suited to accommodate host molecules. The straight channels ensure that the internal surface is readily accessible and accommodate guest molecules.[3] The properties of MCM-41 also provide basis for making use in applications such as heterogeneous catalyst, biomedicine, separation etc.[4-11] Applications related to mesoscopic devices with ordered arrays of metal or semiconductor quantum particles[12] are also known.

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Replica polymers, metals, and semiconductors have been prepared with 1D and 2D porous structures within the pores of zeolites, mesoporous silicates, porous polymer membranes, anodic alumina, and clays.[13-24] Host properties desired for accommodating a conjugated polymer are present in the self-assembled porous inorganic materials. Microporous materials, such as zeolites, have been used to encapsulate polypyrrole,[25] polythiophene[26] and polyaniline.[27] Mesoporous silica based materials may be readily modified as there are many accessible surface hydroxy groups. It has been found that 26-30% of all Si atoms in MCM-41 bear a surface hydroxyl group.[28] The surface derivatization can proceed by well developed silane chemistry.[29] Unger *et al.*[30] prepared polystyrene, poly (methyl methacrylate) and Karge[31] reported polyvinyl acetate in the channels of MCM-41.

However, the process of making nanostructured polymer within the pores of MCM-41 has not been understood clearly. Though monomer could be readily loaded into MCM-41 through sublimation or any other processes, the subsequent use of base of sufficient strength was not possible. Aqueous bases can attack and dissolve the host. Non aqueous bases can solubilize the monomer and extract it from the pores before polymerization could occur.

Nanostructured materials can be produced inside the pores of MCM-41 through creation of a self-assembled environment for the monomer inside the pores and subsequent polymerization of such self-assembled monomeric units. It is known that a weak aromatic organic base or an amphiprotoic molecule can have donor-acceptor interactions with the silica based hosts. The composition and structure of donor-acceptor association depends on the nature of the adsorption site, whether it is a strong or weak acid or base, or Bronsted or Lewis acid.

Meixiang Wan *et al.*[32] synthesized tubular poly(pyrrole) using template molecules. Microtubes of PANI and PPY were produced in the presence of β-napthalene sulfonic acid (NSA) as a dopant[33-35] through conventional synthesis. A tubular conducting polymer can be prepared inside the pores of MCM-41 by creating a self-assembly of monomer inside the pores. It is expected that tubular conducting polymer can be obtained if one can select a suitable surfactant that can act as a template and dopant, simultaneously.

In the present study, we are reporting the synthesis of tubular form of poly (diphenylamine), PDPA inside the channels of MCM-41. Micelle of DPA and NSA were generated inside the pores of MCM-41 through self-assembly of DPA with the dopant, NSA. Insitu polymerization of self-assembly structure inside the pores resulted tubular PDPA inside the pores of MCM-41. Channels of MCM-41 (C) or MCM-41 (D) prepared with dodecyltrimethyl ammonium bromide (DTAB) or cetyltrimethyl ammonium bromide (CTAB) were utilized for the preparation of tubular PDPA. Evidences were obtained for the presence of PDPA inside the pores through N_2 adsorption-desorption measurements, FTIR spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Ammonium persulphate (APS), β-napthalene sulfonic acid (NSA), diphenylamine (DPA), tetraethyl orthosilicate (TEOS), triethyl amine (TEA) and 1-bromodecane were purchased from Sigma-Aldrich (Germany). Bromodecane trimethyl ammonium bromide (DTAB)[36] and cetyltrimethyl ammonium bromide (CTAB) were prepared and used.[37] For example, DTAB was prepared by the reaction of 1-bromodecane with triethyl amine.

MCM-41 was prepared as follows: The surfactant, CTAB or DTAB was diluted by addition of water, ammonia and ethanol successively till to result a clear solution. The surfactant solution was then added drop wise to an aqueous solution of TEOS and stirred for 210 min. A gel was obtained. The gel was calcined in an oven at 600°C. We designate the calcined materials as MCM-41(D) or MCM-41(C) based on the surfactant used for the synthesis.

2.2 Preparation of tubular PDPA

0.5 g of MCM-41(C) or MCM-41(D) was immersed in a solution of DPA (30 mmol) in NSA and kept for 24 h. The solid material was filtered, washed with water and dried to obtain DPA-NSA loaded MCM-41, designated as MCM-41(D-DPA-NSA) or MCM-41(C-DPA-NSA). The DPA-NSA loaded MCM-41(C) or MCM-41(D) sample was added to a solution of 0.5 M APS and stirred for 2 h at 5ºC. A dark green colored precipitate, NSA doped poly (diphenylamine), PDPA-NSA, loaded in MCM-41, designated as MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA) was obtained.

PDPA formed inside the channels of MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA) was treated with ammonia for 24 h. The blue colored precipitate (neutralized PDPA) was dried in vacuum and designated as MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA). The blue powder was put in 20 mL of DMF and stirred for 48 h. The un-dissolved white mass (MCM-41) was filtered, washed and dried in vacuum dryer. The blue colored solution contained neutral PDPA extracted from pores of MCM-41.

2.3. Characterization

Pristine MCM-41(C), pristine MCM-41(D), MCM-41 (C-DPA-NSA), MCM-41(D-DPA-NSA); MCM-41(C-PDPA-NSA) and MCM-41(D-PDPA-NSA) were subjected to N_2 adsorption-desorption measurements. Measurements were carried out using a quantachrome Autosorb-1 with nitrogen as adsorbate at 77K. Samples were characterized by FT-IR spectroscopy (Perkin-Elmer Lambda 9N-1062 spectrometer). Thermo gravimetric analysis was carried out using a TA instrument 951 at a rate of 10ºC min^{-1} in N_2 atmosphere. Samples were degassed for 12 h at 300ºC in vacuum before measurement. X-ray diffraction patterns were collected employing a D_8-Advanced Bruker AXS diffractometer using CuKα_1 radiation (λ=1.54056 Å) with (θ-2θ) geometry using a scintillation counter (low-angle region). The morphology of the samples was examined by scanning electron microscopy (SEM) (Hitachi, S-4200).

3. Results and Discussion

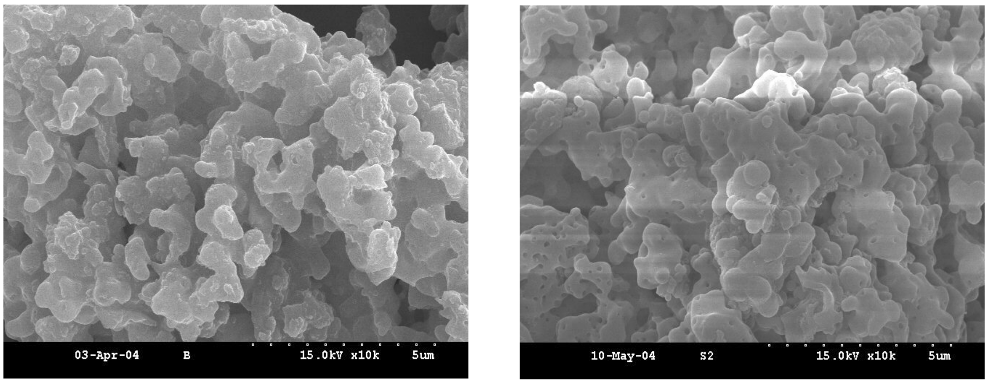
N_2 adsorption-desorption measurements clearly provide evidences for the formation of PDPA inside the channels of MCM-41. The pore volume and surface area were found to decrease from that of pristine MCM-41 upon confining PDPA in MCM-41 (*Table* 1). In both cases of MCM-41, the decrease in surface area and pore volume were noticed after entrapping PDPA inside the channels of MCM-41. The distinct decrease in pore volume and specific surface area informed the presence of PDPA inside the pores. Similar decrease in pore volume and specific surface area has been earlier noticed[37-39] for the entrapment of polymer or enzymes in the pores of mesoporous materials.

However, there are differences in the extent of decrease in specific surface area and pore volume on loading PDPA between the MCM-41(C) and MCM-41(D). Polymerization was performed under similar conditions with these two MCM-41 materials. A decrease in 87% of the surface area and 91% of pore

Table 1. BET surface area[a], pore volume[a] of MCM-41 confined with tubular poly (diphenylamine) and pristine MCM-41

Sample	Specific surface area (m^2/g)	Pore volume (m L /g)
MCM-41(C) pristine	0.86	23.0×10^{-3}
MCM-41(C-PDPA-NSA)	0.11	3.04×10^{-3}
MCM-41(C)-after removal of PDPA	0.78	30.9×10^{-3}
MCM-41(D) pristine	17.3	59.3×10^{-3}
MCM-41(D-PDPA-NSA)	9.5	11.5×10^{-3}
MCM-41(D)-after removal of PDPA	12.8	58.0×10^{-3}

[a]Determined by surface area and pore size analyzer (BJH).



(a) (b)

Fig. 1. SEM morphology of MCM-41(C-PDPA-NSA) (a); MCM-41(C)-after removal of PDPA (b).

volume was observed on forming PDPA inside channels of MCM-41(C) (*Table* 1). In contrast to this, a decrease of 50% surface area and 81% pore volume was noticed with MCM-41(D). These are quite interesting observations as noticed in our earlier papers.[40-41] If one considers PDPA formation inside the pores of MCM-41 through a mechanism based on conventional polymerization, such a difference should not occur. Otherwise, in both cases, the pores should be completely filled with PDPA or should be filled in an equivalent extent. On the contrary, there is a difference in extent of decrease in pore size and pore volume upon loading PDPA. This informs that PDPA formation takes place through a different mechanism to result a different type of PDPA.

We envisage the formation of tubular PDPA inside the pores of MCM-41 which can show dependence on the size of pores. Polymerization of DPA was done by initial sorption of DPA inside the pores of MCM-41 in a medium (NSA) that would provide conditions for self-assembly of DPA inside the pores of MCM-41. On subsequent polymerization of self-assembly of DPA through chemical oxidative polymerization can result tubular type PDPA.

The formation of self-assembly of DPA inside the MCM-41 pores is detailed in our previous publications.[40-41] The formed tubular PDPA could be effectively removed by the method described in the experimental section. N_2 adsorption-desorption measurements after the removal of PDPA from MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA), show that pore volume and surface area were regenerated nearly to the value close to pristine MCM-41(C) or MCM-41(D), respectively. PDPA extracted from MCM-41 shows tubular morphology with an average diameter of 20-30 nm and a length of 130-180 nm.

Fig. 1 represents the SEM photograph of MCM-41 loaded with PDPA. The spheres representing the MCM-41 are held tightly in MCM-41(C-PDPA-NSA) on comparing with pristine MCM-41. This may probably due to the interconnected tubular PDPA network. Otherwise, MCM spheres are threaded into tubular PDPA in a similar fashion to molecule necklace type frameworks.[40-42] The spheres became scattered after the removal of PDPA from the pores of MCM-41(C) (*Fig.* 1).

X-ray diffraction analysis, FTIR spectroscopy and TGA results further provide confirmation for the presence of PDPA inside the pores of MCM-41.

X-ray diffraction of MCM-41(C)-PDPA and MCM-41 (D)-PDPA show additional peaks at 22° and 20.4° *(Fig.* 2) with a concomitant decrease in the peak corresponding to crystalline peak of MCM-41(inset). The presence of additional peaks (22° and 20.4°) over the crystalline peak of MCM-41 corresponds to PDPA (*Fig.* 2)

Evidences could also be seen for the entrapment of PDPA inside the MCM-41 pores from the comparison of position of few important bands in the

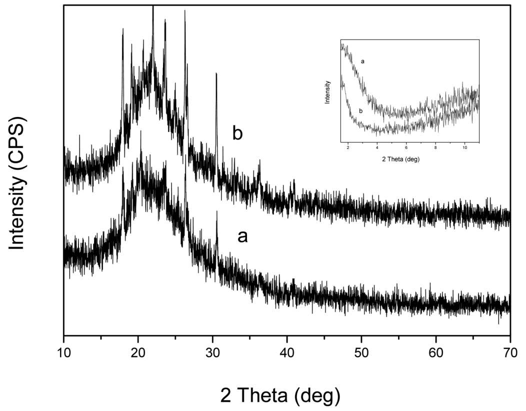


Fig. 2. XRD pattern of MCM-41 (D-PDPA-NSA) (a); MCM-41(C-PDPA-NSA) (b).

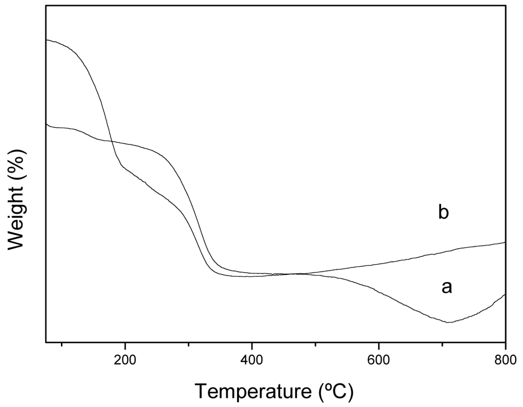


Fig. 4. Thermogram of MCM-41(D-PDPA-NSA) (a); MCM-41(C-PDPA-NSA) (b).

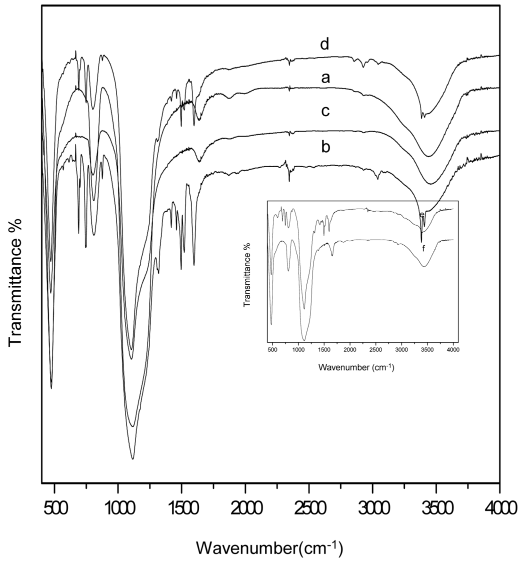


Fig. 3. FTIR spectra of pristine MCM-41(D) (a); MCM-41 (D-PDPA) (b); pristine MCM–41(C) (c); MCM-41 (C- PDPA) (d); MCM-41 (D-after removal of PDPA) (e) and MCM-41 (C-after removal of PDPA) (f).

FTIR spectra (*Fig.* 3) of MCM-41 (PDPA-NSA) and pristine MCM-41. There are characteristic bands in the region 1500 cm^{-1} and 1600 cm^{-1} (*Fig.* 3) which represent the PDPA in the MCM-41 pores. The bands around 1500 cm^{-1} and 1150 cm^{-1} represent the diphenosemiquinone imine and diphenoquinone imine structures of PDPA respectively.[43] These bands are virtually absent in pristine MCM-41. C-H out of plane bending vibration of substituted benzene rings could also be seen.[44] Similarly, the band around 3400 cm^{-1} for PDPA confined in MCM-41 (*Fig.* 3, inset), overlaps with the band around 3400 cm^{1} for the hydroxyl group of silanol units.[45] The N-H bending vibration in PDPA overlaps with Si-O stretching overtone of MCM-41. The characteristic bands of PDPA showed decrease in intensities after removal of the PDPA from MCM-41 pores (*Fig.* 3, inset).

Thermogram of MCM-41 (C-PDPA-NSA) (*Fig.* 4) clearly informs the presence of PDPA. While pristine MCM-41 exhibit thermal stability beyond 250^{0}C, thermogram of MCM-41(D-PDPA-NSA) shows the thermal transitions associate with PDPA. [45]

4. Conclusions

Tubular poly (diphenylamine), PDPA was formed inside the channels of MCM-41 by creating the self assembly of monomer, diphenylamine, in the pores of MCM-41 prior to polymerization. The pore size variations after entrapping PDPA provide evidence for the formation of tubular PDPA inside the channels of MCM-41. The induction of tubular structure to conducting polymer inside the pores of rigid hosts can cause confinement effect to the polymer and that can ultimately modify the electronic properties. We are extending our research activities in these interesting aspects.

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