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A novel self-assembly approach to form tubular poly(diphenylamine) inside the mesoporous silica

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Abstract

MCM-41 materials were synthesized using alkyl(decosane, dodecyl)trimethyl ammonium bromide as structure directing surfactants. X-ray diffraction (XRD) analysis and nitrogen adsorption measurements reveal that the pores are hexagonal with tunable textural properties through the choice of surfactant and experimental condition. Poly(diphenylamine), PDPA was entrapped into the pores of MCM-41 by initial sorption of diphenylamine (DPA, monomer) in a medium (napthalein sulfonic acid) that provides self-assembling of DPA inside the pores and subsequent oxidative of polymerization with peroxydisulphate. Clear presence of an additional peak (around 9–10°) in XRD pattern for the DPA loaded MCM-41 provides evidence for self-assembled structure. Upon polymerization the self-assembly of DPA molecules resulted tubular PDPA inside the pores of MCM-41. PDPA thus formed shows different electronic property than the PDPA prepared by conventional method. XRD and FTIR spectroscopic analysis of PDPA loaded MCM-41 clearly informs that PDPA are entrapped in channels of MCM-41.

Keywords: Mesoporous silica (MCM-41); Napthalein sulfonic acid (NSA); PDPA

1. Introduction

The invention of a new family of mesoporous silicate molecular sieves [1–3] has attracted worldwide interest in many areas of physical, chemical and engineering sciences. In the early 1990s, Mobil scientists as well as Japanese researchers [4,5] reported the first successful synthesis of novel mesostructured materials. The synthesis of such mesoporous materials involves the use of a self-assembled molecular aggregate or supramolecular assembly of surfactant molecules such as cetyl trimethyl ammonium cation as the structure-directing agent. MCM-41, one of the mesoporous materials, is a porous amorphous silica material with a hexagonal honey comb structure and can be prepared with controllable pore diameters by judicious manipulation of conditions of synthesis [6].

Many synthetic modifications have then been formulated and attempted to obtain optimum surface area, well-defined regular pore shape, narrow pore size distribution, large pore volume, and tunable pore size, in conjunction with the high thermal, hydrothermal, chemical and mechanical stability for MCM-41. Such materials subsequently find applications in adsorption and separation [7], ion exchange [8] and polymorphic structure [9–12]. Various templates such as microemulsion [13], block copolymers [14], latex particles [15], colloidal crystals [16], sponge-like polymer gels [17] and bacterial superstructures [18] have been tried for controlling the periodicity and regularity of the porous structure in MCM-41. Also, studies have been directed to tune the pore size without affecting the structural stability of the material [19,20].

Nanostructured organic–inorganic composites based on

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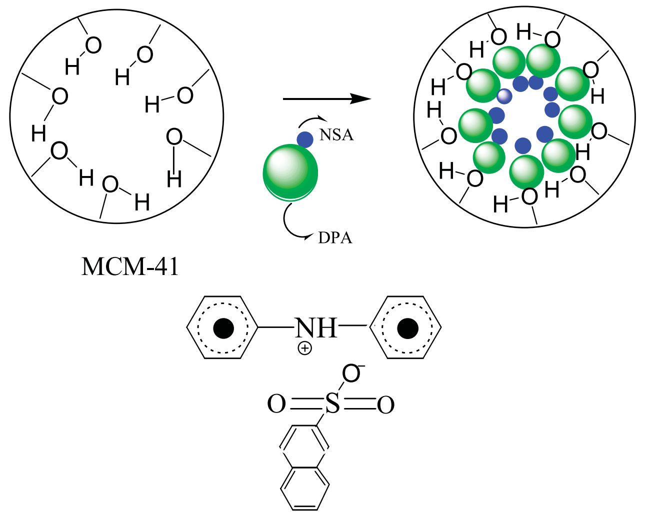


Scheme 1. Sorption of diphenylamine (DPA) in the pores of MCM-41 and formation of self-assembly in NSA.

mesoporous hosts and carbon, polymer, metal, semiconductors have been investigated [21–28] by utilizing the possibility of encapsulation of guest structures in the pores of MCM-41. Conducting polymers such as polyaniline (PANI) have been formed into the channels of MCM-41 hosts for applications in electronic devices [29–32].

Poly(diphenyl amine), PDPA a polymer of N-aryl substituted in aniline, has been reported to exhibit quite a different electrochemistry and electrochromism [33–35] in contrast to PANI and other polymers of N-substituted aniline derivatives. It is understood that electronic properties of the guest materials can be influenced by the confinement effect induced by the inorganic host [36,37]. Hence, preparation of PDPA inside the channels of MCM-41 would produce the polymer with different electronic properties.

For the preparation of polymer nanotubes or nanofibres, template directed synthesis can be employed. While using mesoporous materials as templates for making tubular or fibrous conducting polymer, each pore in the template mesoporous materials can act as tiny reaction vessel having precise diameter and length. Such aligned conducting polymer nanotubes/nanofibres exhibit field emission properties for flat panel displays [38]. Recently, conducting nanotubes/fibres have been prepared by templateless method using organic dopant [39]. Polymer nanotubes were formed by the in situ polymerization of self-assembled supra-molecular structures consisting of monomer and organic dopant molecules [40].

Formation of a conducting polymer inside the channels of mesoporous material through in situ polymerization of self-assembled structures of monomer and organic dopant can result tubular structured conducting polymer in the pores. In the present study, poly(diphenylamine), PDPA, was formed inside the pores of MCM-41 in conditions that could favour tubular structure to PDPA. The encapsulation of PDPA in the pores of MCM-41 has been done by initial formation of self-assembly of diphenylamine (DPA) molecules and subsequent polymerization. Polymerization of the self-assembled structures resulted tubular conducting PDPA. Evidences were provided for the presence of PDPA in the channels of MCM-41 (Scheme 1). The electronic properties of the PDPA formed inside the MCM-41 pores are compared with PDPA prepared by conventional method.

2. Experimental part

2.1. Materials

Tetraethyl orthosilicate (TEOS), cetyl trimethyl ammonium bromide (CTAB), 1-bromodecane, diphenyl amine (DPA), β-napthalein sulfonic acid (NSA) and triethyl amine were purchased from Aldrich Chemicals Co, Milwaukee, USA. Other high purity chemicals were of used as received.

2.2. Preparation of MCM-41

Calcined mesoporous materials (MCM-41) were prepared employing CTAB and decane ethyl ammonium bromide (DTAB) as structure directing surfactants. DTAB was synthesized and used. For the synthesis of DTAB, a solution of 1-bromodecane (7.5 mL) was mixed with triethyl amine (5 mL) in chloroform (30 mL). The mixture was refluxed at 80 °C and stirred for 24 h. A white powder (DTAB) was obtained after evaporation of chloroform and drying at vacuum oven.

Synthesis of MCM-41 was performed as described elsewhere [41–44]. A typical procedure for the preparation of MCM-41 is given. CTAB/DTAB was diluted with water and stirred for 10 min. Ammonia and ethanol were subsequently added under stirring to obtain a clear solution. An aqueous solution of TEOS was prepared. The solution of CTAB/DTAB was added drop wise to TEOS. After continuous stirring for 4 h, a gel (molar) having the compositions: 0.024 TEOS; 0.0024 surfactant (CTAB/DTAB); 0.14 ammonia; 2.568 water; 1.284 ethanol, was obtained. The gel was calcined in an oven at 550 °C and the materials thus obtained were designated as MCM-41(C) and MCM-41(D) corresponding to CTAB and DTAB, respectively.

2.3. Synthesis of tubular poly(diphenyl amine), PDPA, inside the pores of MCM-41 and removal of PDPA from pores

MCM-41(C) (0.5 gm) or MCM-41(D) (0.5 gm) was dispersed in 10 mM solution of DPA in NSA and the mixture was sonicated for 24 h with stirring. After sonication, MCM-41 was filtered, washed three times with NSA and dried to get DPA-NSA loaded MCM-41

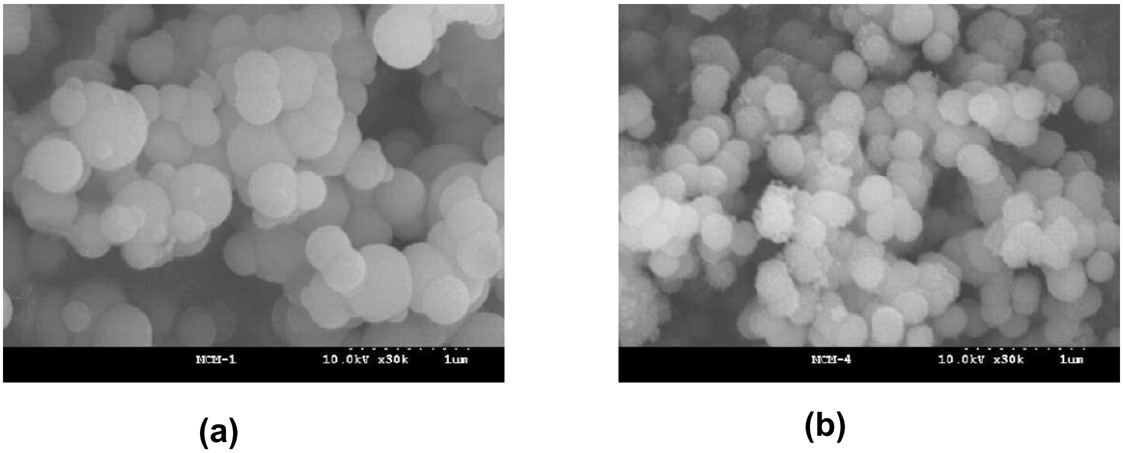


Fig. 1. SEM micrographs of (a) MCM-41(D) and (b) MCM-41(C).

(desginated as MCM-41(D-DPA-NSA) and MCM-41(C-DPA-NSA).

MCM-41(C-DPA-NSA) or MCM-41(D-DPA-NSA) was placed in 20 mL of 0.5 M ammonium peroxydisulphate and then stirred for 2 h at 5 °C. A dark green colored precipitate, NSA doped poly(diphenylamine), PDPA-NSA loaded into MCM-41(designated as MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA)) was obtained. The precipitate was filtered, washed with distilled water and dried at 60 °C in a vacuum oven. Another polymerization experiment was carried out in a similar condition but in the absence of MCM-41.

MCM-41(C-PDPA-NSA) or MCM-41(D-PDPA-NSA) was placed in aqueous ammonia for 24 h and stirred to get dedoped PDPA-NSA. The color of the precipitate changed from green to blue during this process. The blue colored precipitate was filtered, washed with water and dried in vacuum oven. The blue colored MCM-41 containing the dedoped PDPA was put in DMF and stirred for 48 h. The medium becomes blue colored informing the removal of PDPA from the pores of the MCM-41. The un-dissolved white mass (MCM-41) was filtered, washed with DMF and dried in vacuum oven. The blue colored solution contains the PDPA extracted from pores of MCM-41.

2.4. Characterization

The powder XRD patterns of the as-synthesized and calcined MCM-41 materials, were recorded in the 2θ region on a Rigaku diffractrometer using a Nickel filtered Cu K_α radiation. Surface area measurements were made by nitrogen adsorption–desorption method using a Sorptomatic at 77 K. FTIR spectra of the samples were recorded in mid IR (400–4000 cm^{-1}) region on a Jasco 610 spectrometer at 4 cm^{-1} resolution. Compressed KBr pellets containing 6% sample were used for this purpose. Each spectrum was collected after 100 co-added scans.

PDPA extracted from the pores of MCM-41 and PDPA synthesized by conventional oxidative polymerization were characterized by UV–visible spectroscopy and FTIR spectroscopy and scanning electron microscopy measurements (SEM, JEOL JSM-840A). TEM photograph was recorded using energy filtered transmission electron microscope (EF-TEM, EM 912 Omega, Carl Zeiss, Germany) installed at Korea Basic Science Institute, Korea. Elemental composition (% of carbon, hydrogen, nitrogen and sulphur) of neutral PDPA was determined by FISONS EA 1110 elemental analyzer equipped with a flash combustion furnace. Proton (^{1}H) NMR spectrum of neutral PDPA was recorded with 400 MHz Bruker, Advance Digital 400 spectrometer.

3. Results and discussion

3.1. Characterization of MCM-41

There are variations in the morphology of MCM-41 prepared for various conditions with DTAB and CTAB as structure directing surfactants. MCM-41(D) and MCM-41(C) materials with spherical morphology were selected for entrapping the polymer through self-assembly approach. SEM analysis was used to decide the morphology of MCM-41 materials (Fig. 1).

XRD patterns of pristine MCM-41(C) and MCM-41(D) also show spherical morphology corresponding to regular hexagonal channels of MCM-41 structure with a strong (100) peak followed by three minor humps for (110) (200) and (211) in the region of 2–3 °C [45,46].

3.2. Formation of PDPA inside the pores of MCM-41

PDPA was formed inside the channels of MCM-41 by performing polymerization of DPA in NSA that provides an environment for the self-assembly of the monomer (DPA) molecules. Polymerization of DPA was done by initial sorption of DPA inside the pores of MCM-41 in NSA and subsequent chemical oxidation of DPA molecules. We

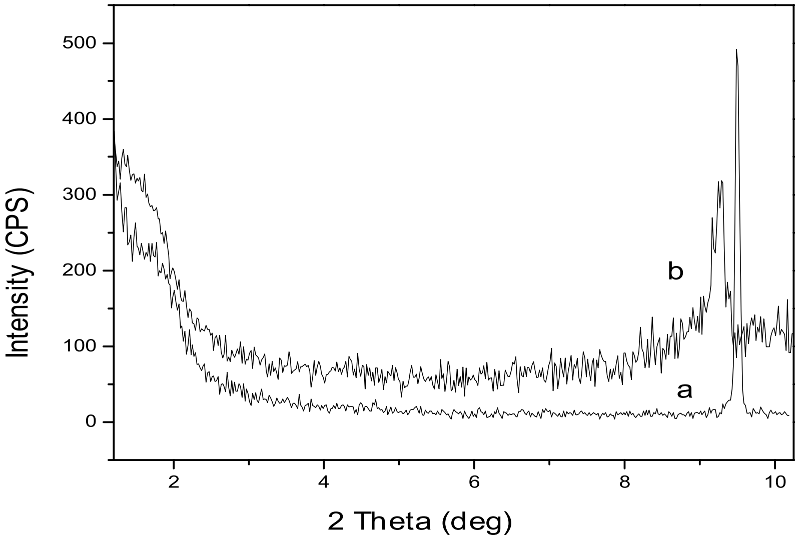
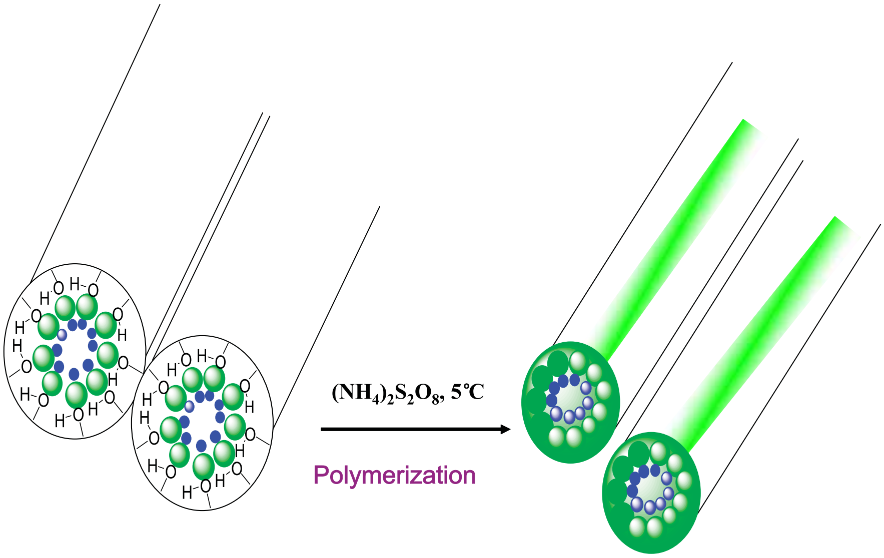


Fig. 2. XRD patterns of (a) MCM-41(D-DPA-NSA) and (b) MCM-41(C-DPA-NSA).



Scheme 2. Formation of tubular poly(diphenylamine).

envisage that the possibility of self-assembly of monomer (DPA) molecules in NSA inside the pores of MCM-41 would subsequently result tubular PDPA.

X-ray diffraction pattern of MCM-41 adsorbed with DPA (Fig. 2) shows an additional peak at 9.31° (for DTAB based MCM-41) and 9.25° (for CTAB based MCM-41) with a significant decrease in the intensity of peak at 2.1° (2θ), which is signature of the highly ordered quasi-two dimensional hexagonal lattice of MCM-41 (2θ) [47–49]. The significant reduction in the peak intensity at 2.1° (2θ) after the loading of DPA in NSA in MCM-41 is attributed to the filling of pores by the self-assembled structure. The decrease in surface area and pore volume after loading MCM-41 with monomer (Table 1) corroborates with pore filling. Similar observations were reported earlier for the filling of MCM-41 pores with carbon [50] or nanoparticles [51]. The loaded monomer molecules are confined to the pores of MCM-41 and reduces the scattering contrast between the pores and the walls of the molecular sieves. Further, we noticed that the structure of MCM-41 does not

Table 1
BET surface areas and pore volume of MCM-41confined with DPA-NSA and PDPA-NSA

Sample	Specific surface area (m^2/g)	Total pore volume (mL/g)
MCM-41(C)	141	5.6×10^{-2}
MCM-41(C-DPA-NSA)	3.35	1.51×10^{-2}
MCM-41(C-PDPA-NSA)	1.14	0.71×10^{-2}
MCM-41(D)	440	1.6×10^{-1}
MCM-41(D-DPA-NSA)	2.52	3.57×10^{-2}
MCM-41(D-PDPA-NSA)	3.22	0.96×10^{-2}

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

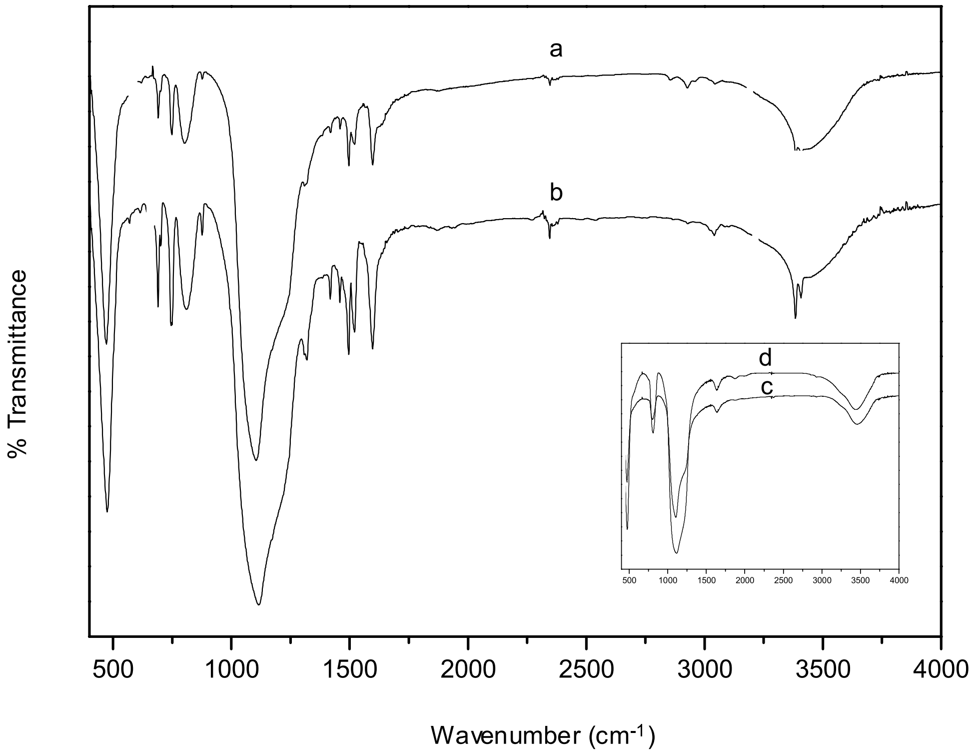


Fig. 3. FTIR spectra of (a) MCM-41(D-DPA-NSA), (b) MCM-41(C-DPA-NSA), inset: (c) Pristine MCM-41(D) and (d) Pristine MCM-41(C).

change permanently. This was evident from the reappearance of the peak at 2.1° (2θ) with an intensity close to the pristine MCM-41 after the removal of loaded DPA from the pores of MCM-41. The presence of the additional peak may correspond to induced arrangement of ordered (self-assembled) molecules of DPA involving NSA (Scheme 1). The self-assembly is envisioned as follows. The amine group attached to aromatic ring in DPA makes the unpaired

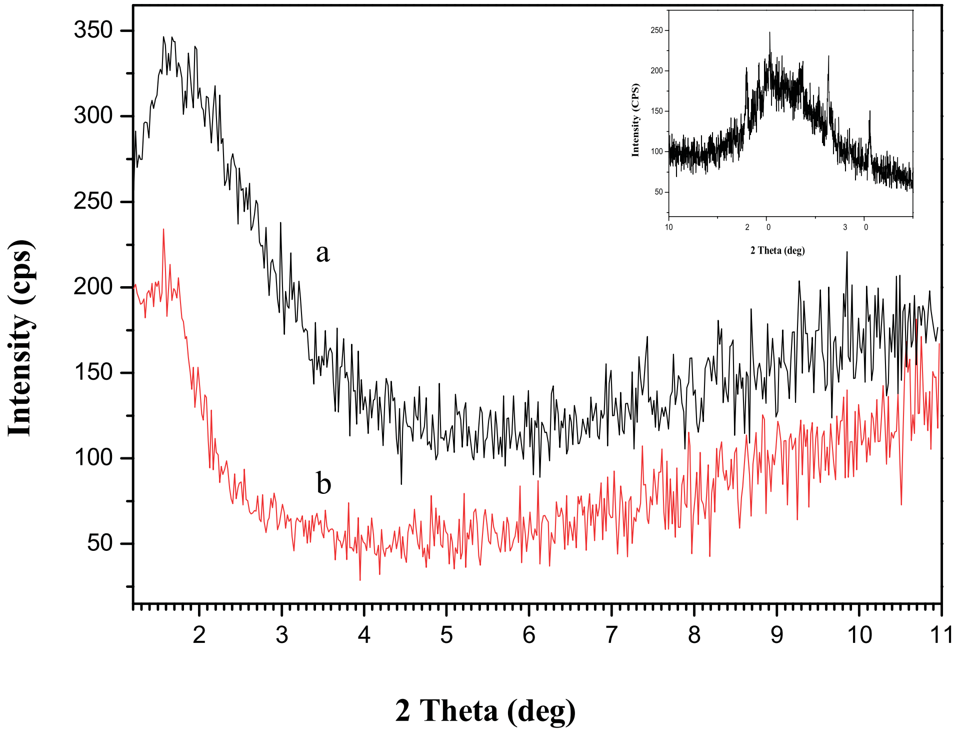


Fig. 4. XRD patterns of (a) MCM-41(D-PDPA-NSA) and (b) MCM-41(C-PDPA-NSA); inset (wide angle pattern for (a)).

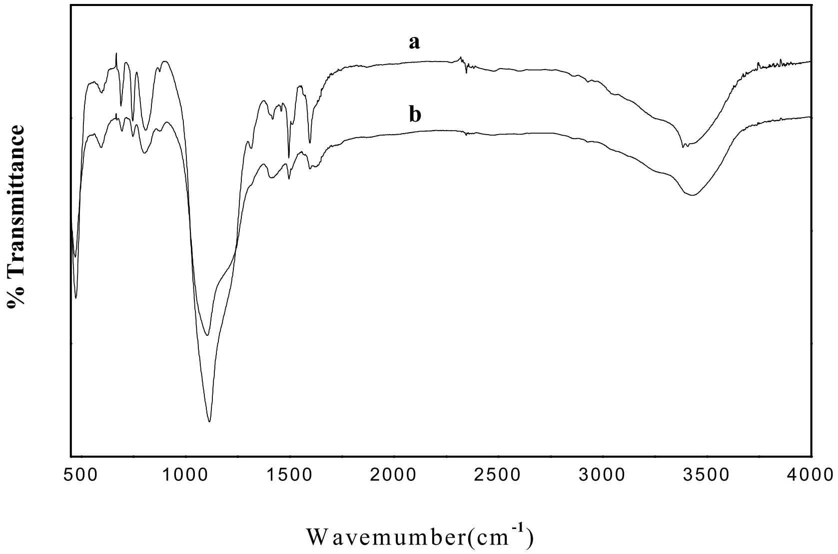
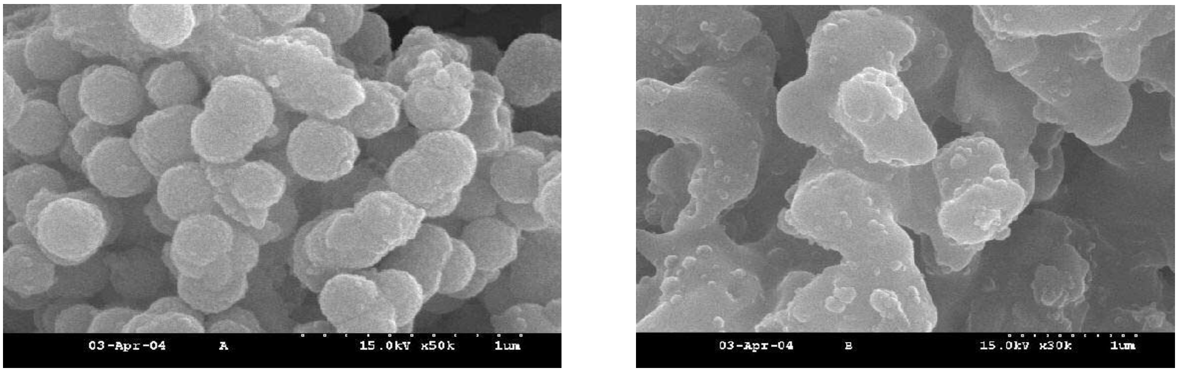


Fig. 5. FTIR spectra (a) MCM-41(D-PDPA-NSA) and (b) MCM-41(C-PDPA-NSA).

electron to delocalize and keeps the electron as part of aromatic ring. As a result of this, π- interaction of aromatic unit of DPA with Si-OH groups in MCM-41 is expected. DPA is expected to be held within the framework of MCM-41 through such donor–acceptor interactions. In acidic medium with the presence NSA, protonated DPA or salt form of DPA gets attached to MCM-41 (Scheme 1), rather than the neutral DPA molecules. The amphiphillic character of NSA by the presence of hydrophilic –SO_3H group and lipophillic –$C_{10}H_7$ (napthyl) groups and the co-existence of NSA with its salt of DPA, provide the possibility of miceller formation. With micelles consisting of NSA-DPA salt attached to MCM-41, the shell of micelles can be visualized (Scheme 2) to have the coexistence of NSA anion and diphenyl amine cation in the form of electrical double layers [52]. Now, the hydrophobic part of NSA can hold further layers of DPA, making a monomer filled miceller structure attached to the pores of MCM-4 [53]. We envisage that this type of miceller structure can act like a template to form tubular for PDPA [54,55].

It becomes now important to know whether DPA molecules are confined in the pores or on the surface of MCM-41 sphere. For obtaining information regarding this, samples of MCM-41 loaded with DPA were subjected to N_2 sorption studies. A significant decrease in the surface area and pore volume in comparison to pristine MCM-41 (Table 1) could be noticed upon loading with DPA. A miceller environment with excess monomer in the matrix of MCM-41 in NSA would fill the pores to a greater extent. Similar decrease in pore volume and specific surface area has been reported upon entrapment of polymer [56,57] or enzymes [58] in the pores of mesoporous materials.

Evidences for the presence of DPA inside MCM-41 pores could be obtained from the comparison of FTIR spectra of pristine MCM-41 (Fig. 3, inset) and DPA adsorbed MCM-41 (Fig. 3). There are characteristic bands in the region 1300–1600 cm^{-1} and 3300–3400 cm^{-1} (Fig. 3) that represent the presence of DPA in MCM-41 pores. Typically, there are bands corresponding to N–H bending and C–C ring stretching vibration around 1590 and



(a) (b)

Fig. 6. SEM micrographs of (a) MCM-41(D-PDPA-NSA) and (b) MCM-41(C-PDPA-NSA).

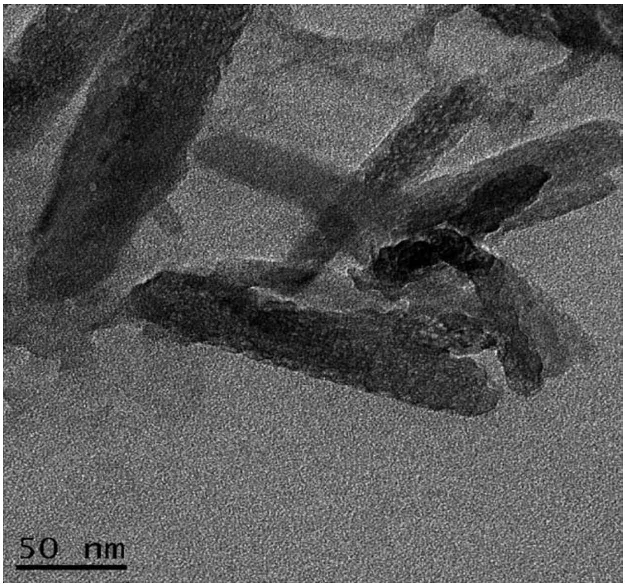


Fig. 7. TEM photograph of PDPA extracted from the pores of MCM-41.

1500 cm^{-1}, respectively. The clear presence of band around 1520 cm^{-1} signifies NH_3^+ bending vibration [59]. The existence of protonated amine units is in accordance with the proposed self-assembly model (Scheme 1).

On polymerization of self-assembly of DPA micellar units, a tubular PDPA was resulted inside the channels of MCM-41(C) or MCM-41(D). XRD measurements, scanning electron microscopy, FTIR spectroscopy, and UV–visible spectroscopy of MCM-41(C-PDPA-NSA) and MCM-41(D-PDPA-NSA) provide evidences for the presence of PDPA inside the channels of MCM-41 (Scheme 2). The peak representing the ordered self-assembled structure of monomer units in XRD disappear indicating the conversion of monomer to amorphous polymer. The presence of new peak around 25° corresponds to PDPA (Fig. 4).

The band in FTIR spectra MCM-41(C-PDPA-NSA) and MCM-41(D-PDPA-NSA) (Fig. 5) around 1400 cm^{-1} can be assigned to dipheno semiquino aminoimine segments [60] in PDPA, which is virtually absent in pristine MCM-41. There are other characteristic peaks which correspond to doped state of PDPA [60,61].

Fig. 6 presents the SEM photograph of MCM-41 loaded with PDPA. The spheres are held tightly in MCM-41(C-PDPA-NSA) and MCM-41(D-PDPA-NSA), probably by the interconnected tubular PDPA network as envisaged in Scheme 2. Otherwise, MCM spheres are threaded into tubular or fibrous PDPA as noted in molecular necklace type frameworks [62]. The PDPA formed inside the pores of MCM-41(C) or MCM-41(D) was removed from the pores. TEM image clearly informs that PDPA has tubular morphology (Fig. 7).

UV–visible spectroscopy was used to know the electronic state of PDPA confined in MCM-41. UV–visible spectrum (Fig. 8) of neutralized form of PDPA (after removal from pores of MCM-41) has a band around 570 nm which is characteristic of dipheno quinine dimine form (Scheme 3) of PDPA or bipolaronic state of PDPA [60,61]. We have checked the extent of neutralization by the elemental analysis of the neutralized PDPA. The elemental composition ($C=75.83\%$, $N=8.04\%$, $H=5.23\%$) is consistent with the repeat unit composition of $C_{12}H_9N$ for PDPA (Scheme 3). The low sulfur content (0.49%) gives a S to N ratio of 0.05 and indicates negligible doping of PDPA. Further, ^{1}H NMR spectrum of neutralized PDPA has signals around 6.8–7.8 ppm for the aromatic hydrogens of the double-substituted phenyl rings of the PDPA backbone and this observation is consistent with the earlier literature on

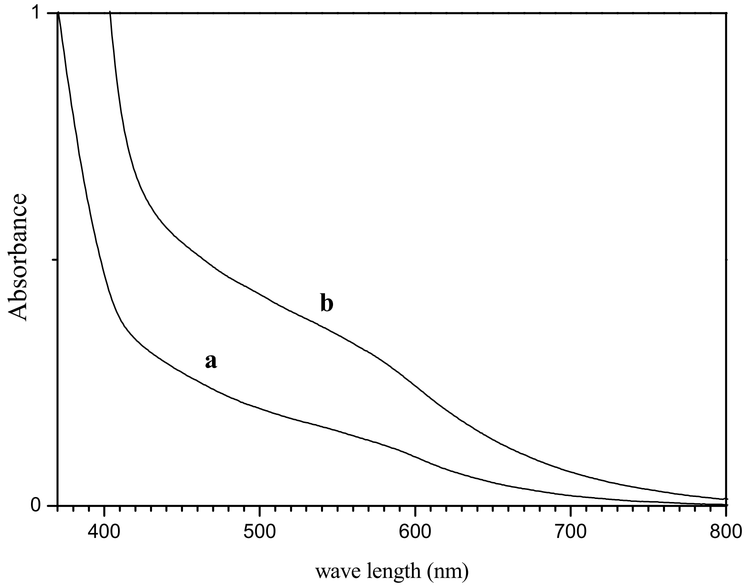
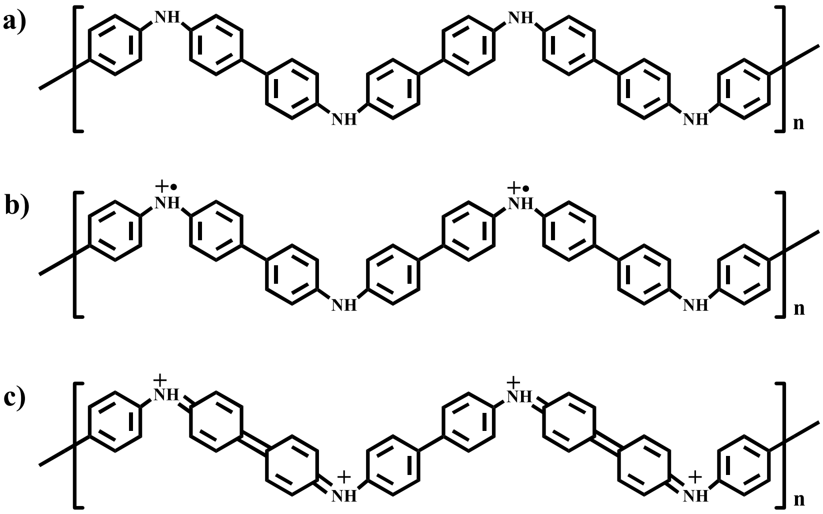


Fig. 8. UV spectra of PDPA extracted from (a) MCM-41(D-PDPA-NSA) and (b) MCM-41(C-PDPA-NSA).



Scheme 3. Redox states of poly(diphenyl amine): (a) fully reduced form, (b) polaronic form and (c) bipolaronic form.

PDPA [63]. Therefore, the existence of the band around 570 nm under this neutralized condition is expected to originate from the confinement effect. The confinement effect may originate from the weak intermolecular (polaron–bipolaron) interactions or co-ordination effect that may cause ‘docking’ of molecular units into the cavities of molecular sieves or surface curvature of the pore walls. Otherwise, PDPA formed from the self-assembled monomeric units exists in bipolaronic state with an interband (polaron–bipolaron) transition. The presence of such a different electronic state for the PDPA was further verified.

For the PDPA prepared through conventional oxidative polymerization route, the band around 570 nm for the bipolaronic state changes to a peak around 420 nm on neutralization [60,61]. However, the spectrum of PDPA formed inside MCM-41 pores shows that PDPA retains the bipolaronic state with a band around 570 nm, even after neutralization. This informs that the electronic state of PDPA-NSA formed inside the pores of MCM-41(C) and MCM-41(D) is different from PDPA formed outside the pores. The confinement of tubular PDPA inside the pores of MCM-41 is expected to alter the electronic states of PDPA [36,37]. Further, research studies to understand the confinement effects on electronic state of conducting polymer formed inside the pores are under progress.

4. Conclusions

We have demonstrated that MCM-41 materials could be prepared with tunable textural properties and used for entrapment of PDPA. Further, this study opens up the possibility of utilizing pores of MCM-41 for keeping self-assembled and micellar arrangement for the monomer, which would eventually result tubular/fibrous polymer on subsequent polymerization. Polymer thus formed inside the pores is expected to have different electronic states than the polymer formed by conventional method.

Acknowledgements

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