

Polyaniline Wires in Oxidant-Containing Mesoporous Channel Hosts

Chun-Guey Wu and Thomas Bein*

Department of Chemistry, Purdue University
West-Lafayette, Indiana 47907

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We report the encapsulation of polyaniline filaments in mesoporous hosts with 3 nm channel diameter. The channel size permits encapsulation of several polyaniline chains, and the resulting filaments show microwave conductivity. Processing of information at the molecular level is an intriguing and important challenge. Efforts to create electronic functions and devices based on molecules instead of bulk semiconductors are inspired by the anticipated enormous increase in computing speed and storage density.^{1,2} However, this approach requires that communication with nanometer structures or molecules can be established. A major challenge is to electrically isolate the conducting structures, and to achieve charge transfer with low fields as in metallic wires. We have recently demonstrated the encapsulation of several different conjugated polymers such as polypyrrole in the well-defined channels of zeolite molecular sieves.³ The synthesis of polyaniline in sol-gel-derived silica gel,⁴ and the template synthesis of conducting polymers in the pores (ca. 0.1–1 μm) of insulating host membranes has also been reported.⁵ Here we demonstrate the stabilization of *conducting* polyaniline filaments in the 3 nm wide hexagonal channels of transition-metal-containing mesoporous aluminosilicate host⁶ MCM-41.

Polyaniline is an unusual conducting polymer because its conductivity is not only controlled by the degree of chain oxidation but also by the level of protonation of $(-\text{BNHBNH}-)_y(-\text{BN}=\text{Q}=\text{N}-)_{1-y}]_n$, leading to the salt $\{(\text{PhNH}-)_x\}_n^{7,8}$. In the conducting salt form (emeraldine salt or PANI) x and y are close to 0.5; B, Q, and Ph are C_6H_4 rings in the benzenoid, quinoid, and inter-

mediate states, respectively, and HA is a strong acid. A proton-induced spin unpairing process on imine nitrogens of the emeraldine salt form of polyaniline is believed to create a conducting polaron lattice. Clays and zeolites ion-exchanged with Cu^{2+} or Fe^{3+} have been shown to oxidatively polymerize various monomers of conjugated polymers such as anilines,⁹ pyrrole,¹⁰ and thiophene and its derivatives^{9c,11} inside their cavities. The in situ oxidative polymerization/intercalation of conducting polymers in layered materials containing strong oxidants has also been demonstrated.¹²

Here we have carried out in situ oxidative adsorption/polymerization of aniline vapor in Cu-MCM (or Fe-MCM), either in the absence or presence of air (details in Table 1). The encapsulated emeraldine salt was formed by first adsorbing aniline vapor into the host;¹³ a maximum of 0.3 g of aniline adsorbed in 1.0 g of Cu-MCM or Fe-MCM (Table 1). Under exclusion of air, the saturated pink adduct (AN-CuMCM-0, AN-FeMCM-0) was then immersed in an acidic aqueous solution of peroxydisulfate, and a drastic color change to dark green was observed. After thorough washing with water, the materials were dried under vacuum. A typical polymer loading is 0.16 g/1.00 g of Cu-MCM host. The following will address the nature of the encapsulated material, its location, and its ac conductivity.

The Cu or Fe ion content in MCM-41 is low due to the low negative charge on the framework (Si/Al = 18) and incomplete ion exchange (Cu/Al ratio equal to 0.21). Therefore there may not be sufficient oxidant to polymerize large amounts of polyaniline inside the host. By carrying out the reaction in air, oxygen could be an indirect oxidant which continues to oxidize the Cu^+ (Fe^{2+}) to Cu^{2+} (Fe^{3+}) during the reaction. This effect has been observed in other cases.¹⁴ However, when the reaction was carried out in air, the resulting product AN-FeMCM-2 is not emeraldine salt ES (nor emeraldine base which shows a strong IR peak at 1594 cm^{-1}), but predominantly the nonconducting leucoemeraldine LEB, as demonstrated with IR and NMR spectroscopy (major IR peaks at 1558 sh, 1497 vs, and 1296 cm^{-1}).¹⁵ The ¹³C MAS NMR spectra of conducting polyaniline are featureless due to the presence of charges, which together with the inhomogeneous character of the materials, results in broadened

* Author for correspondence.

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(13) The host was synthesized with $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_9\text{OH}$ according to ref 6; Si/Al ratio of 18, calcined at 580 °C and evacuated at 400 °C, 10⁻⁵ Torr. To load with copper ions, 1.00 g of the calcined MCM was stirred for 3 h at 25 °C with 100 mL of 0.1 M Cu(II) nitrate (aq), filtered, washed with water. These steps were repeated four times. To load with Fe, 1.00 g of MCM was stirred with 100 mL of 0.1 M Fe(II) nitrate (aq) under nitrogen for 4 h, filtered, and washed with water. The product was treated in an oxygen flow at 100 °C for 10 h, at 350 °C for 4 h, and evacuated at 350 °C for 2 h. Slight decreases in crystallinity were observed. Before loading with aniline, the Cu- and Fe-MCM hosts were heated at 100 °C and 400 °C in oxygen, then evacuated at 400 °C for 7 h.

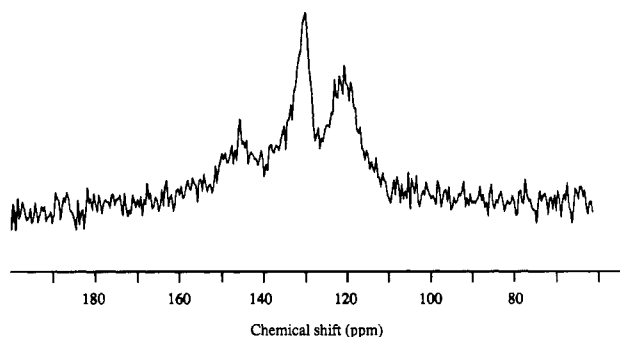
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Table 1. Polyaniline in CuMCM and FeMCM Hosts

sample	reaction sequence ^a	loading ^b (wt %)	product ^c	ac conductivity (S/cm)
AN-CuMCM-0 ^d	vapor	28	radicals/cations	3.6×10^{-4}
AN-CuMCM-1 ^d	A: vapor/S ₂ O ₈ ²⁻	10	ES	1.6×10^{-3}
AN-CuMCM-2 ^d	B: vapor/air/S ₂ O ₈ ²⁻	20	ES and others	
AN-FeMCM-1 ^d	A: vapor/S ₂ O ₈ ²⁻	6	ES	1.6×10^{-3}
AN-FeMCM-2 ^d	C: vapor in air	10	LEB	9.4×10^{-5}
dry CuMCM ^d		0	-	9.4×10^{-5}
bulk polyaniline (as prepared)			ES	1.8×10^{-2}

^a Sequence A: dry CuMCM host was equilibrated with aniline vapor at 40 °C for 4 h, then pumped off for 10 min, and immersed in an aqueous solution of peroxydisulfate under nitrogen at 0 °C for 4 h (mole ratio of oxidant vs aniline 1.25:1, 1 g of sample in 50 mL of 0.2 M HCl). Sequence B: dry CuMCM host was equilibrated with aniline vapor at 25 °C for 24 h, then pumped off for 10 min, exposed to air, and then immersed in an aqueous solution of peroxydisulfate at 0 °C for 4 h (mole ratio of oxidant vs aniline 1.25:1, 1 g of sample in 50 mL of 0.2 M HCl). Sequence C: dry CuMCM host was equilibrated with aniline vapor at 40 °C for 4 h in the presence of air and then pumped off for 1 h. ^b Determined from TGA weight loss between 100 and 600 °C. ^c ES: emeraldine salt; LEB: leucoemeraldine base. ^d All MCM samples indicated were pumped at 10^{-5} Torr for 12 h at room temperature.

Figure 1. MAS ¹³C NMR of sample AN-FeMCM-2.

peaks.¹⁶ The reduced form of polyaniline (leucoemeraldine) has the simplest structure among all modifications of polyaniline. There are only two different types of carbon in the structure. The ¹³C NMR of AN-FeMCM-2 shows two peaks at about 130 and 120 ppm, typical for leucoemeraldine (Figure 1).¹⁶ The same experiment with CuMCM host results in a dark brown material which contains a mixture of products.

As expected, when the exposure to aniline vapor was carried out under vacuum, no polymer was formed (sample AN-Cu-MCM-0). The pink products may contain some radicals and cations of aniline or its oligomers, as indicated by an electronic absorption peak at 410 nm. This peak is consistent with the presence of nitrenium cations (C₆H₅-NH⁺) or nitrenium radicals (C₆H₅NH•).^{17,18} The cations and radicals are quite reactive; upon contact with air, the color turns brown and only a fraction of the resulting products can be further polymerized with (NH₄)₂S₂O₈/HCl to form polyaniline (sample AN-Cu-MCM-2). However, if the pink materials are reacted with (NH₄)₂S₂O₈/HCl aqueous solution before exposure to air, the resulting dark green products, AN-CuMCM-1 and AN-FeMCM-1, both contain the *emeraldine salt form* as shown in Scheme 1 and Figure 2 (IR peaks at 1581, 1497, 1300, and 1230 cm⁻¹).¹⁹ The electronic absorption spectrum of AN-CuMCM-1 and AN-FeMCM-1 presents major transitions at 3.4 and 1.6 eV, typical for the bandgap and polaron transitions of emeraldine salt.^{18,20} The encapsulated, evacuated polymers show a single fairly broad (8–19 G)

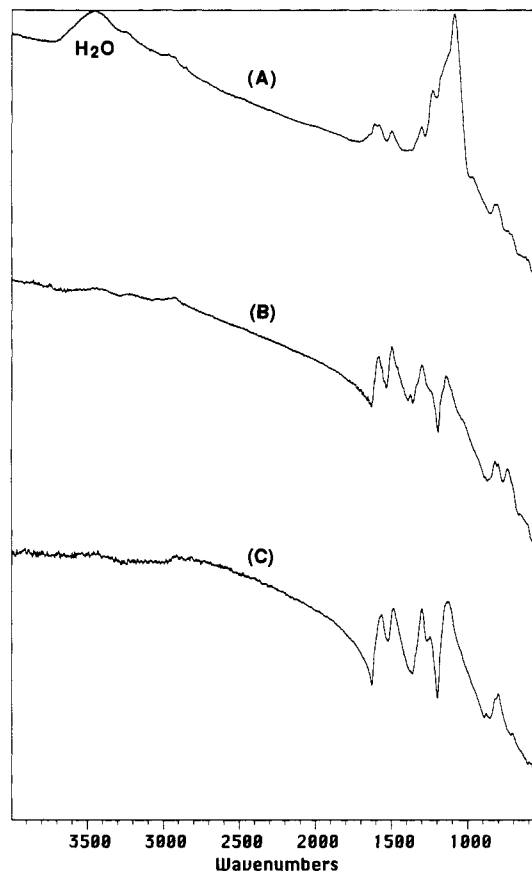


Figure 2. Infrared spectra of (A) AN-CuMCM-1, (B) PANI extracted from the composite in (A), and (C) bulk PANI.

esr line for the polymer (and a weak Cu(II) resonance), as presented in Figure 3, suggesting slightly lower protonation levels than in bulk emeraldine salt²¹ or dipolar interactions with the MCM channel walls or metal cations inside.

The relative chain length of intrachannel polyaniline in AN-FeMCM-1 (vs polystyrene, in *N*-methylpyrrolidinone with 2.5% LiCl) was determined with gel permeation chromatography after decomposition of the host in 5% HF and deprotonation. (Polyaniline is stable toward HF under these conditions; IR spectra and conductivity are unchanged). A correction factor of ca. 0.5 is required to estimate absolute molecular weights.²² The peak mo-

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Scheme 1. Encapsulation of Polyaniline in MCM Channels

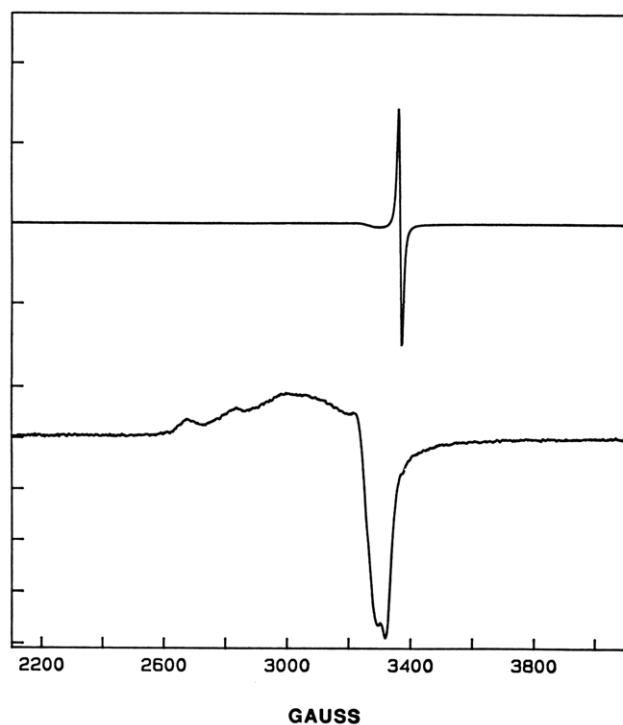
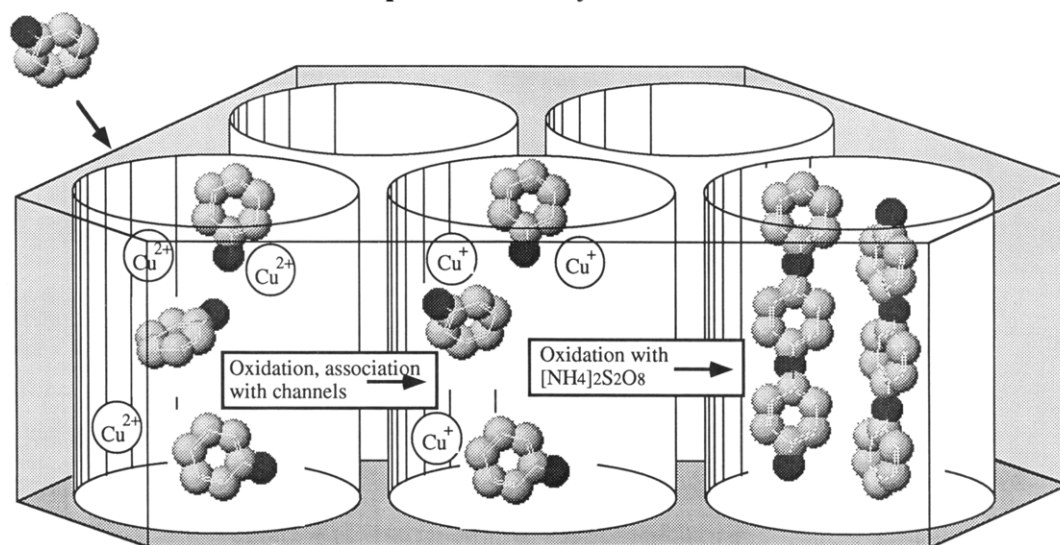


Figure 3. ESR spectra of (top) sample AN-CuMCM-2 and (bottom) CuMCM (scale different from top).

molecular weight of the intrachannel polyaniline (34 000 vs PS; corrected ca. 190 rings) is consistently shorter than that of bulk material synthesized under comparable conditions (52 000 vs PS; corrected ca. 290 rings). This difference suggests that diffusional constraints experienced by the reactants limit the chain growth in the MCM host.

TGA experiments in oxygen show that the stability of AN-CuMCM-1 and AN-FeMCM-1 is much higher (decomposition between 350 and 600 °C) than that of bulk ES (decomposition between 300 and 400 °C). This difference indicates slower diffusion of oxygen and reaction products, similar to observations for polymers in layered hosts.²³ With the sample AN-CuMCM-0 where little polymer forms, most of the weight loss occurs at temperatures below 200 °C.

The location of the polymer (inside vs outside of the channels) is important for the interpretation of the results. Infrared spectra of the hydroxyl region of Cu-MCM-41 before aniline loading show a single peak at 3691 cm^{-1} (in Nujol), due to Si-OH, which disappears on contact with aniline. This indicates complete coverage of the intrachannel surface with aniline. The intrachannel polymerization reaction was probed with nitrogen sorption. The isotherm of AN-CuMCM-1 shows a residual pore volume of 0.43 mL/g of MCM host (it contains 0.16 g of polymer/g of Cu-MCM), compared with 0.64 mL pore volume in the empty host. Assuming a polymer density of 1.3 g/ cm^3 , the loading of 0.16 g/(g of host) is slightly smaller than the change in porosity probed with nitrogen sorption, possibly indicating blockage of some channels. However, the general similarity of the unique isotherm shapes suggests that a tubular structure is even maintained in the polyaniline-loaded host, but the shift of the saturation transition to lower partial pressure shows that the channels are now narrowed.

The electronic conductivity of the encapsulated polyaniline is of primary interest. Detailed studies of bulk emeraldine salt led to the model of a granular metal where charge hopping between metallic bundles dominates the macroscopic conductivity.^{24,25} The dc conductivity of AN-CuMCM-1 and AN-FeMCM-1 is in the 10^{-8} S/cm range, similar to the conductivity of *unloaded* Cu-MCM host under ambient conditions, and more than 7 orders of magnitude lower than for bulk PANI. This shows that the polyaniline is located *inside* the MCM channels and that no percolating conducting paths develop on the external crystal surfaces.

To probe the charge transport of PANI filaments in the insulating MCM host, the contactless microwave absorption technique²⁶ was used. The microwave conductivity of dry AN-CuMCM-1 and AN-FeMCM-1 obtained from the perturbation of a rectangular cavity at 2.63 GHz is *no less than about one-tenth of that of as-synthesized bulk PANI* (with dc conductivity of 0.2 S/cm), after correction

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for the volume fraction of the polymer in the host (Table 1).²⁷ This significant low-field conductivity demonstrates that conjugated polymers can be encapsulated in nanometer channels and still support mobile charge carriers (in contrast to polypyrrole in the 0.7 nm channels of zeolite Y that is not conducting).²⁸ Moreover, the ac conductivity of AN-CuMCM-1 is similar to that of PANI in pristine MCM.²⁹ This indicates that the presence of oxidant ions does not significantly affect the charge-transport proper-

ties of the polyaniline chains in the host. The concept of in situ oxidative adsorption/polymerization of aniline in the oxidant-containing channel host permits us to "lock in" the aniline species as radical cations or short oligomers such that diffusion during subsequent treatment with external oxidant is limited. The factors controlling electronic transport in these and related novel nanostructures are now being studied.

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