Surfactant-Mediated Incorporation of Poly(*p*-phenylene) into MoO_3[†]

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With the realized property enhancements originating from the incorporation of conducting polymers into layered inorganic hosts,[1] interest in nanocomposites remains high. Over the past decade, various combinations of electronic and/or ionic conductive polymers and inorganic hosts have been explored, requiring a wide variety of synthetic methods to effect inclusion of the polymer in the interlamellar gap of the host material.[2] Of the many polymers used in these synthetic methods, poly(*p*-phenylene) (PPP) has *not* been among them, although it has well-established conductive properties in both its n- and p-doped forms[3,4] and is reported to be a promising anode in rechargeable lithium cells.[5] Recent studies by Dubois and Billaud have reported, for example, that poly(*p*-phenylene) can reversibly intercalate $0.5Li/C_6H_4$ between 500 and 0 mV with very low cell polarization.[6]

The paucity of PPP nanocomposites is primarily due to the insoluble and infusible nature of the polymer in its pristine state. To incorporate such a rigid chain polymer, innovative synthetic methodologies must be used. We have recently reported a hydrothermal technique that was used to incorporate the amino-derivative form of PPP (PPP−NH_2) into the van der Waals gap of MoO_3.[7] Taking advantage of the ion exchange properties of the $[(Li/Na)H_2O]_{0.25}MoO_3$ bronze ["(Li,Na)MoO_3"], under such hydrothermal conditions, we were able to induce exchange of the gallery cations for protonated $(C_6H_3NH_3^+)_n$. The promising characteristics of both PPP and $Na_{0.25}MoO_3$[8] as anode materials in lithium ion cells, along with substantial amounts of polymer surface impurities resulting from the hydrothermal method, have led us to develop a new technique for the inclusion of PPP in MoO_3. Here we report on the entrapment of PPP in MoO_3 via a novel surfactant mediated route.

Unlike many conjugated polymers, PPP is relatively crystalline and demonstrates high thermal and oxidative stability, with combustion not occurring until over 500 °C. We have utilized this characteristic to design a new synthetic method that involves surfactant-mediated intercalation. The layers of (Li,Na)MoO_3 are first prised apart using an alkylammonium surfactant. The lipidlike bilayer arrangement of the surfactant molecules between the MoO_3 sheets, with the hydrophilic headgroups nestled adjacent to the oxide surface, results in a hydrophobic region contained at the interface of the alkyl chains. This permits hydrocarbons such as PPP to preferentially adsorb into this region from polar solutions, giving rise to incorporation of the polymer within the layers. Exploiting the high thermal stability of the PPP, the material can then be calcined to selectively remove the surfactant from within the interlamellar region.

The surfactant dodecyltrimethylammonium hydroxide was used as a transport medium material. PPP was prepared using the Kovacic method,[9] which results in an average degree of polymerization of the PPP of about 15−20. This was confirmed by determining the ratio of the infrared (IR) absorptions at 806 cm^{-1}/693 cm^{-1}.[10] Both PPP and $[Li/Na]_{0.25}MoO_3$[11,12] were dispersed in separate concentrated aqueous solutions (∼30%) of surfactant. The PPP does not dissolve in the mixture but is rather suspended by the dense concentration of surfactant micelles. After 12 h, the two solutions were mixed and stirred for 24 h. The suspension was then filtered and the solid washed with copious amounts of water to remove residual surfactant. X-ray diffraction (Figure 1a) reveals an increase in the interlayer distance of the hydrated parent oxide, $[Li/Na(H_2O)]_{0.25}MoO_3$, from 9.6 to 23 Å, indicating substantial incorporation of organic material between the layers. IR spectra of this material showed the presence of strong surfactant and oxide absorptions that obscured the polymer bands. The presence of both polymer and surfactant within the layers was evident by thermal analysis, however (Figure 2a). A weight loss characteristic of surfactant occurs at 310 °C, followed by combustion of the PPP at approximately 460 °C. The latter value is substantially lower than the decomposition temperature of PPP itself, 610 °C (Figure 2b), suggesting that the close proximity of MoO_3 promotes a catalytic oxidation process in the nanocomposite that may involve oxygen from the lattice.

[†] Dedicated to Jean Rouxel in honor of his contributions to solid-state chemistry.

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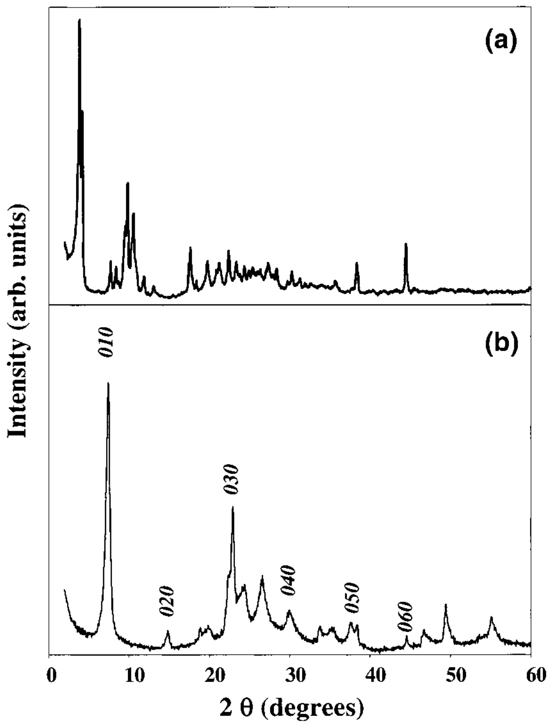

Figure 1. X-ray diffraction patterns (random powder mounts), Cu-Kα radiation, of (a) surfactant/PPP cointercalated in MoO_3 and (b) PPP$-MoO_3$ nanocomposite after heat treatment at 250 °C for 36 h.

Treatment of the co-intercalated surfactant/polymer$-MoO_3$ composite in air at 250 °C for 36$-$48 h results in a decrease of the interlayer spacing to 11.96 Å (Figure 1b), consistent with removal of the surfactant. This corresponds to a 5.0 Å increase of the gallery height vs that of pristine MoO_3, in good agreement with the dimension of a phenylene unit perpendicular to the polymer chain axis (~4.5$-$5.5 Å). It suggests that a monolayer of polymer is intercalated between the oxide layers and that the plane of the phenyl rings are disposed in a perpendicular orientation with respect to the oxide sheets, rather than parallel. The orientation cannot be determined unequivocally from the d spacing, however, since the dimensions of the phenyl ring ("width" and "thickness") are similar (5.3 vs 3.3 Å). Some retention of crystallite ordering occurs, albeit reduced compared to that of the precursor bronze, as shown by the presence of harmonic ($0k0$) reflections (as labeled) and mixed reflections in the random powder mounts. Scanning electron microscopy images of the material also reveal that the layered morphology of the parent oxide is maintained (Figure 3).

The presence of interlamellar PPP and absence of surfactant in the composite material was confirmed by infrared spectroscopy. Its IR spectrum displays several characteristic bands attributable to PPP (Table 1), in particular those at 806 and 1482 cm^{-1} (Figure 4c). The former corresponds to adjacent C$-$H vibrations on para-substituted phenyl rings. The intensity and location of this band remains unchanged in the nanocomposite, suggesting the absence of strong interactions with the oxide layers. Upon dissolution of the oxide with NaOH, isolation of the remaining polymer yields a product which displays an identical IR spectrum to that of virgin PPP (Figure 4b). The ratio of the bands from the para-substituted (806 cm^{-1}) vs the monosubstituted (693 cm^{-1}) rings also remains unchanged, indicating that cross-linking has not occurred during the calcination process. The absence of substantial PPP cross-linking following calcination is indicated by the lack of diagnostic bands at 1600 and 860 cm^{-1} that arise from isolated C$-$H out-of-plane vibrations.[13] A broad band appearing in the composite spectrum at ~1620 cm^{-1} is attributed to some residual water in the KBr pellet. Three bands at 986, 820, and 574 cm^{-1} are assigned to molybdenum oxide lattice vibrations. These are similar to the bands observed in MoO_3 (985, 850, and 560 cm^{-1})[14] and are sufficiently shifted from the two bands characteristic of $Li/NaMoO_3$ (946 and 588 cm^{-1})[15] to suggest that partial oxidation of the reduced bronze has occurred during removal of the surfactant by heat treatment in air, as would be expected. This is in accordance with two-point dc-conductivity measurements of pressed pellets of the nanocomposite material, in which no measurable conductivity was observed. Comparison of the IR spectra of PPP$-MoO_3$ composite after calcination with that of the surfactant-intercalated $(Li/Na)MoO_3$ (Figure 4d) and that of the surfactant

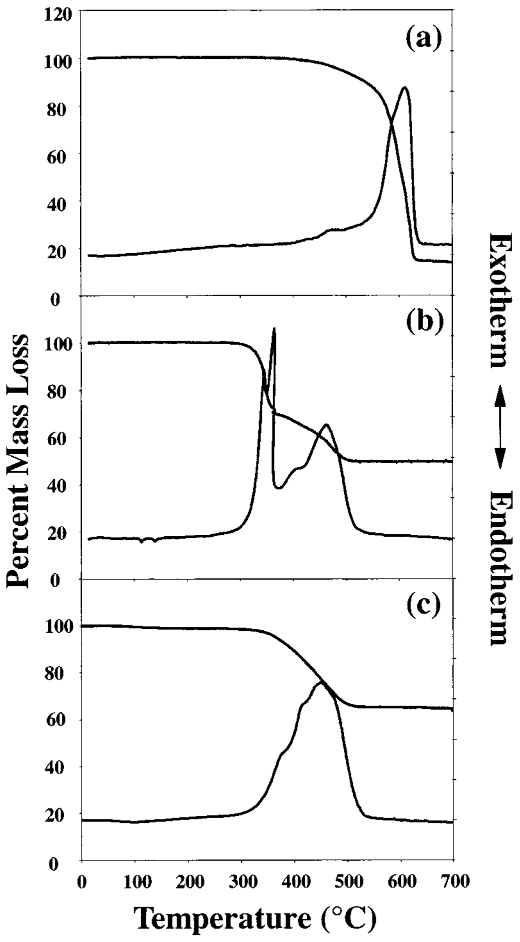

Figure 2. TGA$-$DTA curves taken in air: (a) PPP, as prepared, (b) surfactant/PPP cointercalated in MoO_3, (c) PPP$-MoO_3$ nanocomposite after heat treatment at 250 °C for 36 h.

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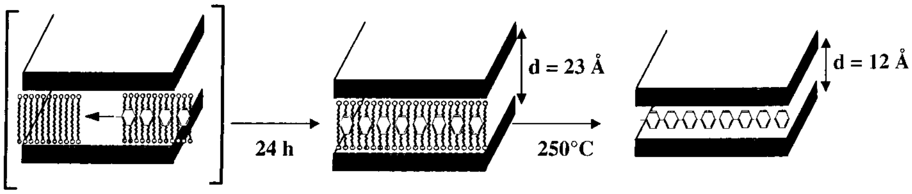
Scheme 1. Schematic Showing Surfactant-Mediated Incorporation of PPP in MoO_3.



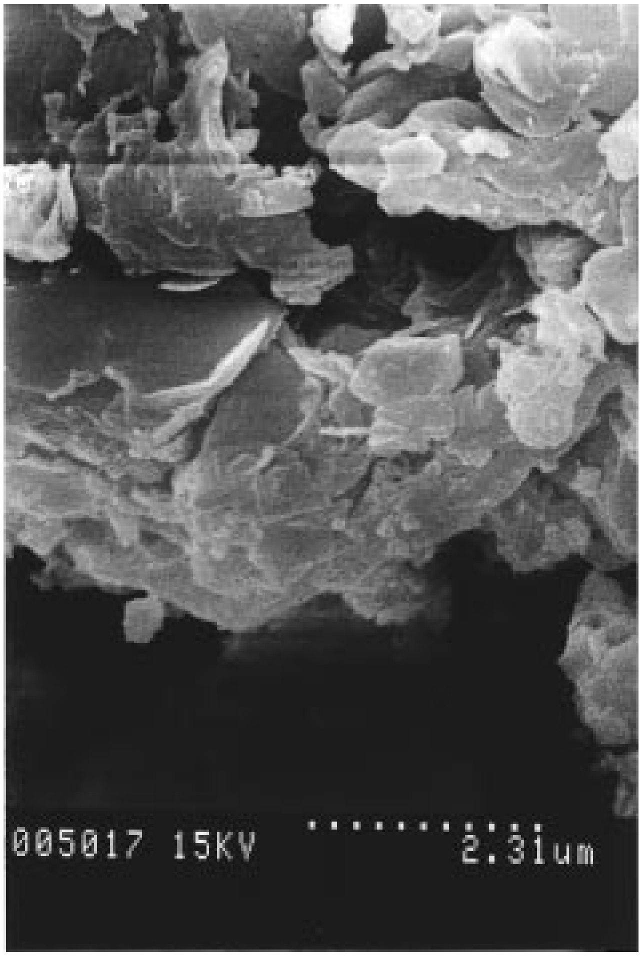


Figure 3. Scanning electron micrograph of PPP−MoO_3 after heat treatment at 250 °C for 36 h.

Table 1. IR Spectral Data Used for Analysis (data from refs 8, 9, and 17−19)

frequency (cm^{-1})	assignment
575	ν(O−Mo), triply bound O^{2-}
693	ν(C−H) out-of-plane, terminal phenyl ring
764	para- and monosubstituted phenyl
806	ν(C−H) out-of-plane, para-disubstituted phenyl
820	ν(O−Mo), doubly bridged O^{2-}
986	ν(O=Mo), terminal O
1000	para-substituted C_6H_4
1482	ν(C=C) in-plane
1575	νC=C) in-plane
1603	ν(C=C) in-plane

alone (Figure 4e) also confirms the substantial loss of surfactant during heat treatment. Specifically, the complex absorptions due to the surfactant between 1400 and 1475 cm^{-1} are absent in the composite material, as are absorptions between 650 and 750 cm^{-1}. A broad weak band at 920 cm^{-1} is still visible, whose origin is unknown, but may be ascribable to residual traces of surfactant.

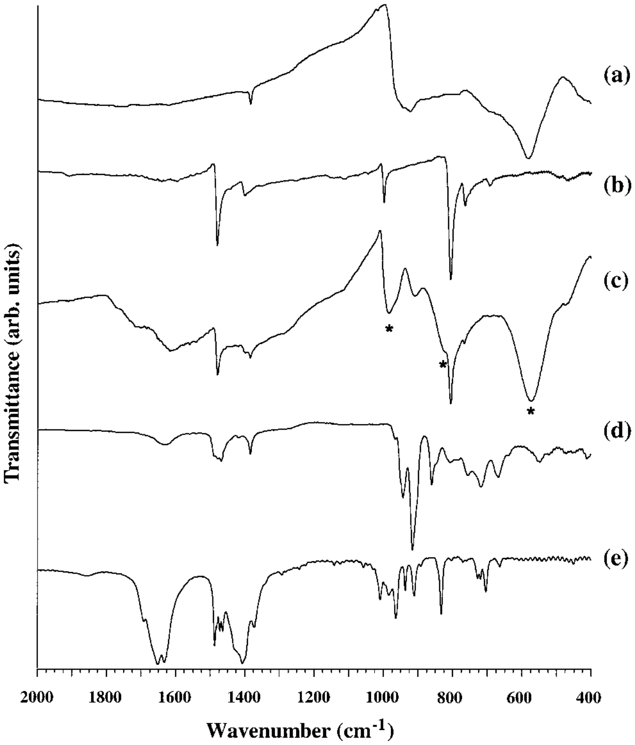


Figure 4. FTIR spectra (KBr pellets) of (a) $[Li/Na(H_2O)_2]_{0.25}$-MoO_3, (b) PPP, as prepared (c) PPP−MoO_3 nanocomposite after heat treatment at 250 °C for 36 h, and (d) surfactant-intercalated MoO_3; dodecyltrimethylammonium hydroxide is shown for comparison. Absorption bands marked with an asterisk are due to MoO_3.

The TGA trace of the heat-treated material (Figure 2c) shows only one weight loss (35%) centered at 450 °C as before, corresponding to combustion of PPP from a composite with a stoichiometry of $[C_6H_4]_{1.0}MoO_3$. The volumetric constraints of the interlayer region do not allow for such a large polymer content in a monolayer arrangement, indicating that a small fraction of polymer is also present on the surface of the crystallites, although it is not visible on the SEM micrographs.

In conclusion, surfactant-mediated transport of insoluble, hydrophobic polymers can be exploited to produce a novel interleaved composite containing poly(*p*-phenylene). The overall synthetic route is illustrated in Scheme 1 whereby the surfactant bilayer within the MoO_3 is displaced by the PPP/surfactant dispersion. Subsequent heat treatment results in concomitant combustion of the surfactant and collapse of the oxide layers, entrapping the residual PPP chains and forming the nanocomposite. The resultant interlayer expansion of 5.0 Å is in good agreement with the dimensions of a phenylene unit perpendicular to the polymer chain axis, suggesting that monolayers of PPP are primarily incorporated via this route. As the insoluble PPP appears dispersed within the surfactant, and “not dissolved”, it suggests that the interlamellar forces or interaction of the polymer with the interlamellar surface after surfactant removal is sufficiently strong to result in partial or complete disaggregation of the PPP chains. This surfactant-transport route is expected to be generally applicable to a wide range of host and insoluble polymers. In this case, since both PPP and $NaMoO_3$ have been shown to have very good characteristics as anode materials in lithium ion batteries, the interleaved composite may possess substantial advantages over either material alone. Preliminary experiments on electrochemical Li insertion−deinsertion into the nanocomposite show a charge capacity of 863 mAh/g for $[C_6H_4]_{1.0}MoO_3$, compared to 773 mAh/g for MoO_3 carried out under identical conditions.[16] These results, together with those of other polymer/MoO_3 composites will be reported in full in a forthcoming paper.

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(16) The material was evaluated vs Li; electrodes were prepared from active material and carbon black using PVDF as a binder in the mass ratio 80:15:5, respectively, with $LiPF_6$ in dimethyl carbonate and ethylene carbonate as an electrolyte. Swagelock type cells were assembled in an argon filled glovebox containing less than 2 ppm of water and oxygen. Discharge was to 5 mV at a current density of 20 mA/g. The contribution from the carbon binder is removed in the quoted capacities.

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