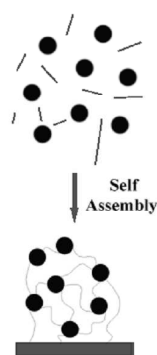


Conducting Polymer-Inorganic Nanoparticle (CPIN) Nanoarrays For Battery Applications

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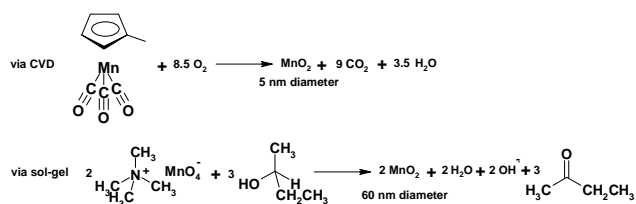
Highly efficient rechargeable batteries (high specific energy and power) constituted with more environmentally friendly materials have been required for different applications. The rechargeable lithium-ion battery fulfils many of these crucial features, due to its high cell voltage and gravimetric energy density.¹ The advantages of these batteries has prompted intensive research in synthesis of new lithium insertion compounds as cathodes. Transition metal oxides, such as manganese oxide, have been receiving special attention as potential candidates, principally because of environmental compatibility and low cost.^{2,3} However, the use of such compounds as cathodes has revealed some undesirable features, such as capacity fading upon cycling due to irreversible structural modification,⁴ relatively poor electronic conductivity and slow Li⁺ diffusion, features that have been attributed to the use of bulk materials.⁵

Our goal is to produce self-assembled nanostructures of these metal oxides, using conducting polymers and/or oligomers as connecting agents ("molecular wires") to form 3D structures with high electronic and ionic conductivities (Figure 1). Sexithiophenes and poly(thiophene)s were chosen as the molecular bridges, because these compounds are stable and can be synthesized with many different pendent and end groups using well known reactions.



Example of a self-assembly process

The MnO₂ nanoparticles were obtained by two different methods (Scheme 1). The first one involved homogeneous nucleation in a CVD reactor, where an organometallic precursor (methyl(CP)Mn(CO)₃) was reacted in presence of O₂ at carefully controlled temperature and mass flow rate, resulting in a powder with particles of 5 nm of diameter. In the second method, colloidal manganese oxide has been prepared *via* reduction of tetramethylammonium permanganate in aqueous solutions with 2-butanol, producing nanoparticles of 60 nm of diameter. TiO₂ nanoparticles were commercially available.



Scheme 1

The sexithiophenes and precursors were obtained using known reactions and these compounds were characterized spectroscopically (¹H and ¹³C NMR and FTIR) and using elemental analysis. Different capping groups were attached to these oligomers, such as dimethylchlorosilane (-SiCl(Me)₂), carboxylic acid (-COOH) and phosphonic acid (-P(O)(OH)₂).

Two different strategies are being attempted to produce the CPIN nanoarrays (Figure 2). In the first one, the bridges having various end groups are used to cap the nanoparticles. In the second method, a monosubstituted bithiophene is used to cap the nanoparticles and then this whole assembly is polymerized chemically or electrochemically, producing the molecular wire (poly(thiophene)). Figure 3 shows TEM images of TiO₂ nanoparticles treated with 2,2'-bithiophene-5-diylphosphonic acid.

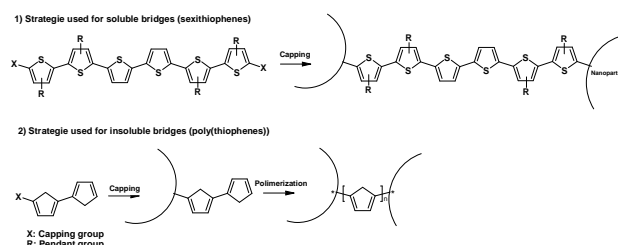


Figure 2: Different strategies to produce the CPINs

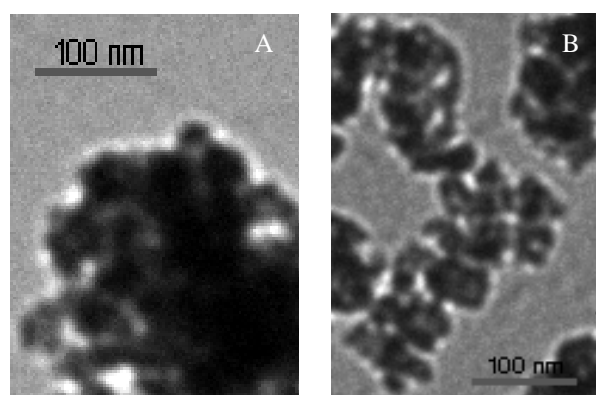


Figure 3: TEM images of the TiO₂ before (A) and after (B) treatment with capping agent

The CPIN nanoarrays are being characterized using TEM, FTIR and elemental analysis. ³¹P solid state NMR is also being utilized in the case of the nanostructures produced with phosphonic acid derivatives. In these cases it is difficult to obtain detailed information from vibrational spectroscopy, due to the complexity of the P-O stretching region.⁶

The electrochemical behavior of these nanostructures is being analyzed and its correlation with their structural, compositional and electrical properties will be discussed.

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