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Synthesis and Study of Zirconium Viologen Phosphonate Thin Films Containing Colloidal Platinum

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Structural control is a key element in the design of molecular materials with desirable bulk properties. An approach that has attracted attention recently is the use of tetravalent metal phosphonates [*e.g.*, $M(O_3PRPO_3)$, $M = M^{4+}$, R = organic group] for the construction and design of molecular materials.[1,2] These structures are reminiscent of Langmuir–Blodgett (LB) multilayers.[3] Unlike LB films, the inorganic layers of metal phosphonate (MP) thin films have very strong bonding, resulting in films that are stable for long periods. MP thin films are prepared by sequential treatment of a substrate with aqueous solutions of zirconium and a bisphosphonic acid.[2a,4–6] Ellipsometric[4–6] and X-ray measurements,[1f,4b] as well as electronic spectroscopy,[2a] show that this incremental growth technique leads to uniform metal phosphonate thin films. MP films have been used as chiral molecular sieves,[7] dielectric layers,[5] and chemical sensors,[1a] as well as to align chromophores for nonlinear optics[1d,6] and study photoinduced electron transfer in layered materials.[1b,2] The present report concerns the synthesis and study of a novel MP film, containing colloidal platinum particles within a photochemically active thin film. The platinum particles of the film make it possible to reduce the film with H_2 and to photochemically reduce water to give H_2.

We have recently reported the preparation and photophysical properties of MP films and microcrystalline samples of a zirconium viologen phosphonate compound, $Zr(O_3PCH_2CH_2$-(bipyridinium)$CH_2CH_2PO_3)X_2$, (X = Cl, Br), **ZrPV(X)**.[2] Photolysis of these white materials leads to deep blue solids. Photophysical studies indicate that the photoproduct is the dialkyl viologen radical cation, produced in the zirconium phosphonate lattice (quantum yield = 0.14).

The chloride ions of **ZrPV(Cl)** thin films are needed to balance the charge of the viologen groups in the solid and are incorporated into the thin film with the bisphosphonic acid. We have found that the chloride ions can be readily ion exchanged for other anionic species (*i.e.*, $PtCl_4^{2-}$). The modified film growth procedure involves sequential treatment of the substrate with aqueous solutions of the viologen bisphosphonic acid, K_2PtCl_4, and $ZrOCl_2{\cdot}(H_2O)_8$. The electronic spectra of these thin films are very similar to those observed for **ZrPV(Cl)**, Figure 1a. The principal difference between the spectra is a tailing into the visible for the **ZrPV($PtCl_4$)** film, due to the expected red shift in the charge-transfer band on exchanging the Cl^- ion for $PtCl_4^{2-}$.[8] The $PtCl_4^{2-}$ ions are trapped inside the **ZrPV($PtCl_4$)** films. The trapping of $PtCl_4^{2-}$ ions in these MP films is consistent with what has been observed for related MP films (Cl^- ions can freely permeate MP films while larger anions are blocked).[5,9] A similar exchange process is not observed when a microcrystalline sample of **ZrPV(Cl)** is treated with a solution of $PtCl_4^{2-}$.

If a thin film of **ZrPV($PtCl_4$)** is suspended in water and hydrogen is bubbled through the solution, significant changes in the film are observed. Hydrogen treatment at room temperature leads to development of a deep blue color in the film, Figure 1b. Raising the temperature to 60 °C under hydrogen turns the film purple, Figure 1c. Pt(II) complexes are reduced to Pt(0) by hydrogen, typically giving colloidal platinum particles.[10–12] In addition to Pt(0), HCl and Cl^- ions are formed in this reduction reaction, converting the thin film into **ZrPV(Cl)·Pt_n**. A similar process has been used to generate colloidal CdS particles in $Zr(O_3PCH_2CH_2COOH)_2$.[1a] The HCl formed should be able to freely diffuse out of the film.[9] The bands associated with the blue film (405 and 605 nm) match those reported for monomeric reduced viologen.[13] The bands associated with the purple film (380 and 540 nm), formed on exhaustive reduction, correspond to a dimer of reduced viologens. The viologen reduction in this material results from platinum-catalyzed hydrogen reduction of the thin film. If HCl is added, the blue or purple color is immediately discharged, giving a gray film, Figure 1d. The gray color is consistent with the formation of colloidal Pt particles. Removing the acid and adding hydrogen regenerates the purple color, demonstrating that the film can readily act as a catalyst for the equilibration of H_2 and H^+. Scanning electron micrographs of a **ZrPV($PtCl_4$)** thin film before and after hydrogen treatment show the same surface morphology, suggesting that the Pt(0) particles are trapped inside the lamellar solid. The inability to exchange $PtCl_4^{2-}$ ions for Cl^- ions in solution also supports the proposal that the inorganic layers of these MP films prevent the migration of the platinum particles to the surface.

A common approach to designing systems for photochemical energy conversion and storage involves photoinduced electron transfer, leading to a high-energy charge-separated state ($A + D + h\nu \rightarrow A^- + D^+$),[14] as observed for **ZrPV(X)**. The photochemical splitting of water to give H_2 and O_2 is a common goal for such systems. While the individual components of the

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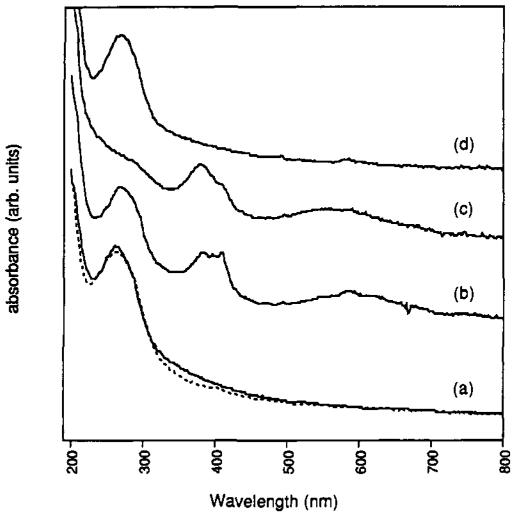

Figure 1. The electronic spectra of (a) a thin film of **ZrPV(Cl)** shown by a dotted line and a thin film of **ZrPV(PtCl$_4$)** shown by a solid line, (b) a film of **ZrPV(PtCl$_4$)** treated with H_2 at room temperature (blue), (c) a film of **ZrPV(PtCl$_4$)** treated with H_2 at 60 °C (purple), and (d) the purple film treated with HCl under anaerobic conditions.

charge-separated state typically have the appropriate potentials to carry out the reduction and oxidation of water, these direct reactions are often kinetically limited, requiring catalysts to overcome these kinetic barriers. Colloidal noble metal particles (*e.g*, Pt) have been found to be ideal catalysts for the reduction of water to give H_2.[15] In order to study the water reduction process independent of oxidation, a sacrificial reductant is typically used (*e.g.*, EDTA, triethanolamine, *etc.*). A typical system for the study of photochemical water reduction consists of an aqueous suspension of colloidal metal particles, a dialkyl viologen, a sensitizer, and a sacrificial reductant.

The photochemical charge separation observed for **ZrPV(X)** and thermal hydrogen equilibration observed for **ZrPV(Cl)·Pt$_n$** suggest that the platinized material may be capable of photochemically reducing water. In order to increase the amount of **ZrPV(Cl)·Pt$_n$** per gram of material to be photolyzed, films of **ZrPV(Cl)·Pt$_n$** four layers thick were grown on silica gel (chromatography grade, measured surface area = 450 m^2/g). On treatment with hydrogen at 60 °C, the **ZrPV(PtCl$_4$)**-derivatized silica gel turns black, consistent with the formation of colloidal platinum. EDAX measurements give a ratio of Zr to Pt in this material of approximately 1:0.3. Thermogravimetric analysis shows a weight loss of 10% for a thin film sample at 200 °C in air. The weight change corresponds to loss of the organic groups, to give $Zr(P_2O_7)\cdot Pt_n$. The expected weight loss for this transformation is 55% of the weight of the platinized thin film. Thus the silica-supported materials are estimated to be 20% **ZrPV(Cl)·Pt$_n$** by weight.

Photolysis of a silica gel supported film of **ZrPV(Cl)·Pt$_n$** suspended in pH 4 water with a 200-W Hg/Xe lamp leads to barely measurable amounts of hydrogen. If the photolysis is carried out in a 0.1 M solution of Na_2EDTA, however, the level of hydrogen produced is increased significantly (0.2 mL/h for the first half-hour). EDTA has been used as a sacrificial reductant in related systems;[14,15] in this capacity it acts to supply the reducing equivalents needed to turn the system over. The rate of hydrogen production gradually decreases on longer irradiation times (the rate averaged over 18 h of photolysis is 0.07 mL/h). Passing the light through a 330-nm cutoff filter decreases the rate of hydrogen production by more than an order of magnitude. The wavelength dependence for photoproduction of hydrogen in this system correlates well with that observed in forming charge-separated states in both microcrystalline and thin film samples of **ZrPV(X)** (X = Cl, Br).[2] Photoexcitation of the viologen group has been proposed as the first step in photoinduced charge transfer reactions in **ZrPV(X)**. A lower limit for the quantum yield for hydrogen formation in this system is 0.008 (2 × mol of H_2/mol of photons incident with $\lambda < 330$ nm).

Photolysis of a platinum-free thin film of **ZrPV(Cl)** on silica in 0.1 M Na_2EDTA generates hydrogen at a rate much lower than that of the platinized material (<0.01 mL/h). An aqueous suspension of colloidal platinum (0.1 M Na_2EDTA) to which 25 mg of $Zr(O_3PC_8H_{17})_2$ was added gave no detectable H_2 on photolysis. If the zirconium phosphonate is replaced with dimethyl viologen, however, H_2 is observed. Photolysis of an aqueous suspension of colloidal platinum (0.1 M Na_2EDTA, 8 mM dimethyl viologen dichloride) gave a rate of hydrogen production which was decreased by 60% relative to photolysis of **ZrPV(Cl)·Pt$_n$** (rate for the suspension = 0.08 mL/h). The increased efficiency for **ZrPV(Cl)·Pt$_n$** relative to the suspension is presumably due to the close contact of the viologen molecules and Pt particles; in **ZrPV(Cl)·Pt$_n$** electron transfer to Pt competes more effectively with back electron transfer. The 0.008 quantum efficiency for hydrogen production by **ZrPV(Cl)·Pt$_n$** is low relative to that for other reported systems.[14,15] The low yield could be due to a number of causes, including photochemical or mechanical degradation of the catalyst as well as poisoning by byproducts of the sacrificial reductant, all of which are being examined at this time. We are also investigating films in which the Cl^- ions have been replaced with other halides and pseudo halides.

Layered metal phosphonates allow a high degree of structural control in designing *very robust* systems for photochemical and electronic processes. In this communication we report the incorporation of colloidal platinum particles into a photochemically reducible metal phosphonate thin film. We are currently investigating the use of these materials as heterogeneous catalysts for the reduction of organic substrates by H_2, as well as studying the photochemical processes catalyzed by these materials. Another area of interest for us is the use of this film growth procedure to prepare novel multilayered materials. The sequential deposition technique can be used to grow films of completely different composition on top of **ZrPV(X)·Pt$_n$** films. A number of different heterostructures could be built in this way, which would incorporate different functions into different regions of the material.

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Supplementary Material Available: Details of the syntheses of thin films of **ZrPV(PtCl$_4$)** and **ZrPV(Cl)·Pt$_n$** on both planar substrates and silica gel particles; a description of the procedure used for photochemical hydrogen generation (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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