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Sensitized Polypyrrole-Coated Semiconducting Powders as Materials in Photosystems for Hydrogen Generation

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TiO₂ powders were coated with polypyrrole layers by irradiating dispersions of them in a solution containing pyrrole, oxygen, and fluoroborate ion with UV light. Polymer-coated and platinized powders were photoactive despite some losses, probably due to absorption by the polymer layer. Incorporating the anionic chromophore fluorescein into the positively charged polypyrrole structure sensitized the photocatalytic generation of hydrogen with visible light.

Introduction

In photoelectrochemical studies, polypyrrole coatings have been used to inhibit photocorrosion of *narrow-band-gap* semiconductors such as n-GaP^{1,2} and CdS,^{3,4} among others.^{5,6} Polypyrrole is a black, porous, stable, electrically conducting polymer. It is generally insoluble and can be prepared easily by the electrooxidation of pyrrole in aqueous and nonaqueous media in the presence of anions such as fluoroborate or perchlorate. It is well established that one counteranion per four pyrrole units is incorporated into the structure during electropolymerization to balance the charge of the positively charged polymer chain.⁷⁻⁹

While *wide-band-gap* semiconductors are more stable, they suffer from intrinsically inefficient use of the solar spectrum. One approach for improvement is the utilization of sensitizers, which shift the photoresponse of these stable materials into the visible region.⁷ Chromophores with high triplet quantum yields such as phthalocyanines,^{10,11} 8-hydroxyquinoline complexes,¹² chlorophyllin,¹³ xanthene dyes,^{14,15} metal porphyrin complexes,¹⁶⁻¹⁸ and ruthenium(II) coordination compounds¹⁸⁻²² have been used.

Photon harvesting using xanthene dyes as "antennas" linked to the backbone of electrically nonconducting polymer matrices such as poly(4-vinylpyridine), poly(vinylpyrrolidone), and polystyrene has been the subject of several recent studies.²³⁻²⁵ The ionic structure of conducting polypyrrole offers the possibility of incorporating *anionic* dyes into the polymeric structure for photon harvesting and sensitization purposes. This procedure has been used previously for incorporation of electrocatalysts, e.g., tetrasulfonated iron phthalocyanines, into polypyrrole on an electrode surface.²⁶ It is also known that polypyrrole improves the charge transfer between some planar semiconductor-ionic conductor-metal electrode interfaces.²⁷

With this in mind, we undertook to coat *particles* of a wide band-gap semiconductor, TiO₂, with polypyrrole by using photogenerated electron-hole pairs in the oxide and to examine, by using visible light, the sensitized production of hydrogen in well-studied sacrificial donor systems. This paper summarizes our results.

Experimental Section

TiO₂ (Degussa P-25, specific surface area of 56 m² g⁻¹) was used. Methanol (Fischer Scientific, spectroscopic grade), EDTA disodium salt (Spectrum Chemical), fluorescein monosodium salt

(Kodak), and tetrabutylammonium fluoroborate (Southwestern Analytical Chemical) were used as received. Deionized water with a resistivity of 18.3 MΩ cm was obtained from a Barnstead Nanopure system. A 1000-W Xe lamp equipped with a water jacket to remove IR was used for UV irradiation (90 ± 5 mW cm⁻²). A 435-nm cut-off filter was used for visible (VIS) irradiation (60 ± 5 mW cm⁻²). In both cases, the irradiated area was about 1 cm².

The details of the polypyrrole preparation and platinization are as follows:

1. **TiO₂/Polypyrrole:** 200 mg of TiO₂, 10 mg of tetrabutylammonium tetrafluoroborate, and 100 μL of pyrrole were placed in the reaction cell, and 30 mL of O₂-saturated H₂O was added. UV irradiation was carried out in air for 2 h.

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Table I. Photoactivities of Semiconductor Powders

| system | sacrificial donor | light source | rate ^a |
|---|---------------------------------|--------------|-------------------|
| TiO ₂ /Pt | CH ₃ OH ^b | UV-vis | 4.16 mL/h |
| TiO ₂ /PPyBF ₄ /Pt | CH ₃ OH | UV-vis | 2.55 mL/h |
| TiO ₂ /Pt/PPyBF ₄ | CH ₃ OH | UV-vis | 1.02 mL/h |
| TiO ₂ /PPyFl/Pt | EDTA ^c | vis | 55 μL/h |
| TiO ₂ /Pt/PPyFl | EDTA | vis | 23 μL/h |
| TiO ₂ /PPyBF ₄ Pt | EDTA | vis | 0 |
| TiO ₂ /Pt + Fl ^d | EDTA | vis | 9 μL/h |
| TiO ₂ /PPyBF ₄ /Pt + Fl | EDTA | vis | 29 μL/h |

^a Based on 2-h irradiation times. ^b CH₃OH/H₂O = 1/1 (vol). ^c [EDTA²⁻] = 0.1 M. ^d Fl in solution.

2. Platinization: 200 mg of the appropriate powder was mixed with 8 mL of H₂PtCl₆ solution (0.0002 g of Pt mL⁻¹), and ≈22 mL of water was added. The slurry was deaerated in argon and irradiated with UV for 2 h.²⁸ The pH was about 5.

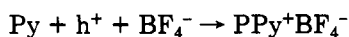
3. Fluorescein: the fluorescein anion sensitizer was incorporated into the polymeric coating by ion exchange of the electrostatically bound fluoroborate anion with a 3 × 10⁻³ M aqueous fluorescein solution (pH 6.5).

All powders were washed thoroughly with deionized water and dried at 90 °C. The presence of fluorescein in the polypyrrole-coated surface of TiO₂ powder was established spectrofluorometrically by using a SPEX Fluorolog photon-counting fluorometer equipped with an RCA C31034 photomultiplier tube. Either EDTA (dianion) or methanol was used as a sacrificial electron donor in the photocatalysis studies.

The reaction vessels were stoppered with rubber septa, and the powders were dispersed by sonication. Deaeration was carried out with an argon purge and sonication for at least 30 min prior to irradiation in all photocatalysis experiments. A headspace of 6–8 mL was maintained in the reaction vessel. The solution was constantly stirred. At timed intervals, 200 μL of argon was injected into the vessel and 200 μL of the headspace gas was removed for gas chromatography (thermal conductivity detector, column packed with 13X 60–80 mesh molecular sieve, argon was the carrier gas).

Results and Discussion

The valence band edge of TiO₂ is located so that the photochemical conversion of pyrrole monomer to polymer can be sensitized by band-gap irradiation of these semiconducting powders²⁹ in the presence of oxygen as a sacrificial electron acceptor and fluoroborate as a counteranion. The process follows



where h⁺ is formed by optical excitation of the semiconductor.

Table I shows the UV photoactivity (over a 2-h period) of the polypyrrole-coated anatase powders in a water-methanol mixture, one of the most efficient hydrogen-producing photosystems known.³⁰ These are given in units of STP volume/h and, unless stated otherwise, are initial rates. Compared to the platinized TiO₂ powders (TiO₂/Pt), the photoactivity is lower for TiO₂ powders which are first polypyrrole-coated and then photoplatinized (TiO₂/PPyBF₄/Pt). The photoactivity is even lower for TiO₂ powders which are photoplatinized first and then coated with a polypyrrole layer (TiO₂/Pt/PPyBF₄).

Presumably, this is mainly due to optical absorption by the dark polymer surface. In addition to the light-filtering effect of the polypyrrole layer, the platinum catalyst underneath the polymeric coating likely works less efficiently as a catalyst for hydrogen evolution than that deposited onto the surface of the polymer coating. We conclude that, not surprisingly, there are no obvious advantages of using polypyrrole with UV excitation. Clearly, however, photoactivity remains.

We now consider sensitization and visible photoactivity. The polypyrrole layer on TiO₂ particles (TiO₂/PPyBF₄) can be doped with fluorescein anions by a simple exchange of fluoroborate anions using a solution of dye at neutral pH (TiO₂/PPyFl). This system fluoresces between 490 and 650 nm when excited with 475-nm light. The liquid phase does not fluoresce, indicating that all fluorescein has been incorporated. This material is active for the visible photocatalytic evolution of hydrogen in the presence of EDTA (Table I). The TiO₂/PPyFl/Pt powders generate hydrogen more effectively than TiO₂/Pt/PPyFl powders, i.e., platinization last is better.

Comparative studies with TiO₂/Pt and TiO₂/PPyBF₄/Pt powders dispersed in fluorescein solution show interesting visible photoactivities. Over the first 2 h, the H₂ evolution rates are about equal. They then slow over the next 2 h, TiO₂/Pt slowing the most. After that, the rates become constant over the next 20 h (Table I). Spectrochemical studies show that both before and after 3 h of illumination of TiO₂/PPyBF₄/Pt the whole amount of fluorescein used (1 mg) was adsorbed on 12 mg of substrate. No traces of fluorescein were found in the liquid phase. The amount of the sensitizer adsorbed on the uncoated TiO₂ surface was much less, and fluorescence was readily observed in the solution. These results show that concentrating the dye in the conducting polymer layer is not harmful and improves the long-term visible photoactivity of the system.

We clearly do not know the detailed structure of the polypyrrole layer. On the basis of photoelectrochemical studies,²⁷ we assume that polypyrrole fully covers the TiO₂ particles. We can assert that the layers function to concentrate the sensitizer and enhance the overall yield of H₂. Because fluorescence of fluorescein from the polypyrrole layer is observed, we know that the efficiency of charge-transfer quenching is less than 100%. This is not surprising considering the heterogeneous internal structure expected in the polymer layer.

In summary, this work shows that polypyrrole can be photochemically formed on platinized TiO₂ powders and that these powders retain significant activity for UV-photoassisted catalytic generation of hydrogen in the presence of a sacrificial electron donor, particularly when platinized after the polymer is added. Adding fluorescein to the polypyrrole layer sensitizes the system for visible-photoassisted production of hydrogen.

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Registry No. EDTA, 60-00-4; CH₃OH, 67-56-1; TiO₂, 13463-67-7; H₂, 1333-74-0; Pt, 7440-06-4; polypyrrole, 30604-81-0; fluorescein, 2321-07-5.

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