

Photocatalysed CO₂-Fixation to Formate and H₂-Evolution by Eosin-modified Pd-TiO₂ Powders

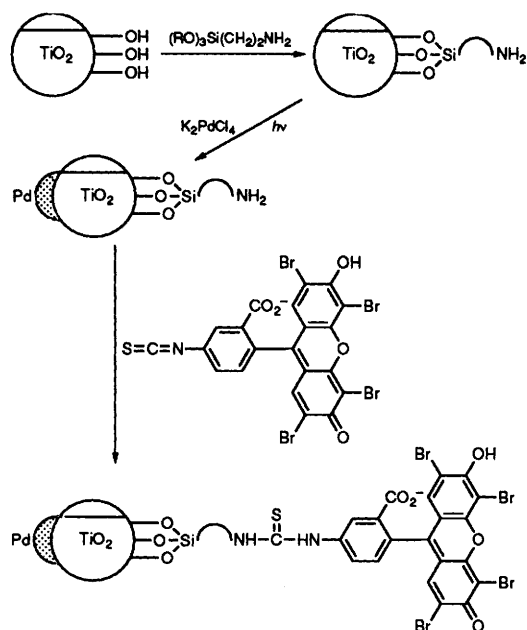
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Covalent attachment of an eosin monolayer to a Pd-TiO₂ semiconductor powder provides an effective photocatalyst for CO₂-HCO₃⁻ fixation to formate and H₂-evolution.

Semiconductor photocatalysed hydrogen evolution and CO₂-fixation are two processes of fundamental interest for solar energy conversion and storage.^{1,2} Extensive efforts have recently been directed towards the utilization of semiconductor catalysts for the mineralization of organic waste products^{3,4} and for the elimination of atmospheric greenhouse pollutants⁵ such as NO and CO₂. TiO₂ semiconductor photocatalysts were applied for the photochemical fixation of CO₂ to various C₁ fuel products.^{6,7} These processes are, however, very inefficient and lead to mixtures of reduced carbon products. TiO₂ powders with metal deposited catalysts such as Ru,⁸ Pd⁹ and Cu¹⁰ revealed improved photocatalytic activities and selective production of methane, formate and methanol, respectively. The photocatalytic activation of TiO₂ requires, however, UV-irradiation, and hence, the semiconductor performance in the solar spectrum is inefficient. Several methods to switch the photocatalytic activities of semiconductor particles to the visible region involve surface modification of the semiconductors by organic dyes or transition metal complexes.¹¹⁻¹³ In the present study, we describe a method to switch the photocatalytic activity of Pd-TiO₂ powders to the visible spectral region by covalent attachment of an eosin-dye monolayer to the semiconductor-oxide particles. We demonstrate effective electron injection from the excited dye into the semiconductor conduction band. The injected electrons drive the selective catalytic reduction of CO₂-HCO₃⁻ to formate. The eosin-modified Pd-TiO₂ acts also as an H₂-evolution photocatalyst.

The organization of the Pd-TiO₂ photocatalyst modified by the eosin monolayer is described in Scheme 1. Surface hydroxy groups associated with TiO₂ (Degussa P-25) were silanated by aminopropyl triethoxysilane.† Palladium metal



Scheme 1 Organization of Pd-TiO₂ powders modified by eosin monolayers

was photodeposited¹⁴ onto the silanated TiO₂ powder, and subsequently was covalently attached to the surface active monolayer. Illumination, $\lambda > 435$ nm, of an aqueous system that contains CO₂-HCO₃⁻ (0.1 mol dm⁻³), Na₂edta (0.01 mol dm⁻³) as sacrificial electron donor, and the eosin-modified Pd-TiO₂, Pd-TiO₂-Eo²⁻ (6.3 mg), results in the formation of formate (HCO₂⁻).‡ No H₂-evolution from the system is detected in the presence of CO₂-HCO₃⁻. Fig. 1 [curve (a)] shows the rate of HCO₂⁻ formation in the system with time during illumination. The quantum yield for HCO₂⁻ formation corresponds to $\phi = 0.008$. Control experiments revealed that no formate production was observed upon exclusion of the Pd-catalyst, the eosin component or Na₂edta, from the photosystem. Furthermore, the rate of formate formation from a photosystem employing the Pd-TiO₂ powder, Na₂edta as sacrificial electron donor and eosin (3.6×10^{-4} mol dm⁻³), as a homogeneous photosensitizer, is also shown in Fig. 1 [curve (b)]. Evidently, the yield of formate production is ca. five-fold higher in the photosystem where eosin is covalently linked to the TiO₂-surface. In the absence of CO₂-HCO₃⁻, the Pd-TiO₂-Eo²⁻ photocatalyst effects H₂-evolution. The

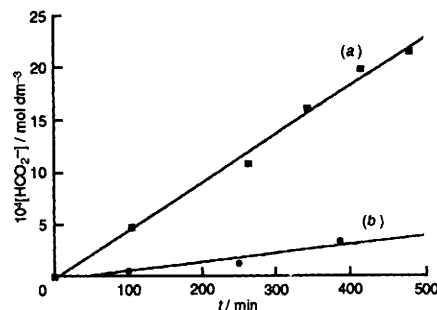


Fig. 1 Rate of formate production at time intervals of illumination: (a) Pd-TiO₂-Eo²⁻ photocatalyst, (b) Pd-TiO₂ and solubilized eosin, (3.6×10^{-4} mol dm⁻³). All systems are composed of 3 ml aqueous solution at pH = 7.6, containing Na₂edta (0.01 mol dm⁻³), HCO₃⁻ (0.1 mol dm⁻³) and the respective Pd-TiO₂ photocatalyst (6.3 mg). All systems were saturated with CO₂ prior to illumination.

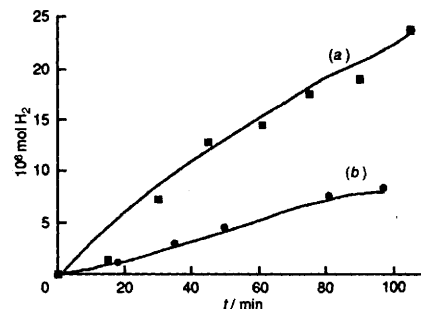


Fig. 2 Rate of H₂-evolution at time intervals of illumination of the photosystems: (a) Pd-TiO₂-Eo²⁻ photocatalyst; (b) Pd-TiO₂ and solubilized eosin (3.6×10^{-4} mol dm⁻³). All systems consist of a 3 ml aqueous solution at pH = 7.6, containing the respective photocatalyst, (6.3 mg), Na₂edta, (0.01 mol dm⁻³), HCO₃⁻, (0.1 mol dm⁻³) and ethanethiol (5×10^{-5} mol dm⁻³).

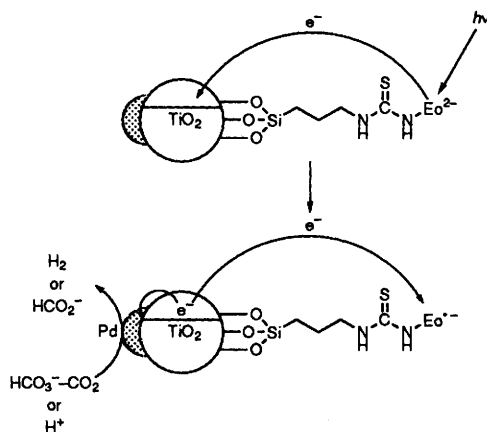


Fig. 3 Photosensitization of TiO_2 by the eosin monolayer and catalysed CO_2 - HCO_3^- fixation and H_2 -evolution

quantum yield for H_2 -evolution from the system is, however, lower than that of HCO_2^- formation and corresponds to $\phi = 0.0004$.

The improved photocatalytic activity of Pd- TiO_2 powders modified by an eosin monolayer is also observed towards H_2 -evolution in the presence of ethanethiol as the sacrificial electron donor, Fig. 2. Irradiation, $\lambda > 435$ nm, of an aqueous solution at pH = 7.6, which contains the Eo^{2-} -modified monolayer TiO_2 (6.3 mg), and ethanethiol (5×10^{-5} mol dm^{-3}), results in H_2 -evolution. The rate of H_2 formation with time during illumination is shown in Fig. 2 [curve (a)] and corresponds to a quantum yield of $\phi = 0.12$.[§] Illumination of this photosystem in the presence of CO_2 - HCO_3^- does not lead to the formation of formate, and the H_2 -evolution proceeds at the same efficiency as in the system in the absence of CO_2 - HCO_3^- . The yield of H_2 -evolution from the system that contains the chemically modified catalyst, Pd- TiO_2 - Eo^{2-} , was compared to that from a photosystem containing the Pd- TiO_2 catalyst and solubilized Eo^{2-} [curve (b), Fig. 2]. The quantum yield of H_2 -evolution is ca. two-fold higher in the photosystem that includes the covalently linked eosin photocatalyst.

The results reveal the enhanced photocatalytic properties of Pd- TiO_2 powders that are chemically modified by an eosin monolayer towards CO_2 - HCO_3^- -fixation and H_2 -evolution. The improved photocatalytic activities of Pd- TiO_2 - Eo^{2-} are attributed to effective photosensitization of the semiconductor by the immobilized dye, Fig. 3. Excitation of the eosin monolayer results in effective electron transfer to the semiconductor conduction band. Electron tunnelling to the Pd catalyst site effects CO_2 - HCO_3^- fixation or H_2 -evolution. That is, the immobilized dye is effectively quenched by the semiconductor, and its natural or radiationless decays are minimized. The results also reveal selective CO_2 - HCO_3^- fixation or H_2 -evolution being controlled by the electron donor employed in the photosystem. With Na_2edta as electron donor, only HCO_2^- was observed and no H_2 -evolution was detected in the presence of CO_2 - HCO_3^- . With ethanethiol as electron donor, only H_2 -evolution occurs.

Previous studies indicated that thiols inhibit the CO_2 - HCO_3^- activation sites on a Pd-catalyst.¹⁵ Also, it has been shown that CO_2 - HCO_3^- reduction on a Pd-catalyst is substantially faster than the competitive H_2 -evolution. Thus, the lack of HCO_2^- formation in the photosystem that includes ethanethiol as electron donor is attributed to the inhibition of the CO_2 - HCO_3^- activation sites by the thiol. It should be noted, however, that the quantum yield for H_2 -evolution is ca. 300-fold higher in the photosystem that includes ethanethiol as compared to the system comprising Na_2edta as sacrificial electron donor. The enhancement in H_2 -evolution from the

system that includes ethanethiol is attributed to its better electron donating properties. That is, upon photosensitization of the semiconductor, back electron-transfer competes with the subsequent catalysed H_2 -evolution. Effective scavenging of the intermediate oxidized eosin dye by the electron donor would prevent the back electron-transfer and direct the conduction band to H_2 -evolution, Fig. 3. With ethanethiol the oxidized eosin dye is effectively scavenged and efficient H_2 -evolution proceeds. With Na_2edta as electron donor, back electron-transfer competes with the irreversible oxidation of the electron donor, and hence, the H_2 -evolution yield decreases.

We conclude that covalent attachment of an eosin monolayer to the Pd- TiO_2 powder provides an effective photocatalyst for CO_2 - HCO_3^- fixation and H_2 -evolution that operates in the visible spectral region.

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Footnotes

† Silanization of TiO_2 was accomplished by refluxing the powder with 1% (v/v) solution of propylaminotriethoxysilane in dry toluene.

‡ Formate was analysed by ion-chromatography using a Shodex column (0.1% H_3PO_4 as eluent). Further complementary analysis of formate was executed by the enzymatic assay of the photolysed solution. The biocatalysed reduction of NAD^+ to NADH by formate using formate dehydrogenase (E.C. 1.2.1.2) was followed spectroscopically at $\lambda = 340$ nm.

§ H_2 -evolution was analysed by gas-chromatography, MS 5A column, Ar as carrier gas.

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