Efficient Visible Light Sensitization of TiO_2 by Surface Complexation with $Fe(CN)_6^{4-}$

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A coloured charge-transfer complex formed by adsorption of $Fe(CN)_6^{4-}$ at the surface of TiO_2 particles and electrodes upon photoexcitation injects electrons into the conduction band of this semiconductor with a quantum yield of at least 37%.

The photosensitization of wide-band-gap oxide semiconductors is a subject of intensive investigation,[1] mainly owing to its importance in electrophotography[2] and solar energy conversion.[3] Optimum results are achieved with systems where intimate contact between dye and semiconductor surface is established.[4,5] Here, we report on a charge-transfer type complex formed between $Fe(CN)_6^{4-}$ and Ti^{4+} ions at the surface of TiO_2 which shifts the onset of the photo-response of this semiconductor from 400 to 700 nm.

The deeply orange coloured surface complex is formed when TiO_2 colloid (particle size 12 nm, prepared as previously described[6]) or powder (Degussa P25, a mixture of *ca.* 75% anatase and 25% rutile) is added to a deaerated aqueous solution of $K_4Fe(CN)_6$. The reaction takes place readily at pH $\leqslant 5$. In neutral solution the presence of electrolyte, *e.g.* 10^{-1} M $NaClO_4$, is required for the complexation of the particles. Figure 1 illustrates the effect of adding 2 g/dm^3 colloidal TiO_2 (protected by 2 g/dm^3 polyvinyl alcohol, PVA) on the optical absorption spectrum of a deaerated solution containing 3.9×10^{-5} M $Fe(CN)_6^{4-}$ and 10^{-2} M $HClO_4$. While $Fe(CN)_6^{4-}$ alone does not absorb any light above 350 nm, a pronounced visible absorption extending until 700 nm develops in the presence of the TiO_2 particles. The maximum absorption is located at 430 nm and the extinction coefficient is 5.2×10^3 dm^3 mol^{-1} cm^{-1}. Cyclic voltammetry experiments showed that practically all the $Fe(CN)_6^{4-}$ present in the solution underwent surface complexation.†

Surface complexation by $Fe(CN)_6^{4-}$ was found to take place also with TiO_2 powders or electrodes. For example, addition of 5 g/dm^3 TiO_2-P25 to a 10^{-3} M $Fe(CN)_6^{4-}$ solution in 10^{-2} M aqueous $HClO_4$ leads to immediate deep orange coloration of the particles, the reflectance spectrum of which displays a broad maximum at *ca.* 450 nm. The visible absorption is attributed to a charge transfer complex formed between $Fe(CN)_6^{4-}$ and surface Ti^{4+} ions. Further evidence for the formation of such a complex was obtained by the reaction of hexacyano-ferrate and -ferrite with titanium ions in acidic solutions. Addition of $Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$ to solutions containing Ti^{3+} or TiO^{2+} ions, respectively, resulted in the formation of an orange coloured precipitate, presumably a titanium analogue of Prussian Blue, with a reflectance spectrum similar to that of $Fe(CN)_6^{4-}$-covered TiO_2.

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† Free $Fe(CN)_6^{4-}$ shows a reversible wave at 0.36 V (normal hydrogen electrode). This disappears in the presence of TiO_2 particles.

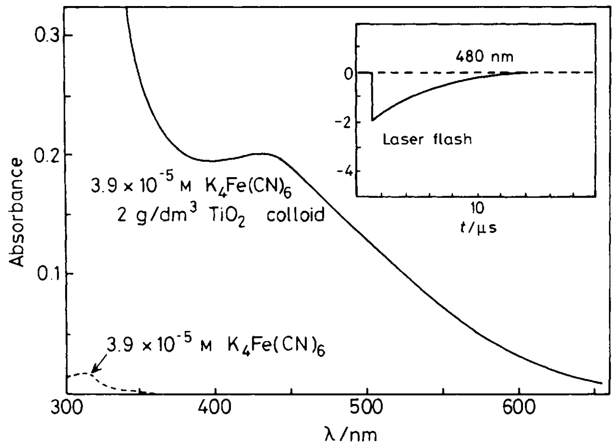

Figure 1. Effect of colloidal TiO_2 (2 g/dm^3 protected by 2 g/dm^3 PVA) on the absorption spectrum of a 3.9×10^{-5} M $K_4Fe(CN)_6$ solution in 10^{-2} M $HClO_4$, optical path length 1 cm. Dashed line: $K_4Fe(CN)_6$ solution, reference 10^{-2} M $HClO_4$; solid line: $K_4Fe(CN)_6/TiO_2$ solution 5 h after addition of colloidal TiO_2; reference solution is 2 g/dm^3 TiO_2 protected by 2 g/dm^3 PVA. Insert: 530 nm laser photolysis of the colloidal $TiO_2/Fe(CN)_6^{4-}$ solution; the oscilloscope trace shows the temporal behaviour of the absorption at 480 nm.

The charge-transfer character of the surface complex would suggest that visible light sensitization of TiO_2 by $Fe(CN)_6^{4-}$ should be possible. This is fully borne out by results obtained with both TiO_2 colloids and electrodes. The insert in Figure 1 shows an oscilloscope trace obtained from the 530 nm laser photolysis of colloidal TiO_2 covered with $Fe(CN)_6^{4-}$. The 480 nm absorption of the charge-transfer complex is bleached within the 20 ns duration of the laser pulse and recovers subsequently with a half-lifetime of 3 μs. This is interpreted in terms of very rapid photoinduced electron injection in the conduction band (cb) of TiO_2 [reaction (1)], followed by the much slower intra-particle back electron transfer [reaction (2)]. The rate constant for the latter reaction is *ca.* 2×10^5 s^{-1}, which is typical for the recapture of conduction band electrons by oxidized sensitizers adsorbed at the surface of colloidal TiO_2 particles.[5,7]

$$[Fe(CN)_6^{4-}]_{TiO_2} \xrightarrow{h\nu} e^-_{cb}\,(TiO_2) + [Fe(CN)_6^{3-}]_{TiO_2} \quad (1)$$

$$[Fe(CN)_6^{3-}]_{TiO_2} + e^-_{cb}\,(TiO_2) \rightarrow [Fe(CN)_6^{4-}]_{TiO_2} \quad (2)$$

Photoelectrochemical experiments employed a three-compartment cell equipped with a quartz window. The working electrode was a cylindrical titanium rod (geometric area 0.28 cm^2) onto which a polycrystalline anatase layer (thickness *ca.* 20 μm, surface roughness factor *ca.* 200) was deposited as previously described.[8,9] The TiO_2 layer was coated with $Fe(CN)_6^{4-}$ by immersing the electrode for 5 h in a stirred deaerated aqueous solution (pH 2, adjusted with $HClO_4$) containing 10^{-2} M $K_4Fe(CN)_6^{4-}$ and subsequent air-drying. Dye release upon immersion of the coated electrode in moderately acidic aqueous solution was negligible. Steady-state photolysis employed a 150 W Oriel tungsten–halogen lamp used in conjunction with a water filter and a Kratos monochromator. The light intensities were measured with a Yellow Springs Institute-Kettering (YSI-K) radiometer.

Figure 2 presents the action spectrum for the photocurrent observed during visible light irradiation of $Fe(CN)_6^{4-}$-coated TiO_2 electrodes. Apart from 10^{-2} M $HClO_4$ the solution contained 10^{-2} M hydroquinone as electron donor. The action spectrum is characterized by a maximum at 420 nm matching the absorption features of the $Fe(CN)_6^{4-}$ complex formed with colloidal TiO_2 particles, Figure 1. The incident monochromatic photon-to-current conversion efficiency (η), defined as the number of electrons injected by the excited sensitizer (and recorded as photocurrent) divided by the number of incident photons, was calculated from equation (3). The current density obtained at 420 nm at an incident light flux of 0.84 W m^{-2} is 10.4 μA cm^{-2} which corresponds to $\eta = 37\%$. In the absence of $Fe(CN)_6^{4-}$ η is $\leqslant 2\%$ for $\lambda > 400$ nm.[5] This shows the remarkable efficiency of $Fe(CN)_6^{4-}$ for sensitizing the visible light response of TiO_2. A monolayer of dye deposited on a flat electrode could at most absorb a few % of the incident light. The high roughness factor of the TiO_2 layer enhances the harvesting of visible photons by allowing the sensitizer to attain a 200 times larger concentration than on a smooth surface. Multiple reflection of the light within the fractal structure of the layer could also contribute to the high efficiency.

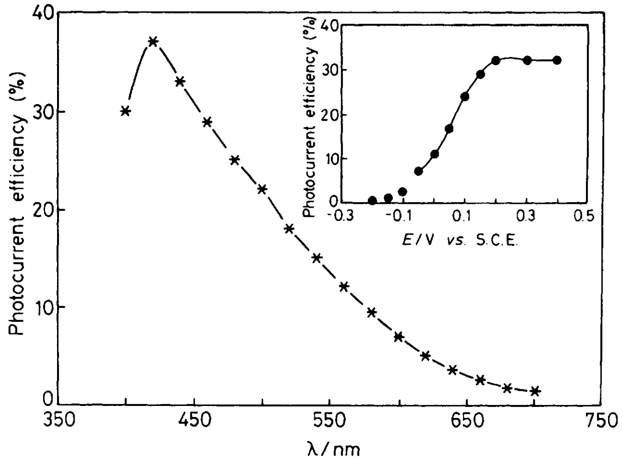

Figure 2. Photocurrent action spectrum obtained with $Fe(CN)_6^{4-}$-loaded anatase electrodes; conditions: 10^{-2} M $HClO_4$, 10^{-2} M hydroquinone electrode potential 0.2 V (S.C.E.), solution deaerated with Ar. Insert: Photocurrent–potential curve obtained under the same conditions at λ 440 nm.

$$\eta(\%) = \frac{1.24 \times 10^3 \times (\text{photocurrent density}/\mu\text{A cm}^{-2})}{(\text{wavelength/nm}) \times (\text{photon flux/W m}^{-2})} \quad (3)$$

The insert of Figure 2 presents the photocurrent–potential curve measured during illumination (440 nm light) of the $Fe(CN)_6^{4-}$-coated electrode under similar conditions as the photocurrent action spectrum. The steady state photocurrent has the onset at −0.2 V (standard calomel electrode, S.C.E.) which is close to the flat band potential of TiO_2. It rises steeply with increasing potential reaching a plateau at 0.1 V.

In conclusion, we have discovered the formation of a stable charge-transfer complex at the surface of TiO_2 involving $Fe(CN)_6^{4-}$. This surface complexation is expected to play an important role in photoelectrochemical studies of TiO_2 electrodes where $Fe(CN)_6^{4-}$ is often employed as electron donor. We have furthermore found that the charge transfer complex is an efficient sensitizer, the incident photon-to-current conversion efficiency being as high as 37% in the visible.

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