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Solid-State Photochromic Device Based on Nanocrystalline TiO_2 Functionalized with Electron Donor–Acceptor Species

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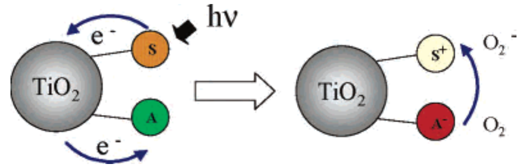
In this Communication, we report on a new type of solid-state photochromic device, S-TiO_2-A, which is based on electron-transfer processes involving a molecular sensitizer (S) and an electron acceptor (A) coadsorbed onto the surface of nanocrystalline TiO_2. The electron-transfer process is mediated by the semiconductor conduction band and leads to a long-lived charge-separated state S^+/A^-. The lifetime of this state can be controlled by oxygen diffusion through a polymeric coating deposited on the device.

Functional nanomaterials based on sensitized wide-band-gap semiconductors have attracted much interest and have been the subject of fundamental studies on interfacial electron transfer. Several applications have been proposed for these materials in the fields of solar photoconversion devices[1,2] and in the development of optical sensors, electrochromic devices,[3,4] and artificial photosynthetic centers.[5] While electron transfer at the molecular level has been widely investigated,[6] electron-transfer kinetics between adsorbed molecular assemblies and semiconductor nanoparticles is at the beginning, and the subject has mainly been addressed in the context of studies related to photocatalysis[7] and photoelectrochemical solar devices.[8] There is a general agreement in the literature that photoinduced charge injection from an adsorbed dye (S) to the conduction band of a wide-band-gap semiconductor, such as TiO_2, is ultrafast (femtosecond to picosecond time domain) and may take place from electronic or vibronic excited states of S*, while charge recombination between conduction band electrons (e^-_{CB}) and the oxidized dye (S^+) may require hundreds of nanoseconds for completion, with a mechanism that may involve a direct electron to S^+ recombination or electron hopping toward S^+. If the molecular sensitizer is firmly bound to the surface, S^+ diffusion can be ruled out.

Scheme 1



In this Communication, we report on a new type of photochromic device, abbreviated as S-TiO_2-A, which is based on electron-transfer processes involving a molecular sensitizer (S) and an electron acceptor (A) coadsorbed onto the surface of nanocrystalline TiO_2 (Scheme 1).

In the scheme, the semiconductor support acts as a shuttle for the electrons injected by the excited sensitizer and charge recombination may either involve direct electron transfer between the reduced A^- and oxidized S^+ or be mediated by oxygen. Photoinduced vectorial electron transfer between a molecular sensitizer and an electron acceptor coadsorbed onto nanocrystalline TiO_2, mediated by the semiconductor conduction band, has previously been demonstrated by the Fitzmaurice group,[9] who obtained, in the presence of an electrolyte solution, a long-lived charge separation on a nanostructured anatase membrane containing coadsorbed [bis(4,4′-dicarboxy-2,2′-bipyridine)(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II)]$^{2+}$ complex and a viologen.

The solid-state device described here is based on molecular sensitizers and electron acceptors previously studied by our

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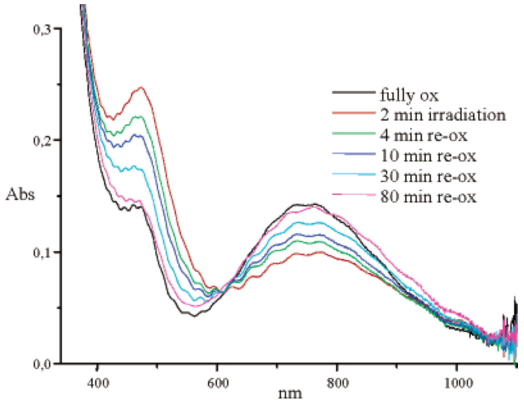

Figure 1. Absorption spectral changes observed after 2 min of irradiation in the visible region of a mixture of **1** and **3**, in a 1:4 molar ratio, coadsorbed onto a 6-μm-thick TiO_2 film.

group.[10−12] The metal-to-ligand charge-transfer (MLCT) sensitizers $[Ru(dcbH_2)_2(CN)_2]$ (**1**)[10b] and $[Os(H_3tcterpy)(dcbH_2)Cl]^+$ (**2**)[11] ($dcbH_2$ = 2,2′-bipyridine-4,4′-dicarboxylic acid; H_3tcterpy = 2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid) were considered for their high electron injection efficiency to TiO_2 nanoparticles, and the mixed-valence (MV) species $[HOOCpyRu^{III}(NH_3)_4(NC)Ru^{II}(bpy)_2(CN)]^{3+}$ (**3**) and $[HOOCpyRu^{III}(NH_3)_4(NC)Ru^{II}(CN)_5]^-$ (**4**) (HOOCpy = pyridine-4-carboxylic acid; bpy = 2,2′-bipyridine), where the Ru^{III} moiety can be bound to TiO_2 via the pyridine-4-carboxylic acid unit, were selected as electron acceptors for the easy reduction of the Ru^{III} units ($E_{1/2}$ = 0.11 V (**3**) and $E_{1/2}$ = 0.10 V (**4**) vs SCE in water),[12] at a potential lower than the TiO_2 conduction band (>−0.6 eV vs SCE[1]), and for the presence of intense metal-to-metal charge-transfer (MMCT) bands in their electronic absorption spectra.[12]

Irradiation, in the presence of a cutoff filter at 400 nm, in the visible region of transparent TiO_2 films supported on glass, functionalized with the mononuclear sensitizers **1** and with the MV complex **3**, in a 1:4 molar ratio,[13] results in a color change from green to red brown (Figure S1 in the Supporting Information), corresponding to the spectral variations reported in Figure 1. Analogous results were obtained in experiments carried out with **2** and **4** coadsorbed onto TiO_2 (Figure S4 in the Supporting Information).

From the molar ratio of the adsorbed components and the molar extinction coefficients at 480 and 780 nm of **1** [ϵ_{480}(MLCT) = 12 000 M^{-1} cm^{-1}; ϵ_{780} = negligible] and **3** [ϵ_{480} = negligible; ϵ_{780}(MMCT) = 3000 M^{-1} cm^{-1}] and of the oxidized $[Ru^{III}(dcbH_2)_2(CN)_2]^+$ [ϵ_{480} and ϵ_{780} = negligible] and reduced $[HOOCpyRu^{II}(NH_3)_4(NC)Ru^{II}(bpy)_2(CN)]^{2+}$ [ϵ_{480}(MLCT) = 11 500 M^{-1} cm^{-1}; ϵ_{780} = negligible], it can be concluded that the observed spectral changes are consistent with a 35% reduction of the acceptor (A). Considering the 4 times excess of adsorbed (A) with respect to (S), this would correspond to a conversion exceeding 100% of the initial S-TiO_2-A state to a final charge-separated state S^+-TiO_2-A^-, a feature that can only be justified by assuming that during film irradiation reduction of the nascent S^+ takes place presumably because of the presence of adsorbed water. This fact is consistent with the high oxidizing ability of $[Ru^{III}(dcbH_2)_2(CN)_2]^+$ species ($E_{1/2}$ = + 1.04 V vs SCE in water at pH 2)[10b] and is supported by previous observations of the behavior of $[Ru^{III}(bpy)_3]^{3+}$ in water.[21] Control experiments on insulating ZrO_2 (S2 and S4 in the Supporting Information) showed that this state could only be reached via electron-transfer processes mediated by the semiconductor support. No spectral changes were, in fact, observed after irradiation of S-ZrO_2-A films in the visible region. As indicated by transient absorbance experiments on TiO_2 films in acetonitrile solutions, formation of the charge-separated state S^+-TiO_2-A^- is clearly limited by charge recombination between conduction band electrons (e^-_{CB}) and the oxidized sensitizer, S^+. In these experiments, two sets of TiO_2 films with adsorbed **1** sensitizer or $[Ru^{II}(NH_3)_5pyCOOH]^{2+}$ complex, chosen to model the behavior of the $HOOCpyRu^{III}(NH_3)_4^-$ electron acceptor unit, were excited at 532 nm (S4 in the Supporting Information) to promote charge injection to the semiconductor. Back electron transfer, $e^-_{CB} \rightarrow Ru^{III}$, was followed by monitoring of the Ru^{III} bleaching decay as a function of time. The results reported in Figure 2 reveal that, despite a difference of ca. 0.6 V in the driving force,[14] charge recombination involving $[Ru^{III}(dcbH_2)_2(CN)_2]^+$ or $[Ru^{III}(NH_3)_5pyCOOH]^{3+}$ occurs on the same time scale.

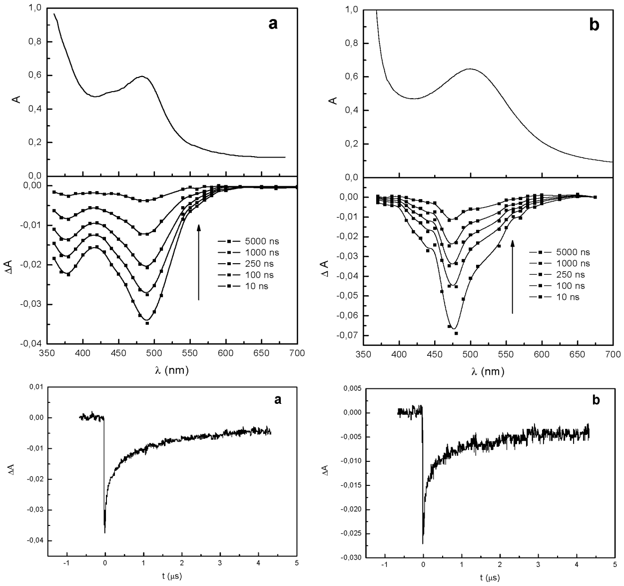

Figure 2. Transient absorbance spectral changes and kinetics of the MLCT bleaching recovery following 532-nm laser excitation of TiO_2 films sensitized with **1** (a) and $[Ru^{II}(NH_3)_5pyCOOH]$ (b) (for experimental details, see the Supporting Information).

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[13] Conduction band electrons can either recombine with the oxidized sensitizer (S^+) or reduce the MV complex (A). The 1:4 (S/A) ratio increases the probability for the reduction of A and was observed to give optimal spectroscopic results.

[14] The difference in the driving force was estimated by the difference between the half-wave potentials of the R^{III}/Ru^{II} couples: for **1**, $E_{1/2}$ = 1.04 vs SCE, in aqueous solution at pH 2, and for $[Ru(NH_3)_5pyCOOH]^{2+}$, $E_{1/2}$ = 0.42 vs SCE in acetonitrile.

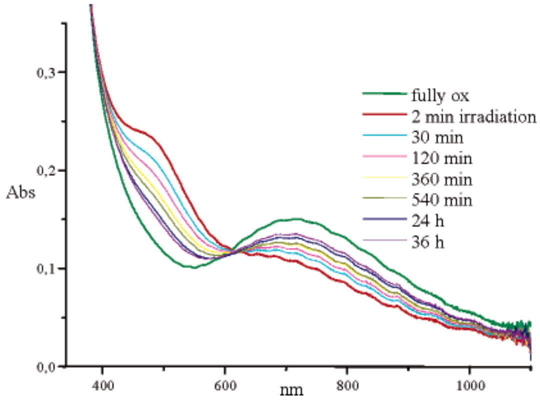

Figure 3. Absorption spectral changes observed after 2 min of irradiation in the visible region of a mixture of **1** and **3**, in a 1:4 molar ratio, coadsorbed onto a 6-μm-thick TiO_2 film coated with a PMMA film under nitrogen.

Kinetic traces in Figure 2 were fitted to a biexponential decay[15] giving weighted average rate constants of $(1.44 \pm 0.03) \times 10^6\ s^{-1}$ (Figure 2a) and $(1.58 \pm 0.04) \times 10^6\ s^{-1}$ (Figure 2b), indicating a slow transport of the injected electrons back to the oxidized species. Although compelling evidence exists that charge recombination falls in the Marcus kinetic inverted region,[16−18] charge recombination has been reported in several cases insensitive to the reduction potential of the sensitizer.[19,2019−20]

Charge recombination from S^+-TiO_2-A^- to the initial S-TiO_2-A state is slow and strongly affected by the presence of oxygen. In experiments where the electron acceptor A on TiO_2 was reduced by band-gap excitation of the semiconductor, reoxidation was observed to take place on a comparable time scale. This points to a dominant mechanism involving electron transfer between A^- and oxygen to form a superoxide, followed by S^+ reduction by O_2^-. Water oxidation from the Ru^{III} center of S^+,[2221−22] as well as direct electron transfer involving coadsorbed A^- and S^+, may also contribute in part to restoration of the initial S-TiO_2-A state. The role played by oxygen in the recombination S^+-TiO_2-A^- → S-TiO_2-A is demonstrated by experiments on S-TiO_2-A films coated with poly(methyl methacrylate) (PMMA; S5 in the Supporting Information). With PMMA coatings, deposited under nitrogen, we were able to observe a delay in the recovery of the initial state of ca. 40 h (Figure 3).

In conclusion, TiO_2 nanoparticles cofunctionalized with dye sensitizers and electron acceptors allow one to obtain a long-lived photoinduced charge separation and storage of redox equivalents at the molecular level. The reversibility of the associated color changes clearly depends on the stability of the oxidized sensitizer and reduced acceptor. TiO_2 films functionalized with **1**−**3** or **2**−**4**, without polymeric coatings, were rewritten and left to erase at least five times without observing significant spectral changes. Writing of S-TiO_2-A films (Figure S1 in the Supporting Information) is limited by light diffraction; near-field spectroscopic experiments on a thin homogeneous distribution of S-TiO_2-A nanoparticles would allow one to gain insight into the optical resolution obtainable with these photochromic materials, behaving as optical storage devices where the lifetime of the stored information can be varied by controlling the diffusion of oxygen through a polymeric coating.[22]

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Supporting Information Available: Materials and methods for the preparation of the Ru^{II} complex and nanostructured TiO_2 and ZrO_2 films and for photophysical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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