

Photoconductivity of an inorganic/organic composite containing dye-sensitized nanocrystalline titanium dioxide

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The photophysical properties of solid films of an inorganic/organic composite composed of dye-sensitized nanocrystalline titanium dioxide (TiO₂) particles, a conjugated polymer, and a [60] fullerene derivative have been investigated. Large charge collection efficiencies of up to 10% at a field of only 10 V/μm were observed. The photoaction spectrum of the composite is interpreted in terms of three major contributions: a weak photocurrent due to the absorption of photons by the polymer, photogeneration of charges involving the fullerene, and a broad region below the onset of the polymer absorption which involves photophysical processes in the dye-loaded TiO₂ nanoparticles. © 1998 American Institute of Physics. [S0003-6951(98)02806-X]

Polymers have been investigated for many years as the photoactive components in photorefractive devices, solar cells, or xerographic layers. These applications require an efficient photogeneration of charges in the solid material. While films of pure polymers often exhibit low photoconductivities,¹⁻⁵ sensitizers have been used to increase the efficiency of charge carrier generation and to broaden the photoaction spectrum.⁶⁻⁸ The process mostly involves a direct photoinduced charge transfer between the polymer and the sensitizer or vice versa. Recently, nearly quantitative conversion of light into electric current was demonstrated for photoelectrochemical cells with nanocrystalline TiO₂ electrodes coated with an appropriate Ru(II) complex.⁹ The large conversion efficiency was explained by the efficient vectorial electron injection from the photoexcited state of the dye into the conduction band of semiconductor particles.^{10,11} In this letter we will show that the photoinduced electron injection process in TiO₂ nanocrystals can be used as an alternative approach to considerably increase the photocurrent in polymer-based composites.

We have investigated the photophysical properties of an inorganic/organic composite of nanocrystalline TiO₂ particles coated with a *cis*-X₂Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (X=SCN⁻) dye [Ru L₂(NCS)₂],¹¹ mixed into a conjugated polymer (LPPP)¹² matrix, which also acts as the hole transport medium. An easy accessible [60] fullerene derivative was added as the electron conducting compound.¹³ This derivative has electronic properties comparable to those of C₆₀ but is more soluble in common organic solvents. TiO₂ was synthesized through hydrolysis and condensation of Ti(OEt)₄ under acid conditions. The modification of the TiO₂ was anatase/brookite (70/30) as determined by x-ray powder diffraction. During preparation the TiO₂ nanocrystals of ~10–20 nm in diameter agglomerated to larger particles with diameters of ~100 nm. The Brunauer–Emmett–Teller (BET) surface area of these agglomerates is 278 m²/g. The particles were sensitized in a solution of RuL₂(NCS)₂ in EtOH, followed by freeze-drying

of the reddish-colored product. From elementary analysis the surface coverage was determined to be 46% (assuming a surface requirement of 1 nm² of one adsorbed dye molecule according to Ref. 10). The reddish powder was redispersed in the solution of the polymer in toluene. The fullerene derivative was dissolved in toluene and added to the mixture. Solid sandwich cells were fabricated by casting from solution onto glass substrates which had previously been covered with semitransparent gold stripe electrodes. Aluminum top electrodes were added on top by thermal evaporation, giving sandwich structures with a surface area of 5.6 mm². The inspection of the cast films with an optical microscope revealed an aggregation of the [60] fullerene and TiO₂, which leads to an inhomogeneity of the local concentration of the two compounds. Spin-coated layers were rather rough because of the large TiO₂ particle size and sandwich devices of these films were short in all cases. Photocurrent spectra were recorded with illumination through the bottom electrode using a home-built setup.⁴

The photoaction spectrum of an LPPP(75 wt %)/TiO₂(12.5 wt %)/fullerene(12.5 wt %) composite is shown in Figure 1. The photocurrent is low within the spectral range of the polymer absorption and raises abruptly below the polymer band gap, followed by a smooth decrease with increasing wavelength. There is a small peak at ~710 nm beyond which the photocurrent drops to zero.

For comparison, the photoaction spectrum of the LPPP(80 wt %)/fullerene(20 wt %) two-component blend (Figure 1) exhibits a broad and structured peak with maxima at 580 nm and 710 nm. Due to the above mentioned variation in the local concentration of the fullerene molecules the photocurrent value varied for different sandwich cells but the shape of the spectrum was almost the same in each case. Steady state photoconductivity experiments on pure C₆₀ films had consistently shown a large photogeneration efficiency in the tail of the C₆₀ absorption.¹⁴⁻¹⁶ The rise in photogeneration efficiency above 2.3 eV was interpreted in terms of intermolecular charge-transfer states. The detailed analysis gave maxima in the photogeneration efficiency at 350 nm, 540 nm, 570 nm and 715 nm.¹⁴ The good agreement with the positions of the photocurrent peaks of our LPPP/

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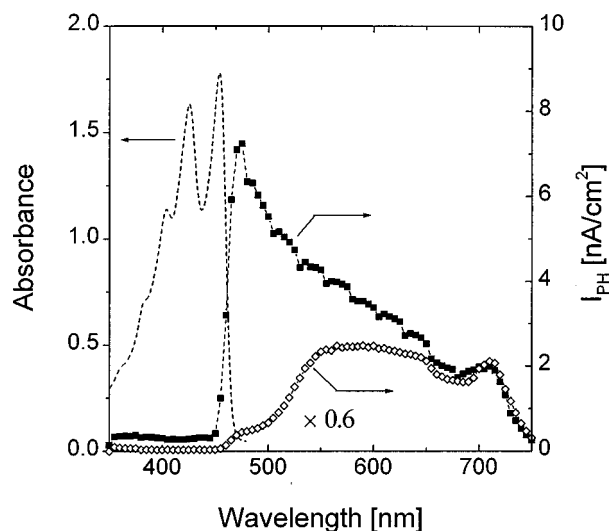


FIG. 1. Photoconductivity spectra of a sandwich device of a $5.6 \mu\text{m}$ thick LPPP/TiO₂/fullerene (75:12.5:12.5) composite film (■) and a $17.2 \mu\text{m}$ thick LPPP/fullerene (80:20) blend layer (◇) between Au and Al electrodes. I_{PH} is defined as the difference in current with and without illumination. The spectra were recorded in dry nitrogen atmosphere ($p=1$ bar) at room temperature. The samples were illuminated through the Au bottom electrode with a constant photon flux of 10^{13} photons/cm² s at the film side facing the light source. In both cases an external voltage of 10 V was applied with the Au electrode biased as the anode. Also shown is the absorbance of a cast film of pure LPPP.

fullerene blend films indicates that the large photocurrent at longer wavelengths can in part be explained by processes involving intermolecular charge transfer within the fullerene aggregates. We do not yet understand the reason for the low photocurrent within the polymer absorption range for the fullerene doped films. Recent work has shown that the addition of [60] fullerene derivatives to semiconducting polymers raises the charge carrier generation efficiency by several orders of magnitude.^{7,17–19} We have observed a pronounced increase in photoconductivity only in 200 nm thick spin-coated layers of LPPP/fullerene.

The comparison between the spectra in Figure 1 shows that the photocurrent of the LPPP/TiO₂/fullerene composite must involve photophysical processes in the dye-loaded TiO₂ nanoparticles. Here, we propose a two-step process for the photogeneration of charge carriers in the composite (Figure 2). In the first step the dye is photoexcited and an electron is injected from the dye into the conduction band of TiO₂. This is followed by a second charge separation process between the TiO₂ particle and a fullerene molecule and between the dye and the polymer, respectively. The proposed scheme is supported by two experimental findings. It has been demonstrated that fullerene radicals can be generated in a suspension with TiO₂ by photoexcitation of the TiO₂ particles with light of energy higher than the semiconductor band gap.^{20,21} Further, electron transfer between a solid organic hole transport material and the photoexcited ruthenium dye after photoexcitation has recently been proven.^{22,23} Provided that the primary electron transfer occurs upon photoexcitation of the dye, the subsequent charge separation can be well expected due to the particular electronic level scheme of the constituents of the hybrid composite. It is quite surprising that the largest photocurrent of the composite arises at the polymer absorption edge and not at the absorption peak of the

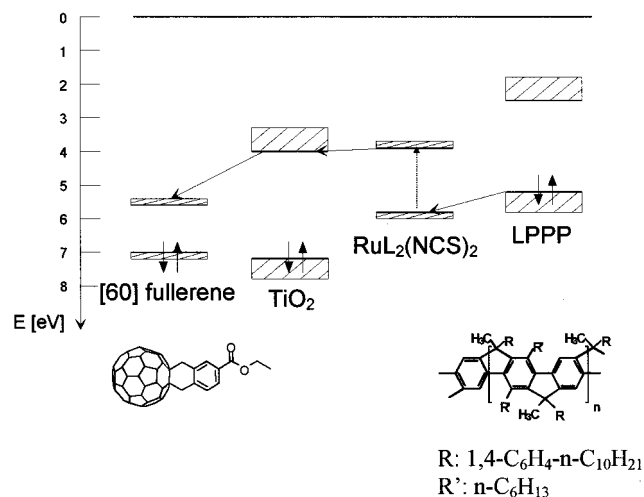


FIG. 2. Schematic energy band diagram of the used compounds and of the proposed charge transfer processes following photoexcitation of the Ru dye.

RuL₂(NCS)₂ dye (at 525 nm). The particular shape of the spectrum suggests a contribution by electron transfer processes at the Al electrode. However, the shape of the spectrum was similar for films measured in a gold surface comb geometry. We could not detect a considerable photocurrent in any films with nonsensitized TiO₂ particles or with pure RuL₂(NCS)₂ pigments dispersed in the polymer matrix below the band gap of the polymer. This indicates that the photogeneration of charges in the composite involves the electron transfer between the photoexcited dye and an electron acceptor species, probably TiO₂.

Figure 3 shows the charge collection efficiency under the assumption that all light is absorbed in the film. The efficiency increases strongly with applied electric field in the entire wavelength range and is up to 10% at a field of only 10 V/ μm . The photocurrent was linear as a function of light intensity at wavelengths above and below the onset of polymer absorption, which indicates that the fraction of photogenerated charges recombining in the film is not significant.

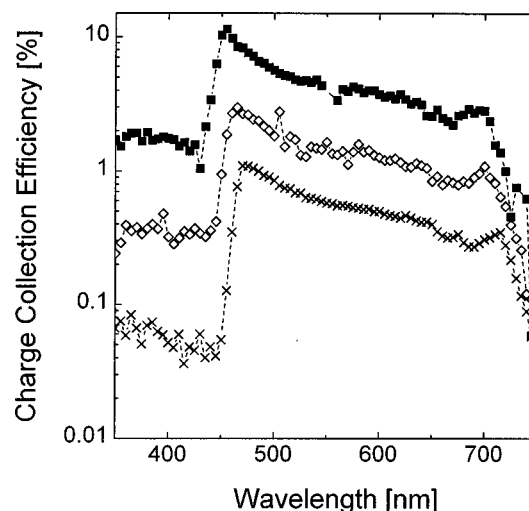


FIG. 3. Charge collection efficiency of a sandwich device of a $5.6 \mu\text{m}$ thick LPPP/TiO₂/fullerene (75:12.5:12.5) composite film. The spectra were recorded under the same conditions as the spectra shown in Figure 1. An external voltage of +20 (x), 40 (◇) and 60 V (■) was applied with the Au electrode biased as the anode.

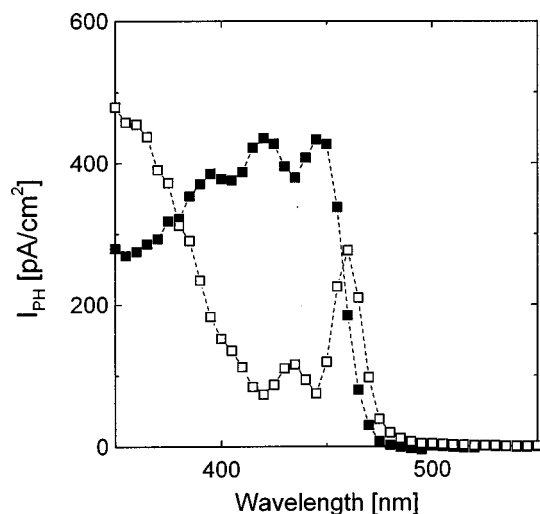


FIG. 4. Photoconductivity spectra of a sandwich device of a 8 μm thick LPPP between Au and Al electrodes. The spectra were recorded under the same conditions as the spectra shown in Figure 1. An external voltage of 4 V was applied with the Au electrode biased either as the anode (■) or the cathode (□).

Furthermore, the spectral dependence of the photocurrent was independent of the scanning direction (increasing or decreasing wavelength) and changed only slightly upon reversal of the field direction. In contrast the photoaction spectra of a pure LPPP cast film as shown in Figure 4 exhibits a pronounced dependence on polarity. In this case photocurrent is only produced by the fraction of the incident light absorbed fairly close to the anode.^{24–26} The enhanced and spectrally broadened photocurrent of the composite indicates that dye-loaded TiO₂ nanoparticles act as efficient centers for the photogeneration of charges in a polymer matrix with further use in photorefractive or xerographic devices.

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- ¹M. Gailberger and H. Bässler, Phys. Rev. B **44**, 8643 (1991).
- ²N. T. Binh, M. Gailberger, and H. Bässler, Synth. Met. **47**, 77 (1992).
- ³V. Cimrova and S. Nespurek, Chem. Phys. **184**, 283 (1994).
- ⁴P. Gättinger, H. Rengel, and D. Neher, Synth. Met. **83**, 245 (1996).
- ⁵S. Barth, H. Bässler, H. Rost, and H. H. Hörhold, Phys. Rev. B **56**, (1997).
- ⁶H.-H. Hörhold, M. Helbig, D. Raabe, J. Opfermann, U. Scherf, R. Stockmann, and D. Weiß, Z. Chem. **27**, 126 (1987).
- ⁷Y. Wang, Nature (London) **356**, 585 (1992).
- ⁸K.-Y. Law, Chem. Rev. **93**, 449 (1993).
- ⁹B. O'Regan and M. Grätzel, Nature (London) **353**, 737 (1991).
- ¹⁰B. O'Regan, J. Moser, M. Anderson, and M. Grätzel, J. Phys. Chem. **94**, 8720 (1990).
- ¹¹M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, J. Am. Chem. Soc. **115**, 6382 (1993).
- ¹²U. Scherf and K. Müllen, Makromol. Chem. Rapid Commun. **12**, 489 (1991).
- ¹³The [60] fullerene derivative was synthesized according to the general procedure described in P. Belik, A. Gügel, A. Kraus, M. Walter, and K. Müllen, J. Org. Chem. **60**, 3307 (1995).
- ¹⁴G. Giro, J. Kalinowski, P. DiMarco, V. Fottori, and G. Marconi, Chem. Phys. Lett. **211**, 580 (1993).
- ¹⁵S. Kazaoui, R. Ross, and N. Minami, Phys. Rev. B **52**, R11665 (1995).
- ¹⁶S. Kazaoui, R. Ross, and N. Minami, Synth. Met. **70**, 1403 (1995).
- ¹⁷N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).
- ¹⁸J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Holmes, and A. B. Moratti, Synth. Met. **77**, 277 (1996).
- ¹⁹A. Haugeneder, C. Kallinger, W. Spirk, U. Lemmer, J. Feldmann, U. Scherf, E. Harth, A. Gügel, and K. Müllen, Proc. SPIE **3142** (in press).
- ²⁰A. Stasko, V. Brezova, S. Biskupic, K.-P. Dinse, P. Schweitzer, and M. Baumgarten, J. Phys. Chem. **99**, 8782 (1995).
- ²¹A. Stasko, V. Brezova, S. Biskupic, K.-P. Dinse, R. Groß, M. Baumgarten, A. Gügel, and P. Belik, J. Electroanal. Chem. **423**, 131 (1997).
- ²²Deutsche Patentanmeldung, DE-1953385 (1997)
- ²³J. Hagen, W. Schaffrath, P. Otschik, R. Fink, A. Bacher, H.-W. Schmidt, and D. Haarer, Synth. Met. **89**, 215 (1997).
- ²⁴T. Ravindran, W. H. Kim, A. K. Jain, J. Kumar, and S. K. Tripathy, Synth. Met. **66**, 203 (1994).
- ²⁵A. Köhler, J. Grüner, R. H. Friend, K. Müllen, and U. Scherf, Chem. Phys. Lett. **243**, 456 (1995).
- ²⁶M. G. Harrison and J. Grüner, Synth. Met. **84**, 653 (1997).