

Conjugated fluorene copolymers as hole transport materials in polymer-metal oxide photovoltaic devices.

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Solid state, high mobility hole transporting materials are needed for applications in dye sensitised and composite donor-acceptor solar cells. Conjugated fluorene copolymers are one of the most promising groups of materials under development for plastic optoelectronics and are attractive on account of hole mobilities of up to $10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ [1]. These polymers absorb in the blue or green and are candidates for both the hole transporting component in dye sensitised structures, and the light absorbing component in unsensitised composite structures.

We focus on a model system consisting of a fluorene polymer in contact with nanocrystalline or thin-film TiO_2 . Metal oxides such as TiO_2 are widely used in dye sensitised solar cells and are attractive for composite photovoltaic devices on account of their stability, electron transport properties and the possibilities for controlling interface morphology. In this paper we report on basic studies of charge transport in thin films of fluorene copolymers, transient optical measurements of charge recombination in composite polymer- TiO_2 structures, and the influence of morphology and device structure on photovoltaic performance.

Hole mobilities in the range $10^{-4} - 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ are measured for films of thickness from 0.2–1.4 μm using the dark injection transient technique. The mobilities agree with values obtained using time of flight in thicker films and confirm the superior charge transport properties of these materials. Dispersive and non-dispersive transport characteristics in different polymers are identified and explained in terms of the presence of trap states.

We observe effective photoinduced charge transfer from polymer to TiO_2 in composite structures using nanosecond-millisecond transient optical spectroscopy. The high yield for charge transfer is accompanied by photoluminescence quenching, and both depend upon the degree of penetration of polymer into the TiO_2 nanostructure. Recombination between the polaron in the polymer and electron in the TiO_2 is remarkably slow, with a half life of around 1 ms (Figure 1), comparable with the recombination time in dye sensitised films at short circuit [2]. Such slow recombination kinetics suggest the availability of high open circuit voltages.

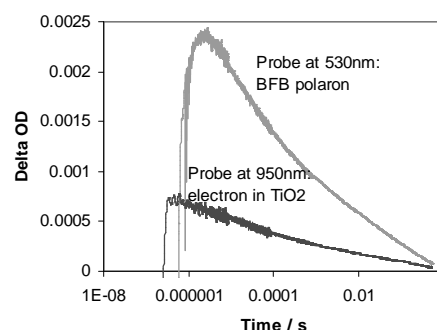


Figure 1. Transient absorption traces for a fluorene co-polymer / porous TiO_2 structure excited by a laser pulse at 400nm. Peaks at 530 nm and 950 nm correspond to the polymer polaron and the electron in the TiO_2 . The half life for recombination is around 1ms, indicating that the charge separated state is long lived.

Photocurrent generation and photovoltage in composite devices are functions of the morphology and the relative compositions of polymer and TiO_2 . Photocurrent quantum efficiencies of 1% are obtained in simple bi-layer devices and are increased by structuring of the interface. We discuss the effect of interface morphology on photocurrent generation and the optimisation of this materials system for solar energy conversion.

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[1] M.Redecker et al. *Adv. Mater.* **11**, 241 (1999).

[2] S.A.Haque *et al.*, *J.Phys. Chem.* **102**, 1745-1749 (1998).