Recombination dynamics in dye sensitised nanocrystalline metal oxide thin films.

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Charge recombination between electrons and photo-oxidised dyes adsorbed on to nanocrystalline metal oxide electrodes may be studied using ms-μs transient absorption spectroscopy. Previous studies have shown that recombination on TiO_2 electrodes is limited by electron transport in the TiO_2, and can be explained in terms of the trap-limited diffusive transport of electrons [1,2]. In the present study we extend this work to alternative metal oxide films (ZnO instead of TiO_2); and address the detailed mechanism of electron transport using recombination kinetics as a probe.

Recombination dynamics for dye sensitised ZnO films show qualitatively the same behaviour as dye sensitised TiO_2 films. They are observed to show slower recombination dynamics at positive applied bias, but these recombination dynamics accelerate more rapidly with negative applied bias. This observation is found to be in good agreement with the rate of charge accumulation in the two metal oxide films, determined by capacitance measurements. We find that the presence of small cations (H^+ and Li^+) has a strong influence upon recombination dynamics and capacitance for TiO_2 films, but virtually no effect upon the behaviour of ZnO films. The implications of this observation for the design of dye sensitised solar cells will be discussed.

To probe the mechanism of charge transport we measure recombination kinetics on TiO_2 films as a function of film thickness, light intensity, and temperature. We find that:

(i) Kinetics are independent of film thickness between 2 and 8 μm. These results imply that the electron density is effectively independent of depth within the film, and that any variation in electron Fermi level near to the substrate is taken up in less than 2 μm.

(ii) Kinetics accelerate continuously as light intensity is increased from a level corresponding to less than 1 to more than 1 electrons per nanocrystal. With the aid of modelling we show that this indicates that inter-particulate electron transport is not the rate determining step.

(iii) In the case of a polymer electrolyte, we study kinetics as a function of temperature in the range 20 to 60°C. Kinetics exhibit a change in shape towards a stretched exponential of lower dispersion parameter, as temperature is increased. This indicates that transport is limited by the thermal activation of electrons out of trap states, and not by multiple step tunnelling.

We conclude that the primary factors influencing charge recombination in nanocrystalline metal oxide electrodes are the distribution of electron trap states and not the film morphology or device thickness. Moreover, the effective distribution of trap states appears to be a function of the material and its chemical environment.

[1] S.A.Haque *et al.*, *J.Phys. Chem.* **102,** 1745-1749 (1998); *J.Phys. Chem.* 104, 538-547 (2000).
[2] J. Nelson *et al. Phys Rev B* **63**, 205321 (2001); J. Nelson, *Phys RevB* **59**, 15374 (1999).