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A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

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THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

Solar energy conversion by photoelectrochemical cells has been intensively investigated[2-11]. Dye-sensitized cells differ from the conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport. In the case of n-type materials, such as TiO_2, current is generated when a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the semiconductor, Fig. 1. To complete the circuit, the dye must be regenerated by

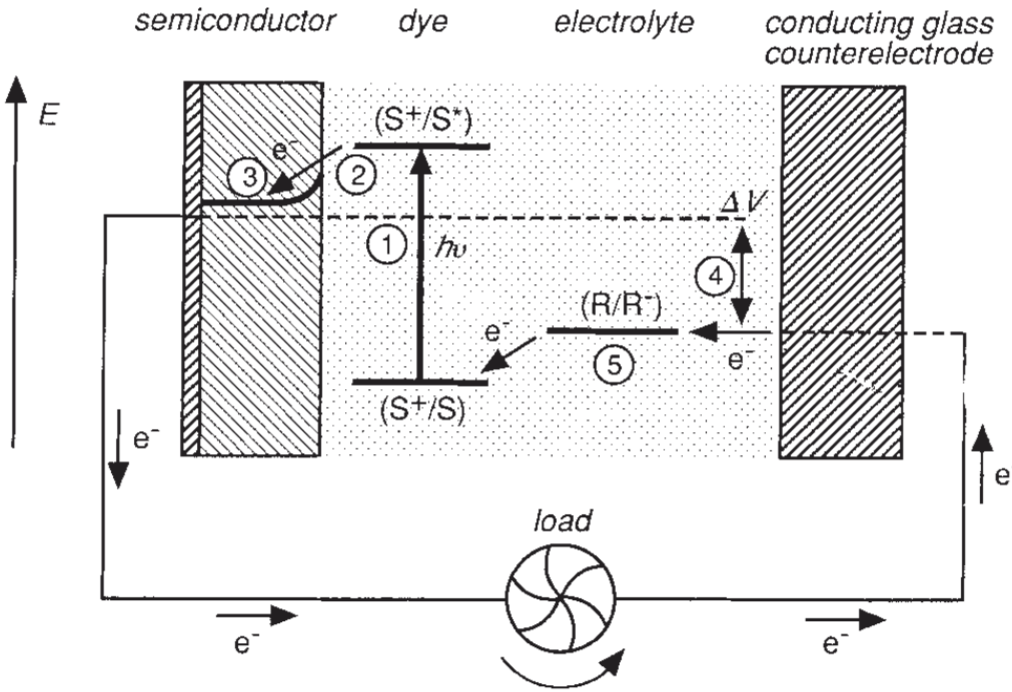

FIG. 1 Schematic representation of the principle of the dye-sensitized photovoltaic cell to indicate the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference, ΔV, between the quasi-Fermi level of TiO_2 under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple (R/R^-) used to mediate charge transfer between the electrodes. S, sensitizer; S^*, electronically excited sensitizer; S^+, oxidized sensitizer.

electron transfer from a redox species in solution which is then reduced at the counter electrode. The monochromatic current yield

$$\eta_i(\lambda) = \mathrm{LHE}(\lambda) \times \phi_{\mathrm{inj}} \times \eta_e \qquad (1)$$

where LHE (light harvesting efficiency) is the fraction of the incident photons that are absorbed by the dye, ϕ_{inj} is the quantum yield for charge injection and η_e is the efficiency of collecting the injected charge at the back contact, expresses the ratio of measured electric current to the incident photon flux at a given wavelength. The photovoltage ΔV in Fig. 1, generated by the cell, corresponds to the difference between the Fermi level in the semiconductor under illumination and the Nernst potential of the redox couple in the electrolyte.

Although attempts to use dye-sensitized photoelectrochemical cells in energy conversion have been made before, the efficiency of such devices has been extremely low and practical applications have seemed remote. One problem is that of poor light harvesting. On a smooth surface, a monomolecular layer of sensitizer absorbs less than 1% of incident monochromatic light. Attempts to harvest more light by using multilayers of dye have in general been unsuccessful. The remaining option is to increase the roughness of the semiconductor surface so that a larger number of dye molecules can be adsorbed directly to the surface and can simultaneously be in direct contact with the redox electrolyte. Matsumura *et al.*[12] and Alonso *et al.*[13] have used sintered ZnO electrodes to increase the efficiency of sensitization by rose bengal and related dyes. Willig, Parkinson and colleagues[14] have reported high quantum yields for the dye sensitization of SnS_2. But the conversion yields from solar light to electricity remained well below 1% for these systems. In addition, the instability of the dyes employed presented a severe practical drawback. By using semiconductor films consisting of nanometer-sized TiO_2 particles, together with newly developed charge-transfer dyes, we have improved the efficiency and stability of the solar cell.

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High-surface-area TiO_2 films were deposited on a conducting glass sheet from colloidal solutions. A transmission electron micrograph of the colloid is shown in Fig. 2. Electronic contact between the particles was produced by brief sintering at 450 °C. The size of the particles and pores making up the film is controlled by the size of the particles in the colloidal solution. The internal surface area of the film is determined by the size of the particles and the thickness of the film. These parameters were optimized to obtain efficient light harvesting while maintaining a pore size large enough to allow the redox electrolyte to diffuse easily. Films of 10 μm thickness consisting of particles with an average size of 15 nm gave linear photocurrent response up to full sunlight and were used throughout. A cubic close packing of 15-nm-sized spheres to a 10-μm-thick layer is expected to produce a 2,000-fold increase in surface area.

Absorption spectra obtained for such nanostructured TiO_2 films are shown in Fig. 3. Bare films are transparent and colourless, displaying the fundamental absorption edge of anatase (band gap 3.2 eV) in the ultraviolet region. Deposition of a monolayer of the trimeric ruthenium complex[15,16], $RuL_2(\mu\text{-}(CN)Ru(CN)L'_2)_2$, **1**, where L is 2,2′ bipyridine-4,4′-dicarboxylic acid and L′ is 2,2′-bipyridine, results in deep brownish-red coloration of the film. The absorption onset is shifted to 750 nm, the light harvesting efficiency reading almost 100% in the whole visible region below 550 nm. Integration of the spectral overlap between a solar emission of AM1.5 and this absorption band shows that 46% of the incident solar energy flux is harvested by the dye coated film ($AM = 1/\sin\alpha$ where α is the angle of incidence of the solar rays at the Earth's surface).

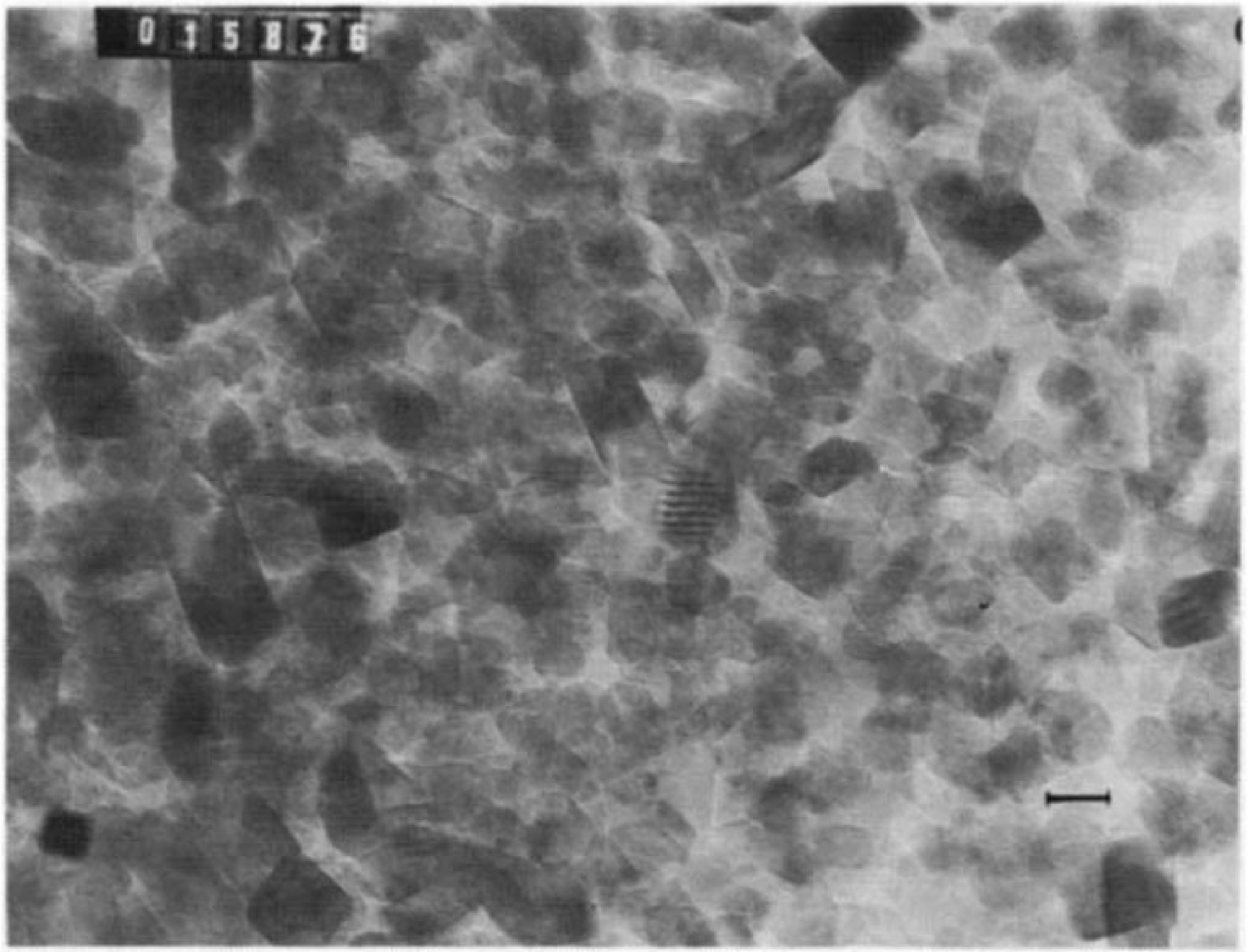


FIG. 2 Transmission electron micrograph of TiO_2 particles used in thin film production. The scale bar represents 10 nm. Particles were prepared by

coloration of the film. The absorption onset is shifted to 750 nm, the light harvesting efficiency reading almost 100% in the whole visible region below 550 nm. Integration of the spectral overlap between a solar emission of AM1.5 and this absorption band shows that 46% of the incident solar energy flux is harvested by the dye coated film ($AM = 1/\sin \alpha$ where α is the angle of incidence of the solar rays at the Earth's surface).

The optical density of the film at 478 nm corrected for the absorption by the conducting glass support was 2.45. Dividing by the extinction coefficient[16] of **1** ($e_{478} = 1.88 \times 10^7\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) yields the dye surface concentration, $\Gamma = 1.3 \times 10^{-7}\ \mathrm{mol\ cm}^{-2}$. As each dye molecule occupies an area[16] of 1 nm^2, the inner surface of the film is 780 cm^2 for each 1 cm^2 of geometric surface. Thus, the roughness factor is 780, which is smaller than the predicted value of 2,000. The difference is attributed to necking between TiO_2 particles. In addition, the large size of **1** prevents its access to very small pores, reducing the apparent surface area.

The photocurrent action spectrum obtained with the dye-coated TiO_2 film is also shown in Fig. 3. It closely matches the absorption spectrum, indicating that the current is due to electron injection from **1** into the conduction band of TiO_2. The photocurrent yield measured at 520 nm was found to depend on the counter ion of the iodide/triiodide redox electrolyte, increasing from 68% for tetrapropylammonium to 84% for Li^+. After correction for the light absorption by the conducting glass, the yields are 80% and 97%, respectively. This shows that the nanostructured TiO_2 films used in conjunction with suitable charge transfer dyes can achieve quantitative conversion of visible light photons into electric current.

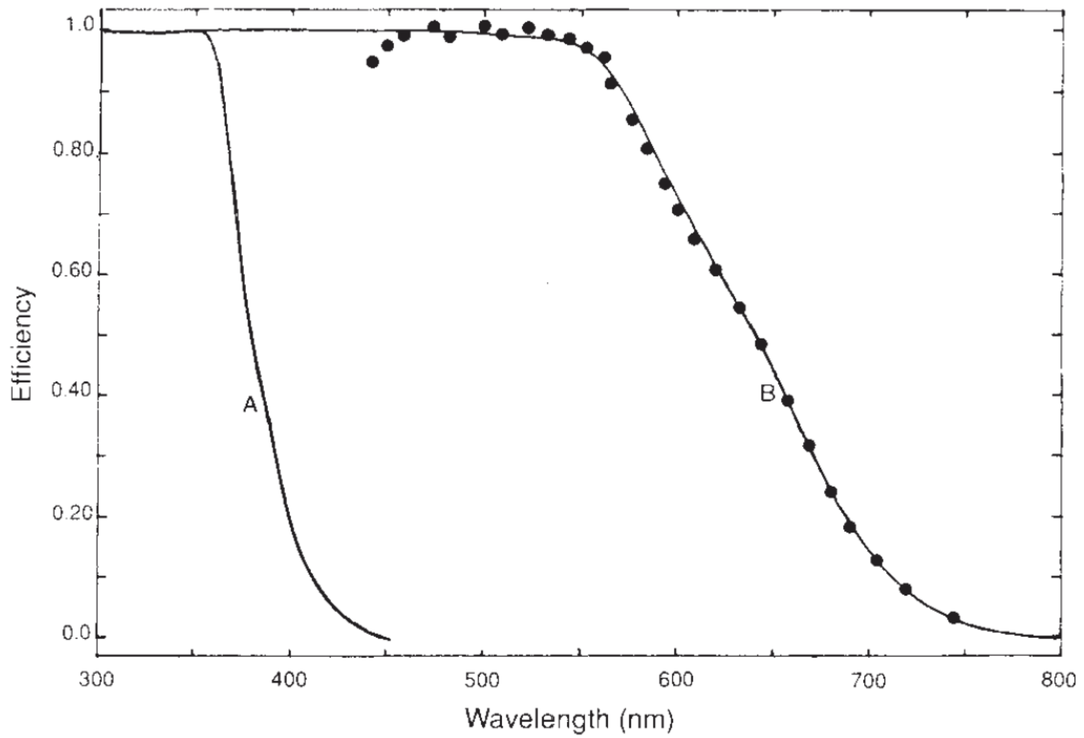
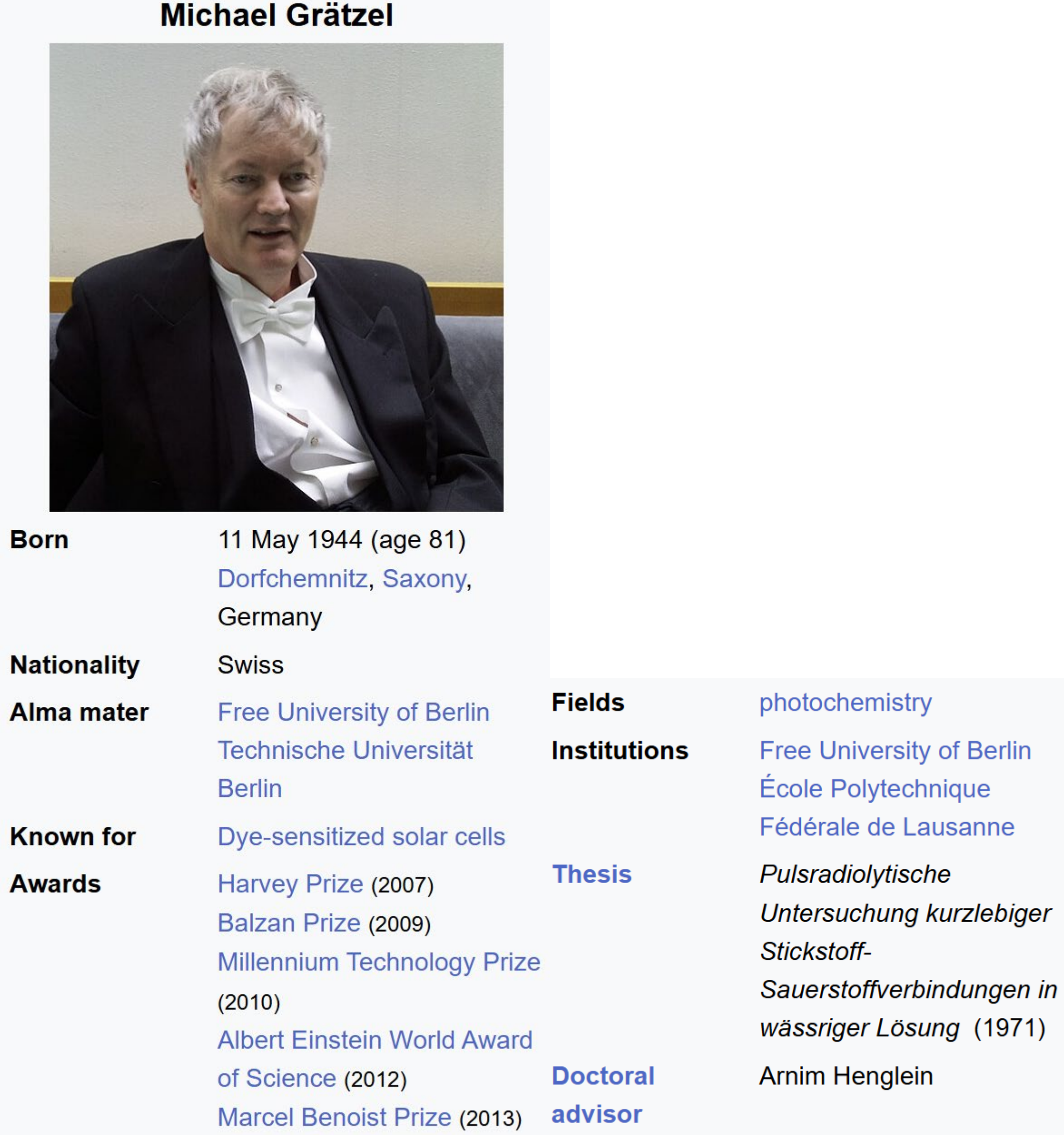


FIG. 3 Absorption and photocurrent action spectra of TiO_2 films supported on conducting glass. A, absorption efficiency of the bare TiO_2 film corrected for conducting glass background; B, absorption efficiency of the same film coated with a monolayer of **1**; full circles, monochromatic current yield at short circuit as a function of excitation wavelength. Yield is corrected for 15% loss of incident photons through light absorption and scattering by the conducting glass support.

Biography



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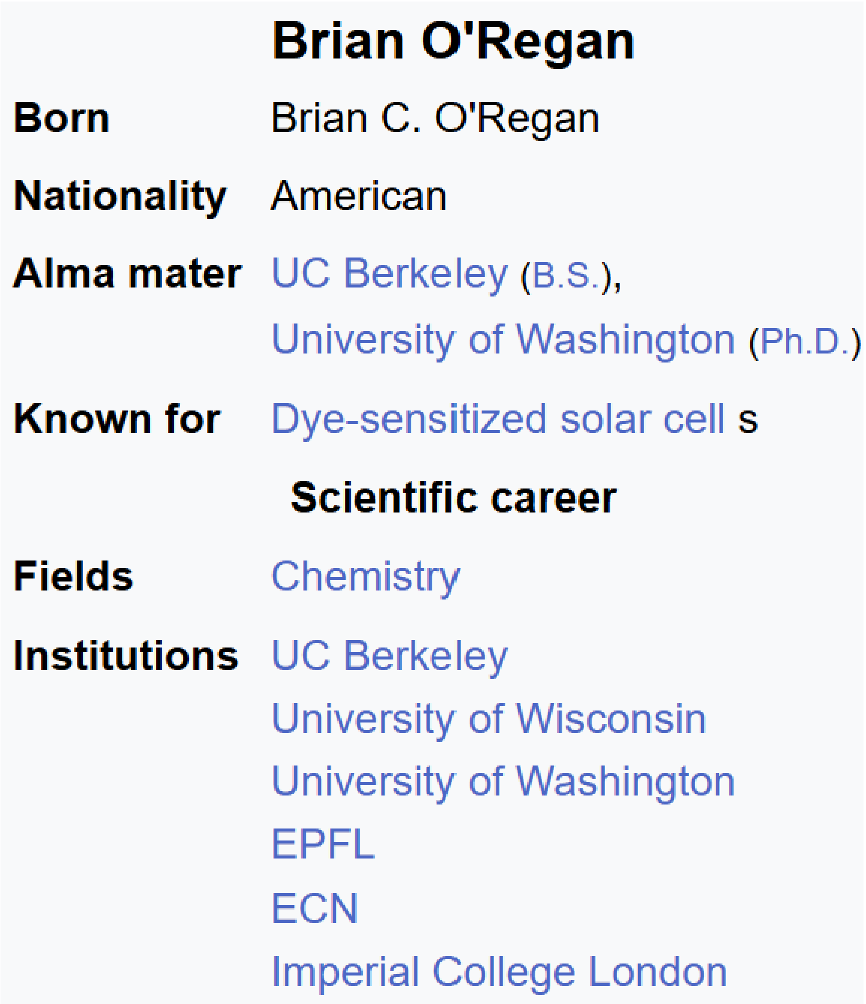

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Cluster sensitized solar cell