

Dye-sensitized near-infrared room-temperature photovoltaic photon detectors

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(Received 5 August 2004; accepted 11 October 2004)

Dye molecules bonded to a semiconductor surface could inject carriers to a band on photoexcitation. This process known as dye-sensitization is used for extending the sensitivity of silver halide emulsions. More recently, dye-sensitization has been adopted to devise solar cells. A near-infrared (NIR) sensitive heterojunction $n\text{-TiO}_2/\mathbf{D}/p\text{-CuSCN}$ (where \mathbf{D} denotes a NIR absorbing dye) is developed to examine the possibility of using dye-sensitization for IR detection. Although the responsivity is lower and response slow compared to silicon detectors, dye-sensitized detectors would be cost effective, especially for large area devices. They are operable at room temperature and have the advantage of insensitivity to noise induced by band-gap excitations (providing high specific detectivity of $\sim 10^{11}$). Furthermore, the spectral response can be adjusted by choosing the appropriate dye. © 2004 American Institute of Physics. [DOI: 10.1063/1.1831562]

The development of devices for sensing IR radiation continues to be an important area of investigation because of the practical utilizations in a diverse variety of applications.¹⁻⁵ Most widely used IR detectors depend on electron-hole generation in low band-gap semiconductor structures by incident radiation. These detectors exhibit good signal-to-noise performance and very fast response. However, in order to achieve this, the semiconductor components of the detector need cryogenic or thermoelectric cooling. Thermal generation of carriers in a low band-gap semiconductor, impurity and defect mediated recombination, or thermally activated intersubband transitions (i.e., in quantum well detectors) are limitations of conventional semiconductor photon detectors. In dye-sensitization (DSN), dye molecules anchored to a semiconductor surface inject carriers into a band leaving dye ions of opposite charge on the semiconductor surface.⁶ The transfer of the charge on dye ions to a counterelectrode through a suitable medium (liquid⁷ or solid^{8,9}) yields a photocurrent having a spectral response (action spectrum) that commensurate with the optical absorption of the dye. An energetic requirement for dye-sensitized electron injection is the location of the excited energy level of the dye molecule above the semiconductor conduction band edge. Similar to hole injection, the ground level of the dye molecule should be positioned above the valence band edge. The possibilities of using high band-gap semiconductors insensitive to background thermal noise and the flexibility of spectral response by choice of the dye are advantages of DSN. Furthermore, DSN produces only one type of carrier in the semiconductor volume, therefore the dye-sensitized photocurrent remains insensitive to recombination at the grain boundaries or impurity sites.⁶ These attractive features of DSN have been exploited to construct solar cells using nanocrystalline films of oxide semiconductors.⁶⁻⁹ Dyes absorbing light in the near-infrared (NIR) region of the spectrum are commercially available for use as photographic sensitizers or

laser dyes. This investigation indicates that some of these dyes sensitize the heterojunctions of the configuration, n -type semiconductor/dye/ p -type semiconductor. A detector based on nanocrystalline TiO_2 (band gap=3.1 eV) film as the dye coated n -type substrate and p -CuSCN (band gap 3.6 eV) as the hole collector is fabricated and tested. Results indicate that these systems could be used as wavelength tailorable, room-temperature, low-cost IR detectors.

Nanocrystalline films of $n\text{-TiO}_2$ were coated on fluorine doped conducting tin oxide (CTO) glass plates ($1 \times 2 \text{ cm}^2$, sheet resistance=15 Ω/sq) by the method reported earlier.⁸ Briefly, the procedure involves painting of a colloidal solution of TiO_2 on to the CTO surface heated to $\sim 150^\circ\text{C}$ followed by sintering at 450°C for 10 min. After removing the loose crust of TiO_2 on the surface, the process was repeated until a film $\sim 10 \mu\text{m}$ is formed. Dyes used in this investigation were anionic dyes IR 783, IR 820 and cationic dyes IR 792, IR 1040 purchased from Aldrich (numbers indicate the peak absorption wavelength of dye solution in nanometers). The anionic dyes readily anchor to the TiO_2 surface and were coated by immersing the TiO_2 film in a solution of the dye in 90% ethanol. The cationic dyes not directly anchoring to the TiO_2 surface were deposited by preadsorption of another molecular species, usually an anionic compound.¹⁰ Thereafter, the film was rinsed with ethanol and immersed in a solution of the cationic dye. The anionic compounds used for this purpose were bromopyrogallol red (BR) mercurochrome (MC) and IR820.

The heterojunction $n\text{-TiO}_2/\text{dye}/p\text{-CuSCN}$ was fabricated by deposition of $p\text{-CuSCN}$ on dyed surface from a solution of CuSCN in propyl sulfide.¹¹ The outer CuSCN surface was coated with graphite and a gold plated CTO glass plate pressed onto the graphite surface served as the backcontact of the detector. A schematic diagram indicating the construction of the device is shown in Fig. 1. Photocurrent spectral responses of the cells were recorded using a monochromatic-light, chopper lock-in amplifier system. Light intensities were measured with a calibrated silicon diode.

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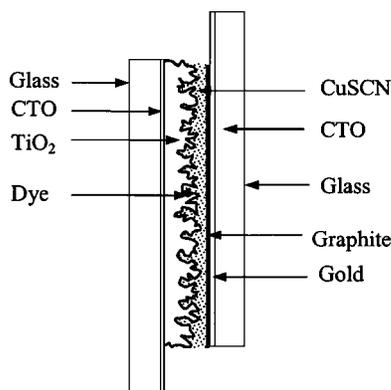
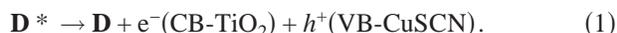


FIG. 1. Construction of the dye-sensitized NIR detector.

Nanocrystalline TiO₂ films prepared by the method described earlier have effective surface areas 200–300 times the geometrical area of the film.⁸ Although the dye covers the TiO₂ surface at the monolayer level, the large roughness factor of the film increases the light absorption cross section. A schematic energy level diagram showing the band edge positions of TiO₂, CuSCN, and ground (*S*₀) and excited (*S*^{*}) levels of the dye is presented in Fig. 2. The photovoltaic effect of the heterojunction originates via the following charge transfer scheme. Excited dye molecules (**D**^{*}) inject electrons and holes to the conduction and valence bands (CB and VB) of *p*-TiO₂ and *p*-CuSCN, respectively, i.e.,



The relative positioning of the ground (*S*₀) and excited (*S*^{*}) levels of the dye and band edges of the two semiconductors (as shown in Fig. 2) energetically permit the above-presented charge transfers. The positions of the band edges of TiO₂ and CuSCN are known¹² and agree with the relative band offsets as shown in Fig. 2. However, the positions of *S*₀ and *S*^{*} in the absolute scale was not measured, which normally requires a cyclic voltammetric determination of the position of *S*₀ with respect to a standard redox couple.¹³ The observation of sensitized photocurrents with IR 783, IR 820, IR 792, and IR 1040 shows that these dyes have ground and excited level positions satisfying the above-noted conditions. Figure 3 gives the spectral responsivities of the detectors sensitized with IR dyes. The redshifts of the peak positions in action spectra are caused by bonding of dyes to the semiconductor surface. The responsivities at the peak absorption wave-

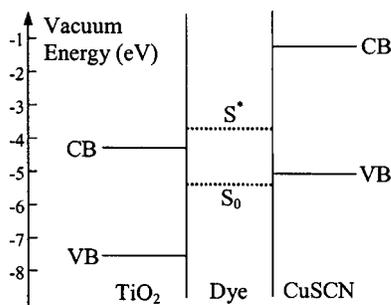


FIG. 2. An energy level diagram showing the band edge positions of *n*-TiO₂, *p*-CuSCN and ground (*S*₀—positioned arbitrarily) and excited (*S*^{*}) states of the dye.

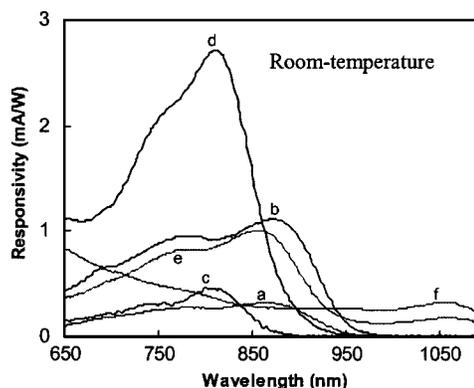


FIG. 3. Spectral responsivity of the heterojunctions (a) *n*-TiO₂/IR820/*p*-CuSCN, (b) *n*-TiO₂/BR-IR820/*p*-CuSCN, (c) *n*-TiO₂/IR783/*p*-CuSCN, (d) *n*-TiO₂/MC-IR792/*p*-CuSCN, (e) *n*-TiO₂/IR820-IR1040/*p*-CuSCN, (f) *n*-TiO₂/BR-IR1040/*p*-CuSCN.

lengths summarized in Table I, are nearly two orders of magnitude smaller than that of silicon detectors.¹⁴ Poor photon-to-photocurrent conversion efficiency could be a result of low probability of injection of carriers by the excited dye molecule. Photophysical properties of the dye, the relative energetic positions of ground and excited states with respect to the band edges, density of states in the bands (i.e., electrons in the CB of TiO₂ and holes in the VB of CuSCN), and mode of anchoring of the dye molecule to the TiO₂ surface determine the injection rate.

When photocurrent transients of the detector sensitized with IR 792 were examined, the rise and fall time constants turned out to be of the order 5 and 3 ms, respectively. Clearly, the response is slower than that of conventional semiconductor detectors. This behavior of the device is a consequence of the slow diffusive transport of electrons in a film consisting of TiO₂ nanocrystallites interconnected to each other by sintering. The response time τ of the detector can be expressed in the form,

$$\tau \approx L^2/D, \quad (2)$$

where *L*=film thickness, *D*=diffusion coefficient (which depends on film morphology and intrinsic material properties of the two semiconductors). Thus, the response time happens to be highly sensitive to the film thickness, i.e., a reduction in film thickness leads to faster response. However, the responsivity of the detector determined by the light absorption cross section of the dye coated nanocrystalline film varies linearly with the film thickness. Optimization would be possible to meet the requirements of specific practical applications.

This investigation demonstrates that dye-sensitization of high band-gap semiconductors can be utilized to devise NIR detectors. They have the advantage of not being sensitive to

TABLE I. Responsivities (*R*) of the detectors at peak absorption wavelengths (λ_{max}) of different sensitizers.

Dye	λ_{max} (nm)	<i>R</i> (mA/W)
IR820	866	0.3
BR-IR820	876	1.1
IR783	808	0.4
MC-IR792	812	2.7
IR820-IR1040	858	1.0
BR-IR1040	1056	0.3

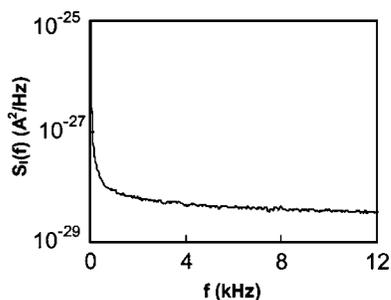


FIG. 4. Power spectral density of the dark current noise of the heterojunction $n\text{-TiO}_2/\text{MC-IR792}/p\text{-CuSCN}$.

thermal noise and radiation that initiate band-gap excitations. As expected, the specific detectivities of dye-sensitized detectors are found to be quite high despite low responsivity. The specific detectivity D^* (noise characteristics measured using the low noise SR560 preamplifier and the SR785 fast Fourier transform Dynamic Signal Analyzer) of the system $n\text{-TiO}_2/\text{MC-IR792}/p\text{-CuSCN}$ was found to be $9.5 \times 10^{10} \text{ cm Hz}^{-1/2} \text{ W}^{-1}$ at 812 nm. Figure 4 shows the variation of the dark current noise spectral density $S(f)$ with frequency at room temperature (292 °C). Beyond a corner frequency of ~ 1 kHz, the noise level is low and largely frequency independent. High band-gap semiconductors remain less susceptible to stochastic intermittency of thermal excitations that contribute to $1/f$ noise.^{15,16}

The peak spectral response of these devices can be readily adjusted by choice of the dye and tuning by structural modifications to the dye molecule. Dye-sensitized NIR detectors would be very cost-effective devices because they are based on polycrystalline semiconductor materials and the processing does not involve vacuum technology. Instead of CTO glass, TiO_2 film could also be deposited on a flexible plastic substrate.¹⁷ However, in the present form the responsivities are of the order 10^{-3} A/W (Table I), i.e., two orders of magnitude smaller than familiar semiconductor detectors. Extensive effort is under way for improvement of the effi-

ciencies of dye-sensitized solar cells. The outcome of these investigations could pave the way for the development of more effective dye-sensitized IR photon detectors. Combination of IR dyes with visible sensitizers may also enhance the efficiencies of dye-sensitized solar cells. In fact, the heterojunctions that incorporate BR or MC in addition to the IR dye are also sensitive to the visible spectrum.

This work is supported in part by the U.S. NSF under Grant No. INT-0322355.

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