A Dye-sensitized Nanocrystalline Solid State Photovoltaic Cell

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Abstract: A new type of dye-sensitized nanocrystalline solid state photovoltaic cell based on the wide band gap n-TiO₂/p-CuI heterojunction was fabricated. Tetra-carboxyphenyl porphyrine (TPP-(COOH)₄), squarylium cyanine derivative (SQ-(CH₂)₃SO₃⁻Py⁺) and ruthenium bipyridyl complex (RuL₂(NCS)₂) were used as photosensitizers. Larger photocurrents and photovoltages were shown in the cell sensitized by ruthenium bipyridyl complex and can be further increased by intercalation of a TiO₂ thin underlayer.

Kewwords: Nanocrystalline TiO₂ electrode, dye sensitization, solid state cell.

Dye-sensitized photovoltaic cells based on nanocrystalline TiO_2 film are of considerable technological interest because of their high conversion efficiency and potential low cost. However the liquid junction photovoltaic cells have a series of technological problems in practical applications. Recently, the replacement of liquid electrolyte by solid state conductors such as ionic conducting polymers¹ and organic hole transport materials² has been tested. In this paper, we report the fabrication of dye sensitized solid state nanocrystalline photovoltaic cell with a wide band gap n-TiO₂(3.0 eV)/p-CuI(3.1 eV) heterojunction.

Figure 1 The construction of the dyesensitized nanocrystalline solid-state cell.



CTO Substrate
TiO₂ Underlayer
Nanocrystalline TiO₂ Film
Dye Layer
CuI Layer
Al Layer

Figure 2 Energy level diagram of the dyesensitized nanocrystalline solid-state cell.



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Nanocrystalline TiO₂ films were prepared by spreading the TiO₂ colloid obtained from the hydrolysis of titanium isopropoxide on F doped SnO₂ conducting glass (CTO) and sintering at 450°C for 10 min. The TiO₂ films of mean diameter ~6 nm anatase crystallites with thickness of 5 μ m were dipped in ethanol solution of dyes for 10h. Transparent CuI layer was deposited on dye-coated TiO₂ films by spreading saturated CuI acetonitrile solution. Electric contact was made by spraying Al on CuI layer surface.

Figure 1 is the construction of n-TiO₂/dye/p-CuI photovoltaic cell. Photoexcited dyes inject electrons into the conduction band of $n-TiO_2$ and holes into the valence band of p-CuI to generate the photocurrents and photovoltages. In order to match the energy diagram shown in **Figure 2**, the dye with D^* level above the bottom of the conduction band of n-TiO₂ and D level below the upper edge of the valence band of p-CuI were used, such as TPP-(COOH)₄, $SQ-(CH_2)_3SO_3^-Py^+$ and $RuL_2(NCS)_2(L=2,2'-bipyridyl-4,4'-dicarboxylic acid)$. The photoelectric performance of the dye-sensitized heterojunction photovoltaic cells is listed in Table 1. As shown in this table, larger open circuit photovoltage (Voc) and short circuit photocurrent (Isc) were obtained in RuL₂(NCS)₂ sensitized cell indicating ruthenium bipyridyl complex is more efficient in the photosensitization of the wide band gap heterojunction than the other two. Voc and Isc of ruthenium bipyridyl complex sensitized cell can be further increased by intercalation of a compact TiO_2 thin underlayer below the nanocrystalline TiO_2 film. This TiO₂ thin underlayer deposited on CTO substrate from titanium butoxide isopropanol solution was used to separate the contact between CuI layer and CTO substrate leading to suppressing the electrons and holes recombinations and improving the photocurrents and photovoltages efficiently.

Dye-sensitized nanocrystalline	solid	Open-circuit	Short-circuit
state cells		photovoltage	photocurrent
		Voc (mV)	Isc (μ A/cm ²)
CTO/TiO2(N)/TPP-(COOH)4/CuI/Al		51	46
CTO/TiO ₂ (N)/SQ-(CH ₂) ₃ SO ₃ ⁻ Py ⁺ /CuI/Al		67	53
CTO/TiO2(N)/RuL2(NCS)2/CuI/Al		200	180
CTO/TiO2(U)/TiO2(N)/ RuL2(NCS)2/CuI/Al		250	220

Table 1. The photoelectric performance of dye-sensitized nanocrystalline solid state cells

250W halogen lamp used as light source; incident light intensity: 60 mW/cm²

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