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Graphene-based cathodes for liquid-junction dye sensitized solar cells: Electrocatalytic and mass transport effects

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ABSTRACT

The optimization of mediator/cathode in a dye sensitized solar cell (DSC) requires detailed knowledge about their electrochemical properties. Particularly, the kinetics of mediator's turnover on the cathode and the mass transport of mediator in the electrolyte solution are the crucial parameters which influence the overall efficiency of solar energy conversion in DSC. This review article aims at critical survey of the works carried out in the field. Attention is paid to graphene-based materials for the counter electrode, which may, eventually, meet all the benchmark parameters for a good DSC cathode, i.e. high optical transparency and electrical conductivity associated with high electrocatalytic activity for the redox mediator. So far, platinum and transparent conducting oxide (TCO) electrodes were used ubiquitously in DSC cathodes, but there is a motivation to avoid Pt and TCO to decrease the device cost without compromising of its performance.

1. Introduction

The dye sensitized solar cell (DSC) is a low-cost, high-efficient device to rival Si-based photovoltaics. It is based on spectral sensitization of wide-band gap semiconductor electrodes by dye molecules absorbing visible light [1–3]. Graetzel et al. [4] pioneered in 1985 the sensitization of polycrystalline TiO$_2$ (anatase) electrode by Ru-bipyridine complex. Subsequently, O'Regan and Graetzel demonstrated in 1991 the first solar cell employing this strategy [5]. Their work triggered great academic and technological feedback during the next two decades [6–10] including a recent highlight of the perovskite-based solar cell [11–13]. The basic concept of DSC is a liquid-junction photoelectrochemical cell which has three principal components: a nanocrystalline TiO$_2$ photoanode, an electrolyte solution with redox mediator and a cathode (counter electrode). The cell has sandwich architecture with a thin-layer ($\delta \approx 10^1$ μm) of electrolyte solution interspaced between both electrodes. Electrocatalytic activity of the cathode for the mediator's redox turnover and the mass transfer in the electrolyte solution layer over the distance δ are among the key parameters influencing the DSC performance. These two problems were analyzed in 2001 by Hauch and Georg [14] for the traditional system, i.e. he platinum cathode and the I_3^-/I^- redox couple in the

electrolyte solution. During the next decade, several new redox couples appeared, as well as many new cathode materials, particularly carbon (graphene)-based. These works will be reviewed below.

The function of a dye-sensitized nanocrystalline TiO$_2$ photoanode is illustrated by the calculation of 'incident photon to current conversion efficiency' (IPCE) also called 'external quantum efficiency':

$$IPCE = \frac{j_{ph} hc}{Pe\lambda} \tag{1}$$

j_{ph} is the photocurrent density, h is Planck's constant, λ is the photon wavelength, c is the velocity of light, P is the incident light power density and e is the electron charge. For a monolayer of a dye (with extinction coefficient ε and surface coverage Γ) the IPCE is expressed as:

$$IPCE = \eta_{inj} \cdot \eta_{coll} \cdot (1 - 10^{-R_F \Gamma \varepsilon}) \tag{2}$$

η_{inj} is the efficiency of electron injection from the photoexcited dye into the TiO$_2$ conduction band, η_{coll} is the efficiency of collection of the injected electron by the back contact of photoanode (for good electrodes $\eta_{inj} \eta_{coll} \approx 1$). The parameter R_F is the so-called roughness factor, defined as the ratio of the total physical area of the electrode material divided by the projected area of the electrode. For a flat TiO$_2$ surface, and for typical parameters of Ru-bipyridine dyes ($\varepsilon \approx 1.3 \cdot 10^7$ cm^2/mol, $\Gamma \approx 9.1 \cdot 10^{-11}$ mol/cm^2) the calculated IPCE equals 0.27%. (The experimental value was 0.11% [15]).

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However, for $R_F = 1000$, the calculated IPCE is as high as 93%, which is achievable experimentally [7,9,10]. The short-circuit photocurrent density for solar light, J_{SC} can be obtained by integration over the solar spectrum:

$$J_{SC} = \int_0^\infty IPCE(\lambda) \cdot P_{sun}(\lambda)d\lambda \qquad (3)$$

$P_{sun}(\lambda)$ is the solar power density at the wavelength λ. The state-of-art DSC achieve $J_{SC} \approx 20\,mA/cm^2$ under full sun illumination [9,10]. This photocurrent density together with the cell voltage define the efficiency of conversion of solar light to electrical energy, Φ_{sol}. It is expressed as the maximum electric power output per solar cell area, divided by the solar power density, P_{sol}. (For AM1.5G solar radiation, $P_{sol} = 100\,mW/cm^2$):

$$\Phi_{sol} = \frac{J_{SC}V_{OC}}{P_{sol}} \cdot F_F \qquad (4)$$

V_{OC} is the open-circuit voltage. The parameter F_F (≈ 0.7) is the so called fill factor describing the non-ideality of the practical current/voltage profile:

$$F_F = \frac{J_{pmax}V_{pmax}}{J_{SC}V_{OC}} \qquad (5)$$

J_{pmax} is the photocurrent density and V_{pmax} is the voltage for which the Φ_{sol} is maximal.

The design of photoanodes (cf. Eq. (2)), should be interfaced to the engineering of mediators and counter electrodes. A straightforward argument for the mediator optimization is the enhancement of V_{OC}. (Note that for $J_{SC} = 20\,mA/cm^2$, assuming $V_{OC} = 1\,V$ and $F_F = 1$, one would get the 'dream' efficiency of $\Phi_{sol} = 20\%$).

The iodine-based redox couple, I_3^-/I^- was used in almost all liquid-junction DSCs prior to 2010 [16]. It is characterized by the following redox reaction and the corresponding standard electrochemical potential, E_0:

$$I_3^- + 2e^- \rightarrow 3I^-;\ E_0 = 0.35\,V \qquad (6)$$

The value of E_0 (more accurately, the actual redox potential in the used electrolyte solution, E_{redox}) is controlling the V_{OC}. The open circuit potential is reached, if the photocurrent in solar cell is exactly offset by recombination of conduction-band electrons with the oxidized form of the adsorbed dye. V_{OC} can be defined by a difference between the quasi Fermi level in the TiO_2 photoanode (E_F/q; where q is elementary charge) and the energy level (W_{redox}) equivalent to the redox potential of mediator, E_{redox}. (Under illumination, electrons in conduction band are no more in equilibrium with the electrolyte). Assuming a defect-free semiconductor, the V_{OC} is given by [17]:

$$V_{OC} = \frac{E_{CB}}{q} + \frac{kT}{q}\ln\left(\frac{n_{ph}}{N_{CB}}\right) - \frac{W_{redox}}{q} \qquad (7)$$

E_{CB} is the energy of conduction band edge, k is Boltzmann constant, n_{ph} is the number of photoelectrons in TiO_2, N_{CB} is the total number of conduction band states in TiO_2. Hence, the V_{OC} is enhanced either by (i) upshift of E_{CB} or by (ii) downshift of W_{redox} (this means by *enhancement* of the mediator's redox potential in the electrochemical scale). In the first case, the available shifts in band energetics are limited to tens to hundreds of meV through engineering of the TiO_2 structure [18] or by electrolyte additives [9,10] but the engineering of the mediator's W_{redox} is theoretically limited only by the electrochemical potential of the dye's ground state, which is usually near 1 V vs. SHE. However, small overpotential (≈ 0.1–$0.2\,V$) is needed as a driving force for dye regeneration [7,9,10,19].
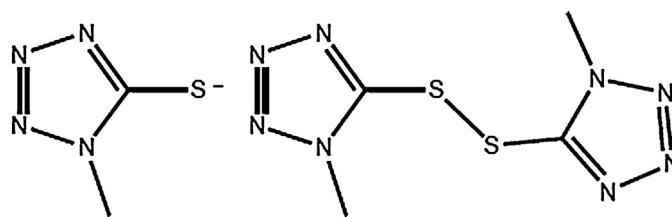
Scheme 1. Structural formulae of T^-: 5-mercapto-1-methyltetrazol and T_2: bis(1-methyltetrazol-5-yl) disulphide.

2. Redox mediators: beyond iodine

Equations 6 and 7 evidence that I_3^-/I^- is hardly the best mediator for DSC, because its $E_0 \approx 0.35\,V$ is too small, leaving $\approx 0.7\,V$ overvoltage for the dye regeneration [16,20–22]. Other problems of iodine are (i) its corrosive nature, e.g. towards metallic contacts in DSC, (ii) its complicated (two-electrons) redox chemistry, including possible formation of higher polyiodides, such as I_5^-, I_7^-, I_9^- and (iii) partial absorption of light near 430 nm wavelengths causing optical loses in DSC.

The search for alternative redox pairs for DSCs is a non-trivial task, because various other parameters, beyond the redox potential, need to be taken into account, such as the dye/mediator compatibility (for review see [20,22]). In 2010, Graetzel et al. [23] introduced an iodine-free redox mediator based on the disulphide/thiolate, T_2/T^- (T^- is 5-mercapto-1-methyltetrazole and T_2 its dimer, i.e. bis(1-methyltetrazol-5-yl) disulphide):

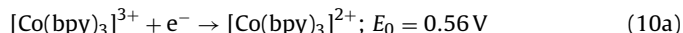$$T_2 + 2e^- \rightarrow 2T^-;\ E_0 \approx 0.4 - 0.5\,V \qquad (8)$$

In their DSC with a Ru-bipyridine dye, and a platinized FTO (fluorine doped SnO_2) counter electrode, this redox mediator yielded $\Phi_{sol} = 6.4\%$, which was the record value in the iodine-free system at that time [23]. Subsequently, the $\Phi_{sol} = 7.9\%$ was reported for a similar DSC employing poly (3,4-ethylenedioxythiophene) (PEDOT) as the counter electrode [24]. The T_2/T^- redox couple is a member of larger family of similar organosulfur compounds based on disulphide, polysulfides, thiourea, cysteine etc. which were also tested in DSCs [20,22,24–27]. Since the redox potential of T_2/T^- is close to that of I_3^-/I^-, there is almost no improvement in V_{OC} and Φ_{sol} as compared to the reference I-mediated DSCs. However, this redox shuttle rivals I_3^-/I^- because it is non-corrosive and free from optical losses in the electrolyte solution [23] (Scheme 1).

Daeneke et al. [28] found that ferrocene/ferrocenium, Fc/Fc^+, interfaced to special organic donor-acceptor dyes sensitizer is among the promising candidates to avoid iodine in DSC and to tune V_{OC} at the same time. Ferrocene has simple redox chemistry:

$$Fc^+ + e^- \rightarrow Fc;\ E_0 = 0.62\,V \qquad (9)$$

This work confirmed that the V_{OC} is, indeed, enhanced through the more positive E_0 redox potential of Fc/Fc^+ (cf. Eqs. (7) and (9)), although the V_{OC} increase was ca. 100 mV only, as compared to the reference DSC with the I_3^-/I^- redox couple owing to faster recombination. The optimized ferrocene-mediated DSC achieved $\Phi_{sol} = 7.5\%$ [28].

Particularly promising redox shuttles with appropriate and well tunable E_0 are the Co-polypyridine complexes [16,19,21,22,25,29–36]. Two examples follow:

$$[Co(bpy)_3]^{3+} + e^- \rightarrow [Co(bpy)_3]^{2+};\ E_0 = 0.56\,V \qquad (10a)$$

$$[Co(bpy-pz)_2]^{3+} + e^- \rightarrow [Co(bpy-pz)_2]^{2+};\ E_0 = 0.86\,V \qquad (10b)$$

bpy = 2,2′-bipyridine; bpy-pz = 6-(1H-pyrazol-1-yl) 2,2′-bipyridine. The Co-mediators were introduced already in 2001, but provided low efficiency, $\Phi_{sol} = 2.2\%$ at that time [37]. The idea was revitalized in 2010 by Feldt et al. [30] and by Yella et al. [34] who