



Influence of 4-tert-butylpyridine/guanidinium thiocyanate co-additives on band edge shift and recombination of dye-sensitized solar cells: experimental and theoretical aspects



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ABSTRACT

The co-additives of 4-tert-butylpyridine (TBP) and guanidinium thiocyanate (GuSCN) in electrolytes can prominently affect the photovoltaic behavior of dye-sensitized solar cell (DSSC) due to their advantages fitting with energy levels and charge transfer. Mott-Schottky analysis is used to quantify the TiO₂ band edge movement to clarify the change of open-circuit voltage. The corresponding kinetic investigations are carried out using cyclic voltammetry, electrochemical impedance spectroscopy, intensity modulated photocurrent/photovoltage spectroscopy and charge extraction. Theoretically, the density functional theory (DFT) method is performed to explore the details of the adsorption, including the interacting energy, Fermi energy and frontier orbitals properties. The results show that the frontier orbitals between TBP and TiO₂ are sufficiently overlapped to induce the negative shift of Fermi energy, increasing the open-circuit voltage. The Gu⁺ cations can be tightly absorbed on TiO₂ surface to by electrostatic attraction form a passivated layer due to the Coulomb attraction, depressing the recombination rate and improving the short-circuit photocurrent. The different proportion of TBP and GuSCN would produce a competitive effect, which would be caused by their volume and electrostatic effect. The photovoltaic performance might be as a result of a synergistic effect of co-additives. DSSC based on the optimal molar ratio (9:1) of TBP and GuSCN achieves its optimized short-circuit current density of 13.74 mA cm⁻², open-circuit voltage of 0.74 V, fill factor of 0.70 and overall efficiency of 7.12%.

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1. INTRODUCTION

For over the past two decades, dye-sensitized solar cells (DSSC) have undergone considerable developments in a brand-new field of nanoscale science and technology [1–5]. Compared to the conventional p-n junction solar cell, like silicon-based cells, the significant difference is that DSSC separates the light absorption and charge separation processes. The main reason is that the use of electrolyte solution in DSSC has created a series of new interfaces between TiO₂ electrode and Pt-based counter electrode. Therefore, the internal structure of DSSC could be considered as a multi-functional interface system, typically consisting of TiO₂/electrolyte

and Pt/electrolyte interfaces. The TiO₂/electrolyte interfaces might interact with the specific chemical additives, which plays an important role in the band edge movement of TiO₂ electrodes and the surface passivated of active recombination sites [6–8]. Consequently, it is the most convenient access to enhance the photovoltaic behavior by adding the appropriate additives into the electrolyte solution to optimize the TiO₂/electrolyte interface state.

In general, 4-tert-butylpyridine (TBP) and guanidine thiocyanate (GuSCN) are believed to contribute to the negative and positive shift of TiO₂ conducting band (CB), leading to higher and lower open-circuit voltage (V_{oc}), respectively [9–10]. The negative shift of TiO₂ CB edge could be assigned to TBP due to the surface adsorption [11,12]. On the contrary, the positive movement is induced by the adsorption of guanidinium cations ([CH₆N₃]⁺ or abbr. Gu⁺) at the TiO₂ surface [13,14]. As a result, the CB position might depend on the density and the electronic structure of the

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adsorbed additives by influencing the interfacial Helmholtz layer [15,16]. Considering the molecular structural features, TBP can be recognized as a Lewis base due to the lone electron pair located at the nitrogen, giving the molecule a dipole character. GuSCN can be acted as an organic salt including Gu^+ cations, suggesting that the guanidinium is the conjugate acid of guanidine. This means that the negatively charged surface in the case of Lewis base will lead to a negative shift of CB edge, and similarly the positively charged surface in the case of Lewis acid will cause a positive shift. On the other hand, the band position change also has an impact on the charge recombination at the TiO_2 /electrolyte interface. As an example, since TBP is expected to occupy the dye-absent TiO_2 surface, this effect is supposed to depress the reversed electron transfer from TiO_2 CB to triiodide [17]. GuSCN is also found to slow down electron recombination on account of Gu^+ cation adsorption on the TiO_2 surface [14,18]. Although these additives can improve the device efficiency, their capacity and limit might be restricted by the working principle of DSSC, which is further governed by the thermodynamic and kinetic factors in essence. Fig. 1 represents the classic working principle of DSSC when the device is placed under sunlight. The sensitized dyes absorb light energy and are excited to produce an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The photogenerated electrons would be injected into TiO_2 CB and collected by the conductive substrates, and then go through the external load circuit and reach the counter electrode. The effective electron transport routes are defined as four green arrow lines. However, the damaging steps indexed by three red arrow dash-lines would directly hurt the charge transport. The most recombination reaction occurring at the interfaces of TiO_2 /electrolyte is as follows: $\text{I}_3^- + 2e^- (\text{CB}) \rightarrow 3\text{I}^-$, arising from the triiodide reduction by CB electrons. Meanwhile, the band bending at TiO_2 surface depends on the depletion layer at the TiO_2 /electrolyte interface, which is determined by the flat band potential (V_{fb}) and Helmholtz layer capacitance (C_{sc} , also called space charge capacitance). This also means that we could use Mott-Schottky (MS) analysis and even density functional theory (DFT) calculations to estimate V_{fb} instead of the difficult determination of TiO_2 Fermi level (E_{F}) [19–22]. It is worth mentioning that the electrical impedance spectroscopy (EIS) analysis and in particular the variation of the chemical capacitance as a function of the actual (corrected) potential of TiO_2 working electrode can provide a direct means to determine the TiO_2 CB edge shift [23,24], which is crucial for the underlying mechanism of TBP/GuSCN. Therefore, their EIS data could obtain complementary information to MS analysis.

Additionally, the energy levels of the iodide/triiodide (I^-/I_3^-) redox couple depend on whether the state is reduced (R_{ed}) or oxidized (O_{x}), owing to the different solvent-sheath energies (λ), around the R_{ed} and O_{x} species [25]. The density of redox states and its redox potential (E_{redox}) can be described by the separate Gaussian distributions and Nernst equation, respectively. The V_{oc} of cells is usually considered as the difference between E_{F} and E_{redox} , when TiO_2 is at its flat-band potential. But above all, the thermodynamic and kinetic aspects would determine V_{oc} and short-circuit photocurrent density (J_{sc}) of DSSC, respectively. For that reason, it is particularly important to clarify the relationship between the band edge shift and recombination process based on the thermodynamic and kinetic viewpoints.

Nowadays TiO_2 CB edge movement is often estimated by the MS procedure and calculated by the density functional theory (DFT) method, respectively [19–20]. The charge transport and recombination are investigated by EIS, intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) and charge extraction approaches to characterize in detail individual steps of photoelectrochemical reactions [26–29]. In this work, we report the effects of TBP and GuSCN co-additives on the V_{fb} position, and interfacial electron transport characterization, such as electron lifetime (τ_{n}), electron transport time (τ_{tr}), extracted charge (Q_{oc}) and exchange current density (J_0). Furthermore, the DFT calculated results, including the surface adsorption energy and Fermi energy shift, would help to explain the experimental data. We hope that these studies may pave the way to design a high efficiency DSSC using multivariate additives.

2. EXPERIMENTAL SECTION AND THEORETICAL CALCULATION

2.1. Electrolyte preparation and DSSC assembly

The basic electrolyte (E1) consists of 1-methyl 3-propyl imidazolium iodide (0.8M) and iodine (0.02M) in propylene carbonate. The others (E2~E8) contain different proportions of TBP and GuSCN with the molar ratio range of 0:10, 1:9, 3:7, 5:5, 7:3, 9:1 and 10:0, respectively. As an example, 0.05 M GuSCN was added into E1 to obtain E2. TiO_2 working electrode was prepared by a screen-printing approach, including mesoporous and scattering films with a total thickness of 13 μm . Ru-dyes (N719) were selected to sensitize TiO_2 electrode. The sandwich-type cell is composed of TiO_2 electrode, electrolyte and Pt-coating conductive glass with a Surlyn film of 25 μm .

2.2. Photoelectrochemical measurements

Current-voltage (IV) and dark current curves were measured by Keithley 2400 under Newport Oriel 91.192 simulated illumination (AM1.5, 100 mW cm^{-2}) and in the dark, respectively. Gamry Reference600 potentiostat was employed to monitor the electrochemical behavior, including MS analysis, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). MS and CV were obtained using three-electrode cell: dye-sensitized TiO_2 as a working electrode, platinum wire as the counter and saturated calomel electrode (SCE) as a reference electrode. EIS on complete DSSCs was estimated in the frequency range of $10^{-2} \sim 10^5$ Hz with 10 mV AC amplitude and under the modulated light (20~100 mW cm^{-2}) with the open-circuit voltage as an applied bias potential. The impedance parameters were fit to equivalent circuit models using ZSimpWin3.10 software. Zahner CIMPS system with a white LED ($\lambda_{\text{max}} = 564 \text{ nm}$) as the light source was used to investigate IMVS, IMPS and charge extraction (CE). The electron lifetime (τ_{n}) and charge transport time (τ_{tr}) can be estimated by IMVS and IMPS, respectively. As for CE, the device was illuminated

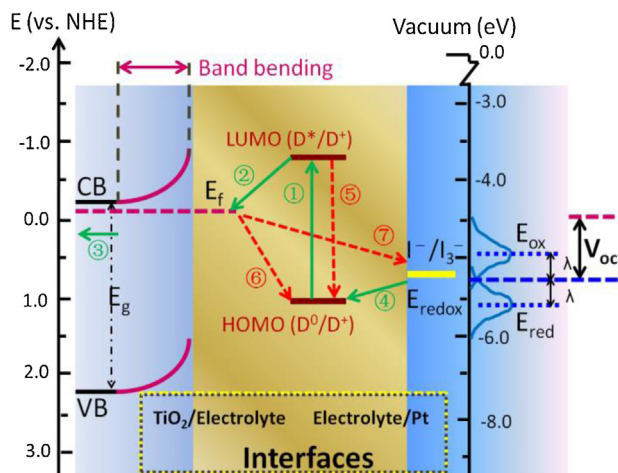


Fig. 1. Schematic of thermodynamic and kinetic mechanisms of DSSC based on I^-/I_3^- redox couple in liquid electrolyte.

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