Electrochemical evaluation of the frontier orbitals of organic dyes in aqueous electrolyte

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\section{A R T I C L E  I N F O}

Article history:
Received 19 February 2013
Received in revised form 2 April 2013
Accepted 3 April 2013
Available online 11 April 2013

Keywords:
DNA
DNA–CTMA
Band gap
Dye
Electrochemistry

\section{A B S T R A C T}

The frontier orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, of organic dye \{5-(4-(di-p-tolylamino)-phenyl)-4-hetaryliophen-2-yl)-2-cyanoacrylic acid (TT) and (5-(5-(4-(di-p-tolylamino)-phenyl)-4-hetaryliophen-2-yl-methylen)-4-oxo-2-thioxothiazolidin-3-yl)-acetic acid (TS) are evaluated by the electrochemical cyclic voltammetry in aqueous electrolyte. Both dyes are electrochemically active and conduct redox processes when the dyes are blended with DNA–CTMA(DNA-cetyltrimethylammonium). The redox processes of the dyes can be carried out under fast potential scanning, e.g. 1.5 V/s, which indicates the fast charge transfer between the dyes and the electrodes. Well-dispersed dye molecules in DNA–CTMA, rather than the aggregated molecules, result in well-defined redox peaks in the cyclic voltammetry. In addition, the conductive DNA is also proposed to be responsible for the fast charge transfer. HOMO and LUMO levels of TT and TS are –5.40 eV and –3.04 eV for TT, –5.42 eV and –3.40 eV for TS, respectively.

\section{1. Introduction}

Dye-sensitized solar cells (DSC) have been attractive due to its flexibility on the choice of light-absorbing materials, the dyes with designed chemical structure, to a large extent [1–5]. Well-designed organic dye molecules should act as the panachromatic absorber to the sunlight, support the efficient charge injection into TiO\textsubscript{2} substrate, and have long-life redox cycling, etc. [6–14]. The most important point is that the band gap structure of the dye should match the valence band of TiO\textsubscript{2} and the redox potential of holeconducting materials, typically I\textsubscript{2}/I\textsubscript{-} redox couple. Therefore, the electrons on the LUMO of dye can inject into TiO\textsubscript{2} and holes on HOMO of the dye can transfer to the hole-conducting electrolyte smoothly [5]. As a result, the band structures of the dyes have to be evaluated in order to build an efficient DSC or synthesize satisfying dyes.

The most common way to obtain the band structure of a dye is to measure the redox potential of the dye with cyclic voltammetry. Usually, the dye is dissolved in organic electrolyte in the electrochemical measurements. If the dye has bad solubility in the organic electrolyte, the electrochemical voltammogram could not be carried out, or no well-defined redox current curves can be recorded, though some dyes can be cast to form film modified electrode for the voltammetric measurements [15–18]. In addition, the electrochemical measurements are conducted in non-aqueous electrolyte, the redox behavior and the redox cycling life-time of the dye might be only valid for the organic electrolyte environments. Recently, the development of DSC with aqueous electrolyte which avoids the flammability, toxicity, and volatility of organic electrolytes, leads to the demands of evaluating the redox behavior of the dyes in aqueous electrolyte [19–21].

We found that the solid dye film cannot be employed in the electrochemical voltammetry, while DNA–CTMA is a suitable host matrix in which the dye is blended, especially in aqueous electrolyte. DNA–CTMA is a kind of self-assembled macro-molecular materials, consisted of DNA salt and surfactant CTMA (cetyltrimethylammonium) [22]. It shows potential applications in photonic and optoelectronic devices [23–26]. DNA–CTMA is soluble in most alcohols, chlorofor but not water. The organic dye, dissolved in chlorofor for example, and DNA–CTMA in ethanol can then be mixed to form heterogeneous solution which can be cast to form uniform film for the electrochemical measurements in aqueous electrolyte.

In this paper, the redox behavior of organic dyes in DNA–CTMA is reported. The frontier orbital energy levels of the dyes are derived from the cyclic voltammetry in aqueous electrolyte. The possibility of charge transport through DNA–CTMA, the electro-activity loss of the dyes in the repetitive potential scanning, as well as the dispersion of the dye molecules in DNA–CTMA matrix are discussed.
2. Experimental

DNA–CTMA was prepared with the reported method [22]. Both dyes, TT ((5-(4-di-p-tolylamino)-phenyl)-4-hexylthiophen-2-yl)-2-cyanoacrylic acid) and TS ((5-(5-(4-di-p-tolylamino)-phenyl)-4-hexylthiophen-2-yl-methylene)-4-oxo-2-thioxothiazolidin-3-yl)-acetic acid), were synthesized and fully characterized in our lab, the corresponding chemical structure is given in Scheme 1. DNA–CTMA in ethanol was mixed with certain amount of dye in chloroform agitatedly. The resulted blend solution was dropped on the working electrode in air. The blend film of dye/DNA–CTMA was formed in the air by dropping blend solution on the electrode. The film was further dried with air blow before the electrochemical measurements.

The electrochemical measurements were carried out with CHI 750D electrochemical workstation. A glassy carbon (GC) electrode with diameter of 3 mm, a Pt wire, and a saturated calomel electrode (SCE) were employed as the working electrode, counter electrode, and reference electrode, respectively. 0.1 M KNO₃ aqueous solution was used as the supporting electrolyte which was degassed with N₂ for at least 15 min unless otherwise noted. The UV–vis absorption spectra were recorded on Shimadzu-UV3101 Spectrophotometer. Film thickness was determined with Ambios XP-2 depth profiler. The dye/DNA–CTMA film thickness on the working electrode was around 1 μm.

3. Results and Discussion

Dye TT/DNA–CTMA undergoes redox reaction in the potential range from −0.8 V to 1.2 V quasi-reversibly. As shown in Fig. 1a, Cyclic voltammetry on TT/DNA–CTMA gives a clear and sharp oxidation peak while the reduction peak is not clear under potential scan rate of 50 mV/s. When the potential scan rate is increased, the reduction peak becomes pronounced, but the reduction peak current is much lower than the oxidation peak current. No change is found in the ratio of oxidation peak current to reduction peak current with the increase of the scan rate. This means that the reduced peak current, compared with oxidation peak current, is probably due to the coupled chemical reactions rather than the loss of oxidized species by diffusion under low scan rates.

It is noted that the oxidation peak potential shifts positively a little with the scan rate. The oxidation peak potential of TT/DNA–CTMA is ~1.03 V at 50 mV/s and, surprisingly, ~1.08 V at 1.5 V/s. This indicates that the redox behavior of TT/DNA–CTMA could be roughly described by a surface wave model, though the oxidation peak current does not increase with the scan rate in strictly linear relationship (see Fig. 1b). Such a non-linear relationship of peak current to scan rate could be resulted from the film screening to the electric field, especially for high-scan-rate cases, and/or the ion diffusion in the non-uniform film. The charge transfer rate is very high in the oxidation process of TT/DNA–CTMA as indicated by the high scan rate of 1.5 V/s. However, the evaluation of the kinetic processes of TT/DNA–CTMA should be careful due to the coupled chemical reactions occurred during the electrochemical oxidation and the continuous loss of electro-activity.

Fig. 2 shows the background current curves from bare GC electrode, DNA–CTMA film, and TT dye film in the aqueous electrolyte. The redox current from dye TT is negligible as compared with others, which means that the redox reaction of dye TT is greatly suppressed. DNA–CTMA is electroactive, but the oxidation current is still lower and nearly negligible. Only TT/DNA–CTMA gives a pronounced redox current. It is obvious that the redox current is mainly contributed from the dye TT in DNA–CTMA matrix, not DNA–CTMA.
Fig. 3. Redox behaviors of TT film, DNA–CTMA film, and TT/DNA–CTMA film at the potential scan rate of 50 mV/s in the cyclic voltammetry. Enlarged curves of TT films are shown in the insert.

Fig. 4. Electrochemical reduction of TT/DNA–CTMA film in the aqueous electrolyte at the potential scan rate of 1.5 V/s. The cyclic voltammetric curves of bare GC electrode, TT film, and DNA–CTMA are also available for reference. The arrow indicates the peak current decreases with the repetitive potential scanning.

itself. The coupled chemical reactions in the oxidation process of TT/DNA–CTMA induce the loss of electroactivity of TT, as shown clearly in Fig. 2, the peak current of TT/DNA–CTMA decreases with the repetitive potential scanning. The redox potential of dye TT is derived to be ∼−1.03 V from the oxidation peak potential of 1.08 V and reduction peak potential of 0.93 V.

It is found that the low electroactivity of TT film is not related to the limited diffusion of ions in the solid TT film under high potential scan rate, e.g. 1.5 V/s. TT film shows lower electroactivity under low potential scan rate of 50 mV/s, as shown in Fig. 3. In addition, the backward current is higher than the forward current in the potential range from −0.95 V to 1.20 V, which results in loops in the current curves. This indicates there forms new phase in TT film [27,28], which supports the proposal of coupled chemical reactions in the oxidation of dye TT. The Faraday current of TT decreases with the scanning without defined redox peaks.

As comparison, TT/DNA–CTMA only gives oxidation peak at the scan rate of 50 mV/s. The missing of reduction peaks of TT arises from the loss of oxidized species of TT due to the coupled reactions. DNA–CTMA film shows broad oxidation peak current, comparable with the “charging” current of TT/DNA–CTMA which includes the charging current and Faraday current of DNA–CTMA matrix. The Faraday current from DNA–CTMA must be subtracted from the total current of TT/DNA–CTMA when the accurate Faraday current of TT is considered.

The reduction of TT/DNA–CTMA in the potential range from 0.0 V to −1.6 V was also investigated under different scan rates. Fig. 4 shows the cyclic voltammetric curves of TT/DNA–CTMA, DNA–CTMA, dye TT film, and bare GC electrode in the electrochemical reduction processes. TT film shows a nearly undistinguishable reduction peak at ∼−1.47 V. Faraday current of TT film is surely negligible. This means the direct reduction of dye TT is greatly limited in the aqueous electrolyte. The introduction of DNA–CTMA on GC electrode suppresses the background current in the more negative potential than −1.0 V. DNA–CTMA shows irreversible reduction, the reduction current peaks at ∼−0.70 V, and the electroactivity will gradually lose in the repetitive potential scanning which is similar to that of DNA–CTMA in the oxidation process.

In contrast to the reduction of TT film, TT in DNA–CTMA gives a well-defined reduction peak at ∼−1.44 V, the peak potential shifts positively slightly with the repetitive scanning, and the peak current decreases at the same time. The electrochemical reduction of TT/DNA–CTMA is irreversible with a very small re-oxidation peak at ∼−1.28 V and a sharp and pronounced peak at ∼−1.44 V in the first potential scan. It is suggested that the reduced TT species is too active (short lifetime) to survive even in the electrochemical re-oxidation process. The gradually shifted peak potential of TT from −1.44 V to 1.40 V in the repeating scan probably indicates the coupled chemical reaction as that happened in the electrochemical oxidation (see Fig. 2 for reference).

It is worthy to note that the reduction of TT is not affected by the residual oxygen in the electrolyte. Compared the reduction of TT/DNA–CTMA films in degassed and undegassed aqueous electrolytes, the peak current at ∼−0.7 V from DNA–CTMA decreases while the peak current at ∼−1.44 V of TT remains. The oxygen is not responsible for the irreversible reduction of TT in DNA–CTMA but the coupled chemical reactions. Usually, the electrochemical reduction of dyes should be conducted in water-free electrolyte strictly [29–31]. Our results indicate an alternative way, using DNA–CTMA as the host matrix, to investigate the electrochemical reduction of dyes in aqueous electrolyte.

The well-defined redox potentials of dyes can derive reliable HOMO and LUMO levels for constructing analytical model for the band structures of DSCs. Herein, we can calculate the HOMO level and LUMO level of dye TT from the redox potentials determined by the cyclic voltammetry, given the energy level of SCE is about 4.4 eV below the vacuum [32,33]. The HOMO level of TT is −5.40 eV (HOMO = −Eox − 4.4 eV = −[(1.08 + 0.93)/2 − 4.4 eV] = −5.40 eV), the LUMO level of TT is −3.04 eV (LUMO = −Ered − 4.4 eV = −(1.44 − 1.28)/2 − 4.4 eV = −3.04 eV), and the band gap of TT is 2.36 eV (Eg = 5.4 − 3.04 = 2.36 eV).

Similarly, the band structure of another dye, TS, is also obtained by the cyclic voltammetry of TS/DNA–CTMA in aqueous electrolyte. As shown in Fig. 5, the oxidation process of TS is quasi-reversible while the reduction process is totally irreversible. Both oxidation and reduction of TS are suffered from the electro-activity loss, probably from the coupled chemical reaction as that in TT, in the repetitive potential scan. The redox potential of TS in the oxidation process is −1.02 eV (Eox = (1.10 + 0.93)/2), the HOMO level is 5.42 eV. Owing to irreversible process of TS reduction, the peak potential of −1.00 V is used instead of redox potential to calculate the LUMO level (the shoulder before the reduction peak at −1.00 V is contributed from DNA–CTMA matrix). The LUMO level of TS is −3.40 eV. Consequently, the band gap of TS is derived to be 2.02 eV.

Fig. 6 presents the peak current of TT/DNA–CTMA films with different content of TT. It shows that the peak current of TT/DNA–CTMA increases with the TT content, but drops down suddenly as the content of TT in DNA–CTMA is greater than 8 mmol/g. It is suggested reasonably that dye molecules, e.g. TT molecule, must
be well-dispersed in DNA–CTMA matrix under lower concentration instead of close packing or aggregation, like in the solid state, under higher concentration. The well-dispersed molecules in DNA–CTMA matrix exist in a kind of “solvated” state with the assistance of DNA–CTMA molecular chains. The “solvated” dye molecules should be in a relaxed state. Such a relaxed state of dye is fixed as the solvents (ethanol and chloroform) leave, which enables dye molecules to conduct redox processes successfully in the solid state.

The absorption spectra of the condensed solid film of TT and TT/DNA–CTMA film are shown in Fig. 7. Around 15 nm blue-shift is observed for the absorption peak of TT/DNA–CTMA film compared with that of TT film. This indicates that the molecular conformation of TT in DNA–CTMA is greatly different from that in solid state film of TT alone. The assumption of “solvated” TT molecules in DNA–CTMA is thereby supported by the absorption results to a large extent.

It is surprising that the voltammetric measurements on such a thick DNA–CTMA film (∼1 μm) can be accomplished with such a high potential scan rate as 1.5 V/s. Given that the diffusion of the dye molecules in DNA–CTMA is very limited, the charge transfer of dye to the electrode must proceed either by redox conducting or by the DNA–CTMA matrix as the media. As shown in Fig. 6, the redox process of TT occurs smoothly even under low concentration of TT in DNA–CTMA. This implies that the charge transfer process is not affected by the distance between the dye molecules. We then propose that the charge transfer between the dye and electrode is achieved via DNA–CTMA matrix. It has been reported that DNA is conducting despite of controversy [34–39]. Our experimental results support that the DNA is conducting (CTMA is insulating). It is DNA chain that wires the dispersed dye molecule with the electrode and facilitates the redox processes of dye. According to the reported results, only guanine and adenine bases in DNA chains are electroactive in the electrochemical window of our experiments [40,41]. We noted that the electrochemical passivation of DNA/CTMA at 0.8 V has unobservable effects on the redox processes of dye TT, see Figs. 1a and 2. This means that the passivation and the electroactivity loss of guanine and adenine bases have little effects on the conduction of DNA. DNA–CTMA is a good conducting matrix for the dyes in the electrochemical measurements.

4. Conclusions

The redox processes of organic dyes, TT and TS, have been investigated in the aqueous electrolyte when the dyes are blended with DNA–CTMA. TT shows electrochemically quasi-reversible redox processes for both oxidation and reduction, while TS conducts quasi-reversible oxidation and irreversible reduction electrochemically. The electro-activity loss of TT and TS in the repetitive potential scanning is attributed to the coupled chemical reactions. Well-dispersed dye molecules in DNA–CTMA matrix are the key for the successful electrochemical measurements. Conductive DNA–CTMA matrix is believed to be responsible for the fast charge transfer between the dyes and the electrode, which results in the surface-wave behavior of the dyes in the electrochemical cyclic voltammetry.

We have shown here that the band structure of the organic dyes can be obtained by the cyclic voltammetry of dyes/DNA–CTMA blend in the aqueous electrolyte. In contrast, the redox processes cannot be conducted with the solid dye films electrochemically. The successful evaluation of organic dye dispersed in DNA–CTMA film with aqueous electrochemistry implies that the electrochemical investigation of organic dyes can be conducted in “green” aqueous electrolyte rather than in large amount of organic electrolyte with dyes dissolved in. It is expected that the aqueous electrochemistry of other materials which can be well dispersed in DNA–CTMA film is also feasible.
Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 61108063 and 61077022) and the National Science Foundation for Distinguished Young Scholars of China (No. 61125505). The author (A.W. Tang) is also grateful to the support from Basic Scientific Research Fund of Beijing JiaoTong University (2010BZ006 and 2011JBM301).

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