Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

In-situ Exchange Mechanism for Dye Molecules and Cations On the Nano-semiconductor Film/Electrolyte Interface

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1. Experiments

Materials: The TiO_2 paste (Dyesol-18NR-T) and N719 dye used in the experiments were purchased from Dyesol, and the quartz wafer was provided by JJK Electronic Co. Ltd. $TBAPF_6$ was provided by Shanghai Yuanye Biological Technology Co. ltd. Acetonitrile and absolute ethanol were provided by Sinopharm Chemical Reagent Co., Ltd.

Preparation of nano TiO_2 modified quartz electrodes: 5MHz quartz wafer was blown dry with nitrogen after being cleaned. The TiO_2 paste was printed on the surface of the quartz wafer and sintered in a muffle furnace at 510 °C for 30 minutes to obtain a nanoporous TiO_2 semiconductor film. The quartz wafer coated with a TiO_2 film was immersed in the 0.5 mM N719 ethanol solution for 12 hours to obtain dye-sensitized TiO_2 film quartz electrodes.

EQCM characterization: A three-electrode-system tetrafluoroethylene electrochemical cell was used for the electrochemical potentiostatic experiment: The working electrode was a dye-sensitized TiO_2 film quartz wafer; the auxiliary electrode was a platinum plate; and the reference electrode was a silver wire. The support electrolyte was 0.1 M of $TBAPF_6$ in acetonitrile solution. The electrochemical parameters and frequency response parameters on the working electrode were collected by means of an electrochemical workstation (Zahner, Germany) in combination with a quartz crystal microbalance (QCM 200, Stanford Research Systems). The potential was stepped from the open circuit potential (OCP) and held for 300 seconds at each potential. After duration for 300 seconds, the potential returned to the OCP. The current and frequency response were recorded. At last, the remaining dye on the electrode was completely desorbed under a high potential, and then rinsed and dried. The sensitization step was repeated before the next measurements. The potential changed to the five potentials of -0.8 V, -0.9 V, -1.0 V, -1.1 V, and -1.2 V, respectively.

2. Dye structure

One of the mostly employed dye sensitizers, *cis*-bis(isothiocyanato)-bis(2,2'-bipyridy1-4,4'-dicarboxylato) ruthenium (II) bis-tetrabutylammonium (N719), is highly efficient for TiO_2-based DSC[1]. The N719 dye contains two carboxylic acid and two carboxylate groups (–COOH and–COO-). The same series of dye molecules are also known as N3 and N712 dyes. The molecular structures of the three dyes are shown in Fig. S1. The ruthenium series compounds such as N719 were prepared as described in the literature[2].

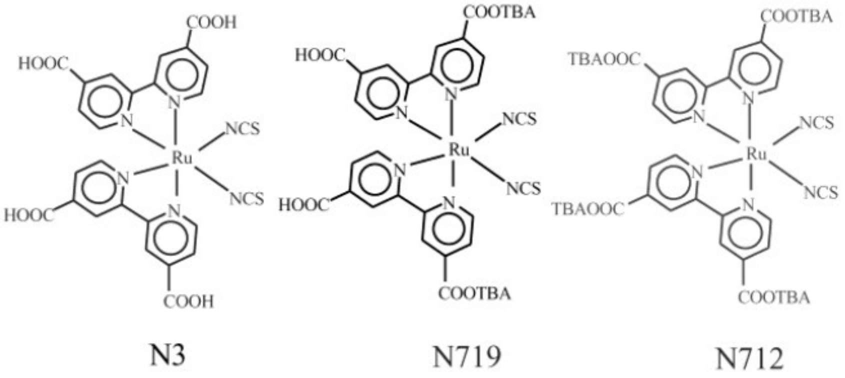

Fig. S1 The molecular structures of the N3, N719, and N712 complexes[3]

3. References

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