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Silicon Compound Decorated Photoanode for Performance Enhanced Visible Light Driven Water Splitting

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ABSTRACT

An efficient dye (**1**) sensitized photoelectrochemical cell (DS-PEC) has been assembled with a silicon compound (3-chloropropyl)trimethoxy-silane (**Si-Cl**) decorated working electrode (WE) TiO_2(**1**+**2**). The introduction of this **Si-Cl** molecule on photoanode leads to better performances on efficiency than untreated ones for light driven water splitting. The firm Si-O layer formed on TiO_2 increased the resistance of the TiO_2/catalyst interface which is assumed to decrease charge recombination from TiO_2 to the oxidized catalyst **2**. The work presented here provides an effective method to improve the performances of DS-PECs.

1. Introduction

Utilization of solar energy to replace traditional fossil fuels is a possible solution to a future sustainable energy supply. Converting solar energy into chemical fuels, such as hydrogen, by visible light driven water splitting using dye-sensitized photoelectrochemical cells (DS-PECs) is a particularly attractive approach. In recent years, much attention has been paid on DS-PECs for light driven water splitting [1–16]. However, quite unsatisfactory results have been achieved in reported systems due to either low efficiencies and/or poor stability of working electrodes (WEs) during the light illumination.

In general, there are several issues to hinder further improvement of the DS-PECs' performances, such as low efficiency of catalysts, desorption of both catalysts and photosensitizers (PSs) from the photoanodes, and charge recombination during the photocatalytic processes. To enhance the performances of DS-PECs, some attempts have been performed, such as application of more efficient catalysts [9–12], assembly of photoanode with electrochemical polymerization or oligoproline methods [17,18]. Mallouk et al. improved their photoanode by inserting a mediator between catalyst and PS to mediate electron transfer process for achieving higher photocurrent density [4]. Meyer et al. decorated photoanodes with a thin film of nanostructured metal oxide to increase the photoanodes' stabilities [20,21]. Despite limited improvement on performance of these DS-PECs, the attempts still provided useful information for designing more efficient DS-PECs.

Core-shell methods are commonly applied to prevent back electron transfers to achieve better performances in decorated systems [19–25]. Therefore, (3-chloropropyl)trimethoxy-silane (**Si-Cl**) was introduced to decorate our photoanode for light driven water splitting, as shown in Scheme 1. As reported [23], organic silicon compounds will attach on TiO_2 through Ti—O—Si bonds and form a Si-O layer with Si—O—Si bonds on the surface of TiO_2. According to our previous work [9], TiO_2-sintered FTO electrodes were immersed into a methanol solution containing both molecular catalyst **2** (2×10^{-4} M) and PS **1** (4×10^{-4} M) to obtain the photoanode TiO_2(**1**+**2**). The obtained photoanode TiO_2(**1**+**2**) was then immersed in a methanol solution of 0.1 M **Si-Cl** for 20 minutes, and then washed with methanol several times, dried in an oven at 45 °C for 5 minutes in the dark to obtain the decorated photoanode. The amount of catalyst and photosensitizer were calculated to be 1.3×10^{-8} mol/cm^2 and 6.4×10^{-8} mol/cm^2 respectively from UV–vis absorption spectrum after desorption in

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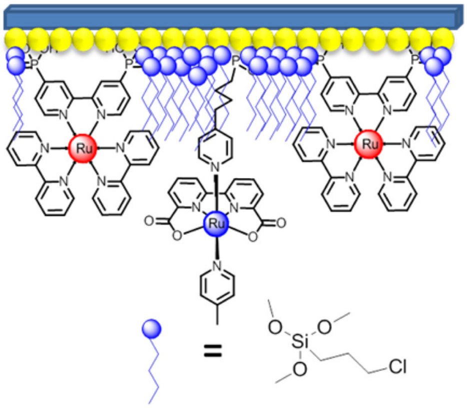


Scheme 1. Scheme for the decoration of the WE TiO_2(**1** + **2**) with **Si-Cl**.

sodium hydroxide solution. We also found nearly same amount of catalyst and photosensitizer still absorbed on TiO_2 surface after the silicon decoration period.

2. Exeperimental

FTO (Fluorine-doped Tin Oxide) glass was purchased from Wuhan Geao science and education instrument company (thickness ~ 2.2 mm, transmittance >90%, resistance ~15 mΩ/cm^2). Other chemicals were purchased from Aladdin chemical company. Solvents were dried and distilled according to the standard methods when needs. Synthetic reactions were carried out under N_2 atmosphere with standard Scheck techniques.

^{1}H NMR Spectra were collected at 298 K using a Bruker DRX-400 instrument. Electrospray ionization mass spectra were recorded on a Q-Tof Micromass spectrometer (Manchester, England). EI-MS analyses were carried out on a gas chromatograph fitted with a mass spectrometer (GC–MS 6890/5973, Agilent, USA). UV–vis absorption measurements were carried out on a HP 8450 spectrophotometer. The light intensity was measured by Nova-II laser power monitor.

Diethyl (4-(pyridin-4-yl)butyl)phosphonate: This ligand was synthesized according to the procedure as reported in literature [31].

2.1. Synthesis of catalyst

As shown in Scheme 2, a mixture of Ru(bda)(DMSO)(4-picoline) (300 mg, 0.6 mmol) and ligand(154 mg,0.6 mmol) in dry CH_3OH (50 mL) was refluxed overnight under N_2 atmosphere. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica gel (CH_2Cl_2:CH_3OH = 10:1) to yield 166 mg (40%). ^{1}H NMR (400 MHz, CD_3OD) δ ppm 1.22 (t, 6H), 1.46 (t, 2H), 1.52 (m, 2H), 1.72 (m, 2H), 2.26 (s, 3H), 2.65 (t, 2H), 4.04 (m, 4H), 7.04 (d, 2H), 7.08 (d, 2H), 7.65(d, 2H), 7.75 (d, 2H), 7.92 (d, 2H), 8.06 (d, 2H), 8.59 (d, 2H). TOF-MS (ES$^+$): m/z$^+$ 731.1183 [M+Na]$^+$. Calcd: 731.1185.

The product (106 mg, 0.15 mmol) was dissolved in dry CH_3CN (20 mL), and then $Si(CH_3)_3I$ (0.03 mL, 0.18 mmol) was added dropwise at room temperature under N_2 atmosphere. The mixture was heated to 45 °C for 2 h then cooled to room temperature. The solution was stirred for 3 h after adding dry CH_3OH (20 mL). The solvent was removed and the product was isolated by gel column (Sephadex LH-20, CH_3OH) to obtain 75 mg (82%) of catalyst **2**. ^{1}H NMR (400 MHz, CD_3OD) δ ppm 1.75 (m, 4H), 2.14 (m, 2H), 2.26 (s, 3H), 2.67 (t, 2H), 7.05 (d, 2H), 7.09 (d, 2H), 7.65 (m, 2H), 7.72 (s, 2H), 7.93 (d, 2H), 8.04 (d, 2H), 8.69 (d, 2H). TOF-MS (ES$^-$): m/z$^-$ 651.0579 [M-H]$^-$. Calcd: 651.0583.

[Ru(bpy)$_2$(4,4-(PO$_3$H$_2$)$_2$bpy)]Br$_2$: This Ru complex was synthesized as reported previously [32].

2.2. Preparation of working electrodes

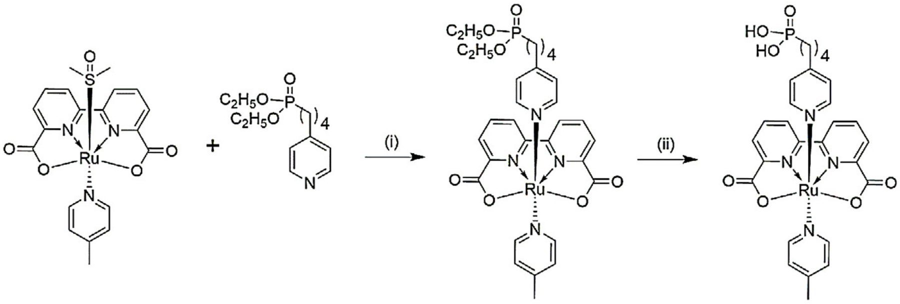
FTO electrode with a 12 μm thickness nano TiO_2 film was made by doctor bladed. It was dried at 120 °C for 30 minutes in oven, then heated to 520 °C in stove for 1 hour, and then cooled to room temperature. Subsequently, it was cut by glass cutter and the active area was made to be 1 cm^2. After that, the FTO conducting glasses sintered by nanostructure TiO_2 (1.0 cm^2 × 2 pieces) were immersed into catalyst **2** (1.3 mg, 2.0×10^{-6} mol) and/or photosensitizer **1** (3.0 mg, 4.0×10^{-6} mol) solution in a mixture of 10 mL methanol and 5 drops of acetonitrile in a closed container for 2 hours. It was then washed with methanol and water for several times and dried in dark at room temperature to obtain working electrodes.

The photoanodes were dipped into a menthol solution of 0.1 M **Si-Cl** for 20 minutes, and then they were dried in oven under dark environment for 5 minutes under 45 °C. Then DS-PECs were assembled with these decorated anodes.

2.3. Electrochemistry and Photoelectrochemical Measurements

The electrochemical measurements were recorded on a BAS-100W electrochemical potentiostat in a three-electrode cell under argon atmosphere. The working electrode was a TiO_2-sintered FTO electrode absorbing with catalyst or photosensitizer. The counter electrode was a platinum wire. The reference electrode was an aqueous Ag/AgCl electrode.

All photocurrent experiments were conducted in 0.1 M Na_2SO_4 aqueous solution under visible light illumination using a 300 W Xe lamp (CEAULIGHT CEL-HXF300) through a cut off filter (λ > 400 nm) to block ultraviolet light. The light intensity in front of the photoanode was 300 mW/cm^2 as measured by a CEAULIGHT CEL-NP2000 photometer. All films were irradiated from the front side of the photoanode, and the irradiated area was 1 cm^2 for all experiments.



Scheme 2. Synthesis route of the catalyst **2**. (i) CH_3OH, reflux, overnight. (ii) $Si(CH_3)_3I$, CH_3CN, 45 °C, 2 h; CH_3OH, r. t., 3 h.