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Triphenylamine-based dye functionalized platinum colloid for photocatalytic hydrogen evolution from water: Synthesis, characterization, electron transfer, and photocatalysis

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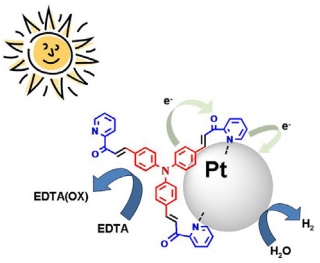
HIGHLIGHTS

- A multibranched triphenylamine dye functionalized Pt nanocomposite was synthesized.
- The multibranched triphenylamine dye demonstrated effective light-absorption.
- Efficient electron transfer from the dye to Pt enhanced the photocatalytic activity.

GRAPHICAL ABSTRACT

Efficient photo-excited electron transfer from the dye-shell to the platinum-core in the photocatalytic splitting of water under UV–vis light irradiation.



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ABSTRACT

A multibranched triphenylamine-based dye (tris(4-(2-(2-(pyridin-2-yl))-carbonyl-vinyl-)phenyl)amine) functionalized platinum homogeneous catalyst was successfully synthesized and characterized by Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet–visible absorption (UV–vis), and fluorescence studies. The FT-IR, TEM, and XRD studies demonstrated that the as-prepared homogeneous catalyst could be described as an organic-inorganic nanosphere composed of an organic multibranched dye shell and a platinum nanocore (ca. 2.9 nm). The fluorescence quenching and fluorescence decay studies indicated that the interfacial electrons transferred directly from the dye molecule to the platinum nanoparticle in this homogeneous catalyst under light irradiation. The homogeneous catalyst could be used as a stable photocatalyst for homogeneous photoinduced hydrogen evolution without an electron relay under UV–vis light irradiation.

1. Introduction

Due to the global energy crisis and environmental protection demand, hydrogen as an environmentally friendly and recyclable energy has attracted great attention. Homogeneous and heterogeneous photocatalytic water splitting to produce hydrogen using solar light is one of the most promising green methods to solving the world energy crisis [1–3]. Homogeneous photocatalysts are very attractive in the sense that their chemical and photochemical properties can be understood and strategically tuned on molecular level. In most cases, homogeneous photocatalytic hydrogen evolution systems usually consist of a dye as a photosensitizer, an electron transfer relay, a sacrificial electron donor, and a hydrogen evolution cocatalyst [4–8]. In fact, these homogenous

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photocatalytic systems are micro-heterogeneous ones because Pt nanoparticles are usually used as cocatalyst. They are often referred as homogeneous systems in many literatures based on the fact that these systems in apparent look like homogenous. In order to achieve high catalytic efficiency, some simplified systems, such as single-component system, have been investigated [9]. These researches revealed that electron-transfer process was enhanced, thus, the efficiency of light induced water splitting into hydrogen was promoted. Our group also investigated some platinum colloid composed by porphyrin derivatives directly anchoring on a platinum nanoparticle surface as catalysts for photoinduced hydrogen evolution. These works demonstrated that efficient electron transfer from excited photosensitizer molecules to the metal occurred and the porphyrin molecules modified by peripheral functional groups could improve the photocatalytic activity [10–13].

Triphenylamine and its derivatives have been wildly employed as photoactive function materials in dye-sensitized solar cells [14–16], two-photon absorption [17–19], organic field-effect transistors [20–22], and light-harvesting systems [23–25] owing to their intriguing optoelectronic and photochemical properties, viz., strong donor character, superior hole transport properties, and the ability to form stable radical cations [26]. Most of triphenylamine-based compounds usually contain a donor–π-spacer–acceptor (D–π–A) structure. Such a structure provides a possible alternative to adjust light absorption and to improve the efficiency of the intramolecular charge separation [27]. Tan and coworkers reported that introduction of vinyl unit into the π-spacer of triphenylamine-based dyes caused red-shifted absorption spectra [28]. Grätzel's group reported several novel triphenylamine-based organic sensitizers for sensitization of mesoscopic titanium dioxide solar cells and increased open-circuit potential of the cells was attributed to the prolonged lifetime of the photoinduced carriers of these novel dyes [29]. However, triphenylamine-based sensitizers have been rarely used as a component to construct homogeneous photocatalysts for photoinducing hydrogen evolution.

Herein, we report synthesis and characterization of an organic-inorganic homogeneous catalyst composed of multi-branched triphenylamine-based molecule, (tris(4-(2-(2-(pyridin-2-yl))-carbonyl-vinyl-)phenyl)amine, abbreviated as TPPA), and platinum nanoparticles, as well as its homogeneous photocatalysis for hydrogen production. This multibranched triphenylamine-based dye demonstrated to be an effective stabilizer and light-harvesting sensitizer. The colloidal solution of the homogeneous catalyst was stable without sign of precipitation at room temperature even for three months. The fluorescence quenching, fluorescence decay and photocatalysis studies revealed that photoexcited electron transferred effectively from the TPPA molecule to the platinum nanoparticles, resulting in favorable photocatalytic hydrogen evolution. The effects of pH value of the system on the photocatalytic activity and the stability of the Pt-TPPA photocatalysts were also investigated.

2. Experimental

2.1. Chemicals

All chemical reagents were purchased from Acros Company and used without further purification.

2.2. Synthesis of (tris(4-(2-(2-(pyridin-2-yl))-carbonyl-vinyl-)phenyl)amine

The synthesis process of TPPA is shown in Fig. 1. In a typical experiment, 3.29 g of tris(4-formylphenyl)amine (10 mmol) and 3.63 g of acetylpyridine (30 mmol) were mixed with 50 cm^3 methanol in a 100 cm^3 three-necked round-bottom flask. To the flask, 2 cm^3 of sodium hydroxide aqueous solution (0.5 M) were added dropwise under magnetic stirring. The mixture was stirred at room temperature for 24 h. The color of the solution turned from light yellow to orange. After evaporation of the solvent, the crude solid was recrystallized from chloroform. The yield was 35% and the melting point of the product is 193–194 °C. Element analysis (%): cald. C, 78.98; H, 4.73; O, 7.51; N, 8.77; Found. C, 78.61; H, 4.12; O, 8.10; N, 9.17. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ, ppm 7.33–7.47 (m, 12H, benzene-H), 7.83–7.96(m, 6H, 4, 5-pyridine-H), 8.07–8.18(m, 6H, 3, 6-pyridine-H), 8.30–8.48(m, 3H, =CH) 8.59, 8.73 (d, 3H, =CH–C=O).

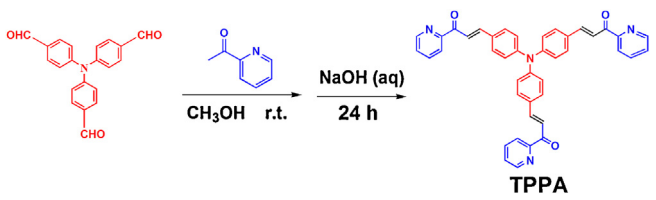

Fig. 1. The synthetic route for TPPA molecule.

2.3. Synthesis of TPPA-functionalized platinum homogeneous catalyst

TPPA-functionalized platinum homogeneous catalyst was prepared by ethanol reduction method [10–13]. In a typical experiment, 2 cm^3 of H_2PtCl_6 aqueous solution (7.723×10^{-3} mol dm^{-3}) and 1 cm^3 of TPPA ethanol solution (7.723×10^{-5} mol dm^{-3}) were mixed with 60 cm^3 aqueous solution of ethanol (V_{water}:$V_{ethanol}$ = 1) at pH 9–10. The solution was heated under reflux for 2.5 h, resulting in a dark brown platinum colloidal solution. For comparison, tris(4-formylphenyl)amine (TFPA) functionalized platinum homogeneous catalyst was also prepared using the same method. The samples were labeled as Pt-TPPA and Pt-TFPA for TPPA and TFPA functionalized platinum homogeneous catalysts, respectively.

2.4. Characterization

^{1}H NMR of TPPA was recorded at 295 K on a Varian NMR System 300 MHz spectrometer using $CDCl_3$ solvent and TMS as internal standard. UV–vis absorption spectra of the samples were recorded on a TU1810 SPC spectrophotometer. Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Nicolet Magna 550 spectrometer. A Philips diffractometer with Ni-filtered Cu Kα radiation was used to obtain X-ray diffraction (XRD) patterns of the samples. Transmission electron microscopy (TEM) studies were conducted on a Tecnai G20 electron microscope operating at an accelerating voltage of 200 kV. The sample for TEM analysis was prepared by dropping about 3 mm^3 of the diluted colloidal solution onto a carbon-covered copper grid and letting the solution air-dry at room temperature. Fluorescence spectra of the samples were taken on an Edinburgh FLS920 fluorospectrophotometer. Fluorescence decays were measured with a time-correlated single-photon-counting fluorometer equipped with a time-correlated single-photon counting card. The lifetime values were calculated by reconvolution fit analysis of the decay profiles with the aid of FelixGX software. In all fluorescence decay profiles, the mono-exponential fit and dual-exponential fits gives acceptable statistics parameters of $c^2 < 1.2$.

2.5. Photocatalytic hydrogen evolution

The photocatalytic reaction was carried out in a 50 cm^3 quartz flask equipped with a flat optical entry window. To the flask, 28 cm^3