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Designing and fabrication of phenothiazine and carbazole based sensitizers for photocatalytic water splitting application

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ABSTRACT

In the present work, we have designed and synthesized two carbazole and phenothiazine donor moieties based metal-free organic sensitizers and their codes are WCBZ2 and WPTZ2 respectively. These sensitizers have been used for photocatalytic hydrogen (H_2) evaluation application. The sensitizers exhibit good light absorption capability and electrochemical properties as well. For increasing water splitting capacity, incorporate platinum salt on TiO_2 semiconductor photoanode was performed and compared hydrogen evolution with pure TiO_2 photoanode. We have also studied the influence of the sensitizer's concentration and the effect of pH of the medium was explored. Using a theoretical measurement optimized both the synthesized dimer dyes structure geometry and the calculated their HOMO-LUMO energy level. Here also reported optimized pH and concentration of sensitizers in the reaction medium and found that the high hydrogen generation efficiency from water splitting is 138.3 μmol (348 TONs) by the WPTZ2 dye.

Introduction

Depletion of fossil fuels and enhanced global demand for energy is an inevitable problem of modern time. An attractive scientific and technological solution of this technique for conversation of solar light into hydrogen (H_2) evolution by water splitting [1]. Generally, the generation of H_2 from water using sunlight has glued the scientists all around the world. In 1972, K. Honda et al. has reported the use of ultraviolet light (UV light) with the TiO_2 semiconductor in separation of oxygen and H_2 from water [2]. Then after the developing of

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appropriate visible range absorb sensitizers and their absorption on *n*-type semiconductor, illuminated visible light has also been used for water splitting [3–7]. While some progress in the development of sensitizers are done already, there should definitely be more extensive studies for more active systems. Now a days, Ru-metal based broad spectrum sensitizers have been used with TiO_2 semiconductor for water splitting [8–11]. During catalytic water splitting operation, the excited electron of sensitizers is transferred to TiO_2 to generate cationic radical which recovers electron from additional losing compounds. In this operation, the sensitizers are decomposed and get a lower turnover number. Hence, still a lot of investigations are required to develop efficient and stable sensitization. According to the literature, cyclic materials such as phenothiazine (PTZ) and carbazole (CBZ) donor groups having sulphide and amine moieties presence and develop cationic radical by electron oxidation [12,13] (see Scheme 1).

Therefore, it can be predicted that PTZ and CBZ donor moieties based sensitizers have excellent stability in photo-excited electron transport from sensitizers to titania. Due to this characteristics, various redox devices have been prepared for efficient light energy conversations [14,15]. It is found that the changes in electrochemical and photophysical behaviour happen due to the substitution of various anchoring and alkyl chains on the main moieties and its nitrogen atom of sensitizers respectively. The present work, we have developed and synthesized dimer of PTZ and CBZ electron donor moieties based organic metal free dyes (Fig. 1) as electron-rich donor moieties contain electron releasing "S" and "N" atoms. Moreover, both the cyclic materials are nonplanar and therefore can hinder the aggregation of both the donor moieties and the generation of intramolecular excimers [12,16–19].

These dimer sensitizers possess substituted butyl chain which is helpful to reduce sensitizer aggregation and also help to increase charge recombination between photo-excited sensitizers and TiO_2 semiconductor. In our present work, we have reported two new dimer metal-free organic sensitizers based on PTZ and CBZ donor moieties (Fig. 1) and they have been used in water splitting (induced photocatalytic hydrogen generation) applications. The change in electrochemical and photophysical properties was studied with the change of donor moieties. It was also calculated that the hydrogen evolution productivity is the function of various effective parameters, such as activation temperature of titania semiconductor, concentration and optical properties of the sensitizers, pH of the reaction medium and charge recombination of sensitizers and TiO_2 interface.

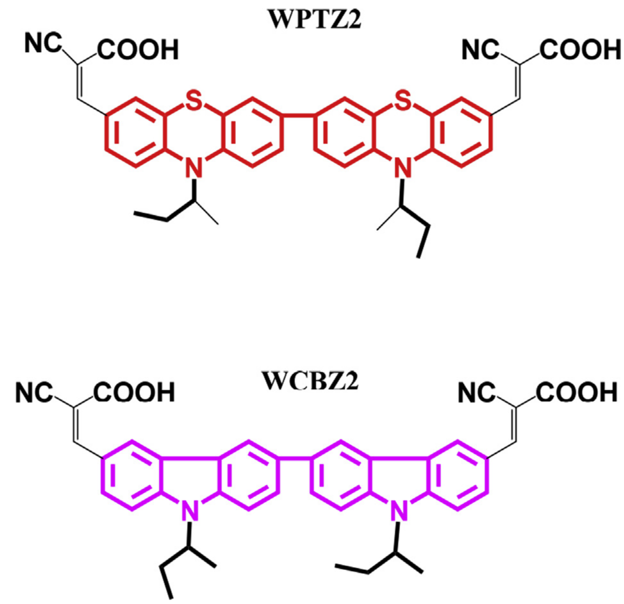
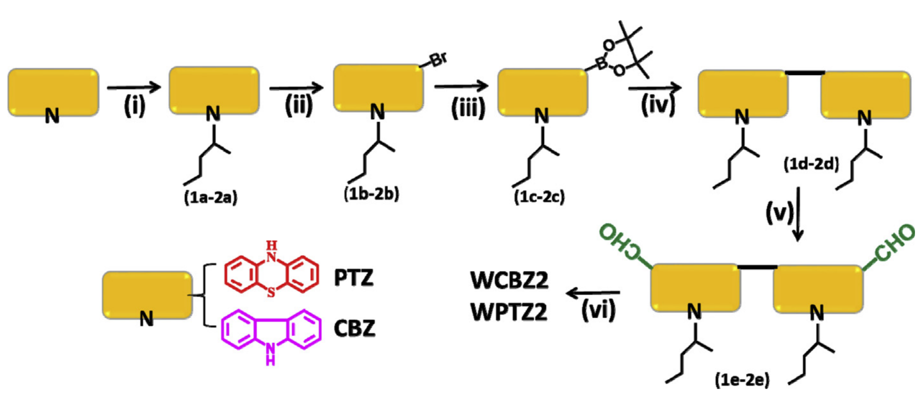


Fig. 1 – Chemical structure of metal-free sensitizers.

Experimental

Materials and reagents

Phenothiazine (PTZ, >98%), carbazole (CBZ, >97%) and 2-bromopentane (>85%) were procured from TCI chemical Ptv. Ltd. China. N-Bromosuccinimide (NBS, 99%), Tetrahydrofuran (THF, 99.9%), Phosphoryl chloride ($POCl_3$, 96%), piperidine (99%), Potassium acetate (>99.0%), Bis (pinacolato)diboron (99%), $Pd(dppf)Cl_2$ (98%), $Pd(PPh_3)_4$ (99%), cyanoacetic acid (99%), acetonitrile (can, >99.8%) and dimethylformamide



Scheme 1 – Synthesis procedure of WPTZ2 and WCBZ2 based sensitizers. (i) NaH, 2-bromopentane, DMF, heat 60 °C, 6 h (ii) N-Bromosuccinimide, Tetrahydrofuran, RT, (iii) KOAc, THF, 65 °C, Bis (Pinacolato)diboron, $Pd(dppf)Cl_2$, (iv) $Pd(PPh_3)_4$, K_2CO_3, (v) $POCl_3$, DMF, 20 h, (vi) cyanoacetic acid, piperidine, acetonitrile, 8 h reflux.