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A two-pronged strategy to enhance visible-light-driven overall water splitting via visible-to-ultraviolet upconversion coupling with hydrogen-oxygen recombination inhibition

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ABSTRACT

Visible-light-driven overall splitting water is a potential and sustainable approach for hydrogen generation. Although many photocatalysts have been reported to be active for this reaction, the efficiency of overall splitting water is still quite low. In this work, a two-pronged strategy is adopted to overcome two key restrictions on visible-light-driven photocatalytic overall water splitting by taking advantages of visible-to-ultraviolet upconversion (UC) effect as well as inhibiting hydrogen-oxygen recombination reaction over the photocatalyst. In order to realize that purpose, a composite photocatalyst with high stability was designed by assembling three components consisting of visible-to-ultraviolet UC Pr^{3+}-Y_2SiO_5, UV-responsive semiconductor photocatalyst $CaTiO_3$ and perfluorodecalin as an oxygen transfer regent. By the first strategy, the visible-to-ultraviolet UC unit is capable of converting visible irradiation to UV light emission, which effectively excites UV-responsive photocatalyst $CaTiO_3$. The photocatalytic activity has been raised up to 200% by regulating the amount of visible-to-ultraviolet UC Pr^{3+}-Y_2SiO_5 in the designed composite photocatalyst Pr^{3+}-Y_2SiO_5/$CaTiO_3$. The photocatalyst exhibited high photochemical stability and catalytic stability in four recycle reactions. By the second strategy, hydrogen and oxygen recombination on photocatalyst surface has been effectively inhibited by an oxygen transfer reagent FDC to capture and take away newly generated oxygen from catalyst surface. This two-pronged strategy is not only convenient and efficient, but exhibits potential versatility for the most stable UV-responsive semiconductor photocatalysts to realize overall split water by visible light irradiation.

1. Introduction

It is urgent to explore new energy resource to replace fossil energy and severe greenhouse effects caused by over-consumption of fossil fuel [1,2]. Hydrogen is considered to be an ideal clean energy carrier to fulfill this purpose due to its high combustion enthalpy and the CO_2 zero-emission property [3–10]. Water splitting to hydrogen has been enlightened as a sustainable and highly potential approach for hydrogen production since Fujishima and Honda found that the TiO_2/Pt electrodes could facilitate water splitting, that is, generating hydrogen from pure water driven by solar energy with the aids of photocatalytic overall splitting water system [11–45].

Many efforts have been done in solar driven water splitting, however, most of the studies concentrated on the half reaction of water splitting in the presence of sacrificial reagents. For example, Cr, Ni, Cu, Nb and N codoped TiO_2 [46], CuOx/TiO_2 [47] and Ni@NiO/TiO_2 [48], redox-mediator-free CdS/Co_9S_8 hollow cubes Z-scheme photocatalyst [49], CdS nanorods with Cu_2MoS_4 as co-catalyst [50], Pt-RuS_2/$Cd_{0.5}Zn_{0.5}S$ photocatalyst [51], showed HER activity under visible light irradiation in the presence of or in the absence of sacrificial agents. And overall water splitting without sacrificial chemicals still remains challenging [52]. On the one hand, although rapid development of photocatalysts for overall water splitting has been triggered, but very seldom visible light sensitive and stable photocatalyst has been reported, for example, sulfide and selenide photocatalysts exhibit high photocatalytic activity for hydrogen evolution under visible light irradiation, but their practical applications are highly restricted due to their poor photochemical stability (photocorrosion) [53–57]. Iwashina et al. [58] used metal sulfide as hydrogen evolution photocatalyst

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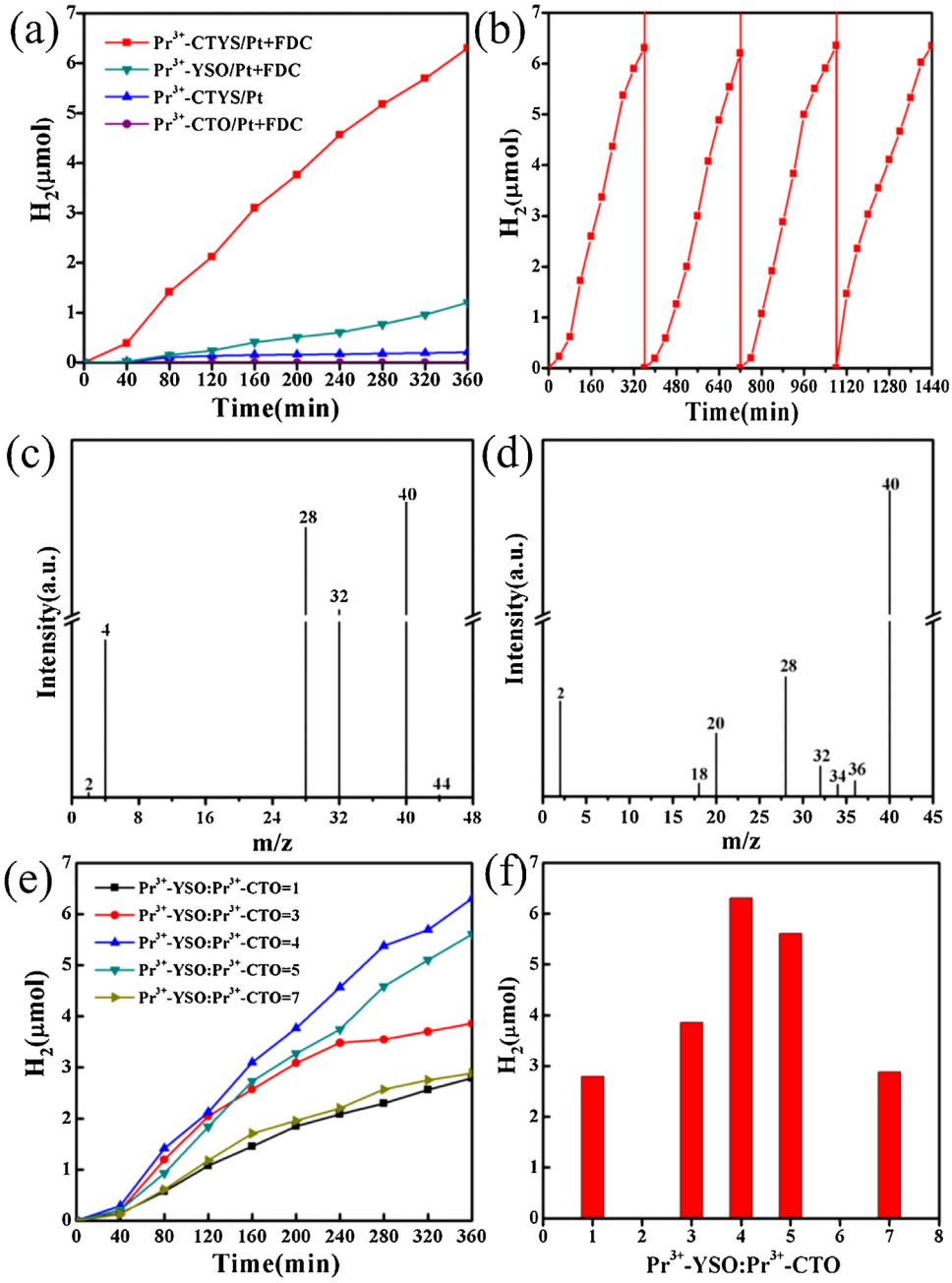

Fig. 1. (a) Photocatalytic activity of Pr^{3+}-CTYS/Pt with and without FDC, Pr^{3+}-CTO/Pt with FDC and Pr^{3+}-YSO/Pt with FDC under visible light; (b) stability testing of Pr^{3+}-CTYS/Pt; GC–MS spectra of water splitting gas products in the presence of (c) D_2O and (d) $H_2{}^{18}O$ over Pr^{3+}-CTYS/Pt; (e) Photocatalytic activities and (f) maximum H_2 evolution over Pr^{3+}-CTYS/Pt in the presence of FDC with the different weight ratio of Pr^{3+}-YSO: Pr^{3+}-CTO = 1,3,4,5,7 respectively.

accompanied with oxygen evolution photocatalyst RGO-TiO_2 in a Z-Schematic system, and they obtained stoichiometric amount of H_2 and O_2 in water splitting reaction, but the stability of their catalyst was not high enough. Zhu [59] and Wang's [60] constructed NiS/Ni foam and three-dimensional (3D) carbon paper/carbon tubes/cobalt-sulfide sheets as electrode for overall water splitting in alkaline medium, however, this photocatalyst dispersion still seems difficult for water splitting. Although some metal oxynitrides and nitrides with d^0 transition-metal cations or typical d^{10} metal cations are reported to be photocatalytic under visible light irradiation for overall water splitting, such as GaN:ZnO [61], TaON [62] and Ta_3N_5 [63], but some of them are unstable under light irradiation [64], resulting from the N^{3-} ions oxidation by photogenerated holes. Carbon nitrides have been used for photocatalytic overall water, for example, MoS_2/Co_2O_3/poly (heptazine imide) composite photocatalyst [65] can catalyze H_2 and O_2 generation using TEOA as a sacrificial hole scavenger. Pt, PtOx, and CoOx modified g-C_3N_4 [66] and Co_3O_4/Janus hollow carbon nitride spheres/Pt photocatalysts [67] were active for water splitting under UV/visible light and UV light irradiation. One difficult problem in photocatalyst development is that TiO_2 and Ti based photocatalysts are stable and active only under UV light irradiation [68–71]. One of options to overcome this obstacle is develop an upconversion (UC) material converting visible light to UV light to excite UV absorbed Ti based photocatalyst, here, the UC material could generate higher energy and shorter wavelength fluorescence under the excitation of the low energy visible photons.