Polymer Composites of Carbon Nitride and Poly (3-hexylthiophene) to Achieve Enhanced Hydrogen Production from Water under Visible Light

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Supporting Information

Experimental details

1. The preparation of photocatalysts

The g-C_3N_4 was prepared by directly heating melamine under a flow of Ar gas [1,2]. Analytical grade melamine powder (10 g) was pressed into a semiclosed cylindrical quartz tube and then placed in the middle region of another quartz tube with 30 mm in inner diameter and 1000 mm in length. The quartz tube was heated to 380 ^oC in 5 minutes and then heated to 600 ^oC in a muffle furnace for 4 h at a heating rate of 1 ^oC min^{-1} in the flow of Ar gas. After the reaction, the quartz tube was cooled down to room temperature in the flow of Ar gas.

The P3HT was synthesized through modified Grignard metathesis polymerization reported by A. Yokoyama et al [3].

The composite catalysts of C_3N_4 and P3HT were prepared by impregnating C_3N_4 (0.5 g) with a chloroform solution of P3HT (0.6 mg/ml) over night, followed by vaporization the solvent under water bath, and then dried overnight at 343 K.

2. Characterizations of the photocatalysts

The structural properties of the polymer composite were analyzed by X-ray powder diffraction (XRD) on a X-Pert Pro diffractionmeter with CuKα radiation (λ = 1.5406 Å) at a scanning speed of 4° min^{-1}. UV-vis diffuse reflection spectra were measured using a UV-vis spectrophotometer (UV2100, Shimadzu) and converted from reflection to absorbance by the Kubelka-Munk method. The photoluminescence measurements were performed in a luminescence spectrophotometer (Hitachi F-7000) operated at room temperature. The morphology of the composite materials was characterized using Tecnai G^2 F20 S-TWIN microscope.

3. Photocatalytic reaction

The loading of Pt (1 wt. %) on the polymer composite was performed by a photodeposition method. The polymer composite (0.5 g) was dispersed in a methanol aqueous solution (H_2O: CH_3OH = 7:1, in volume) containing equivalent molar amount of H_2PtCl_6, followed by irradiation by a 300 W high-pressure mercury lamp for 1 h to reduce H_2PtCl_6 into metallic Pt under airfree conditions. The final product was filtered, washed several times with distilled water and then dried overnight at 343 K.

The photocatalytic reaction under visible light irradiation was carried out in an inner irradiation quartz cell (500 ml). The reaction cell was connected to a closed gas circulation system and the gases evolved were analyzed with an on-line TCD gas chromatograph (SPSIC, GC-102AT, argon carrier). In a typically photocatalytic reaction, 0.3 g of catalysts was suspended in 600 mL of aqueous Na_2S (0.25 M) and Na_2SO_3 (0.25 M). A 300 W high-pressure mercury lamp was blocked by a $NaNO_2$ aqueous solution (2 M) filled in quartz tube. In this case, it is considered that an emission of a high pressure mercury lamp at 436 nm mainly contributes for the reaction.

The apparent quantum efficiency (QE) was estimated by the method described previously [4, 5] with irradiation light at 420±10 nm by using combined band-pass and cut-off filters, and the QE was calculated according to the following equation:

$$QE(\%) = \frac{2 \times H}{I} \times 100$$

where H and I represent the numbers of evolved H_2 molecules and incident photons, respectively. The number of incident photons was 1.3×10^{21} photons h^{-1} which was measured by using a calibrated Si photodiode.

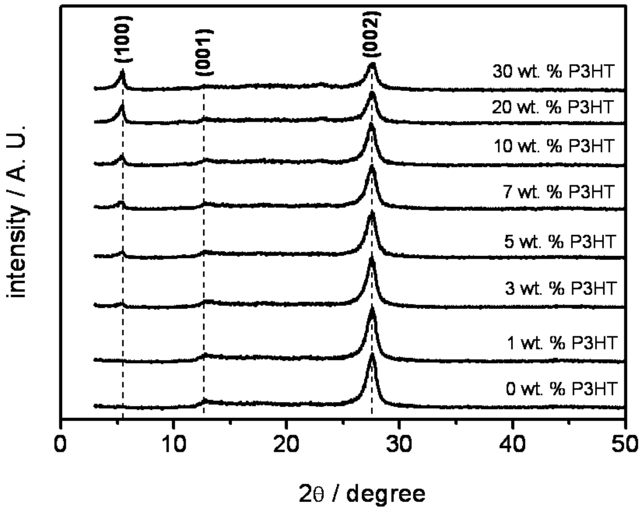

Figure S1 XRD patterns of C_3N_4-P3HT polymer composite

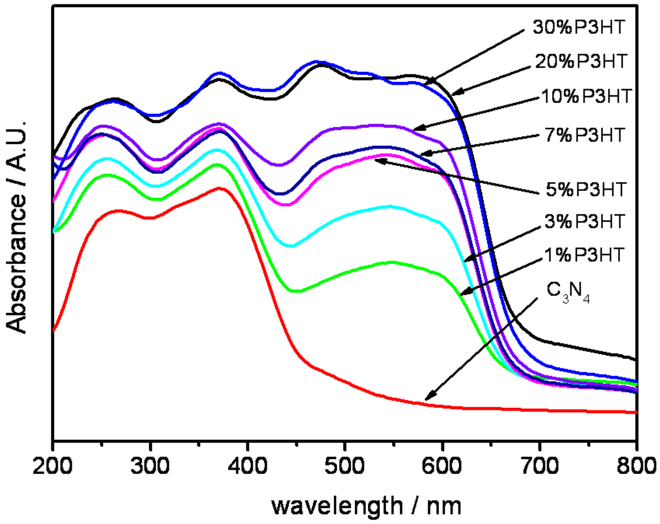

Figure S2 UV-vis of C_3N_4-P3HT polymer composite

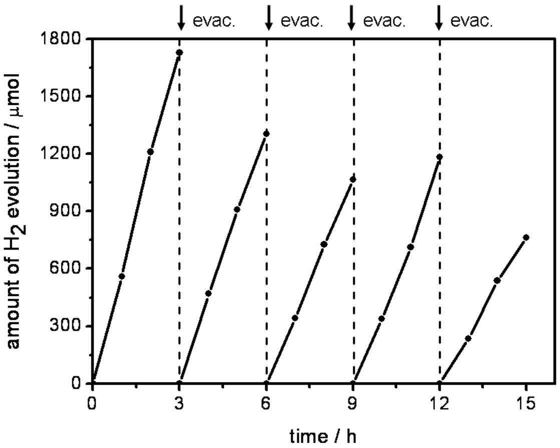

Figure S3 The time course of H_2 evolution on 1 wt % Pt/C_3N_4-3 wt % P3HT under visible light ($\lambda > 400$ nm). Catalyst (0.3 g); 0.25 M Na_2S-0.25 M Na_2SO_3 solution (600 mL); light source, high-pressure mercury lamp (300 W)

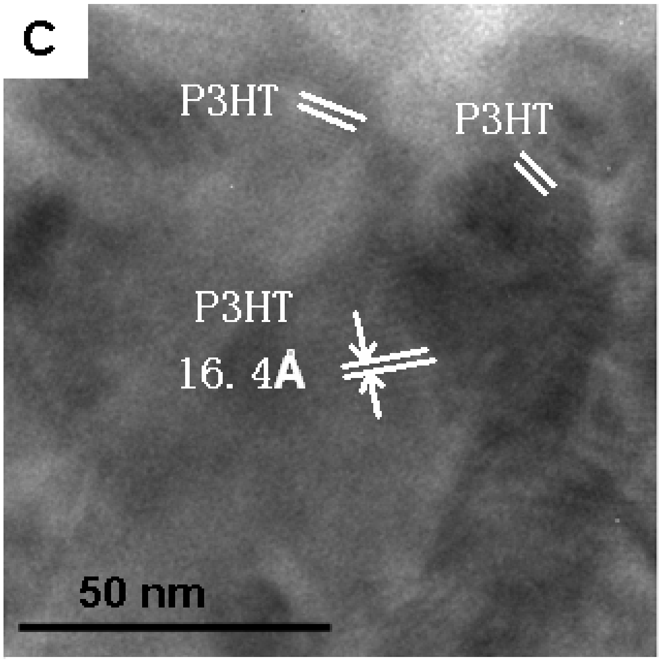

Figure S4 Enlarged marked portions of micrographs of the polymer composite with 3 wt % of P3HT

Reference

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