Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information

# A facile one-step synthesis of ZnO quantum dots modified poly(triazine imide) nanosheets for enhanced hydrogen evolution under visible light

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## Experimental Section

**Synthesis of g-$C_3N_4$.** A porcelain crucible was loaded with cyanamide (CA) (2.00 g) and covered with a porcelain lid. The crucible was placed in a muffle furnace and heated at 793 K for 4 h and then cooled to room temperature. The product was ground to a homogeneous powder.

**Synthesis of PTI/ZnO-QDs.** CA (2.00 g, 47.6 mmol) was thoroughly grounded together with 20.0 g of a mixture of potassium chloride and zinc chloride (48:52 wt %). $ZnCl_2$ plays a role not only as the reactive solvent but also the precursor of ZnO. The reaction mixture was transferred into a porcelain crucible with cover and heated in a muffle furnace at a ramp of 2.1 K min$^{-1}$ to 793 K. The temperature was held for 4 h, and the sample was then cooled to room temperature. After washed with abundant boiling water to remove residual salts, the solid was collected as the product and dried at 333 K. The resulted material was a pale yellow powder.

**Synthesis of PTI.** 0.4 g PTI/ZnO-QDs was added to 200 mL 2 M HCl solution. The mixture was stirred for 1 day at room temperature. After that, the solid was collected, thoroughly washed with water and dried at 333 K. The resulting white solid was transferred to a covered porcelain crucible and heated in a muffle furnace at 623 K for 1 h. Final product was obtained as a yellow powder.

**Synthesis of ZnO quantum dots (QDs).** ZnO QDs were synthesized using a modified procedure in the previous report[S1]. A mixture of zinc acetate ($(CH_3COO)_2Zn\cdot 2H_2O$, 0.291g, 1.00 mmol), poly(vinyl pyrrolidone) (PVP, 0.500 g) and 50.0 mL EtOH was stirred at 333 K for 2 h, and then cooled to 273 K. A solution of NaOH (0.080 g, 2.00 mmol) in 50.0 mL EtOH was added to the above mixture (1.0 mL/min). The resulted mixture was then stirred at 333 K for 3 h to afford a PVP-capped ZnO QDs suspension. Pure ZnO QDs were obtained by adding hexane to the suspension and collected by centrifugation.

**Characterizations.** Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) analyses were carried out on a JEM-

2100 instrument. X-ray diffraction (XRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO using monochromated Cu Kα radiation. BET measurements were carried out on a Micromeritics ASAP 2020 nitrogen adsorption apparatus. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Escalab 250Xi spectrometer using an Al Kα radiation excitation source. The UV-vis diffuse reflection spectra (DRS) were taken on a Shimadzu UV-2450 spectrophotometer using $BaSO_4$ as the reference. Photoluminescent (PL) spectra were detected by a Cary Eclipse fluorescence spectrometer at an excitation wavelength of 350 nm.

**Photoelectrochemical measurements.** All the photochemical measurements (Mott-Schottky plots and photocurrent) were performed by CHI-660E workstation (CH Instruments) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 1.0 $cm^2$, Ag/AgCl electrode (immersed in saturated KCl solution) as a reference electrode, and a Pt sheet as the counter electrode. The electrolyte was 0.5 M $Na_2SO_4$ aqueous solution. Topically, the working electrodes were prepared as follows: 15 mg sample was dispersed in 0.2 mL DMF to afford slurry. The slurry was spread on to an ITO glass. After air-drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. The light source was a 300 W Xe lamp (UV-Vis) equipped with a cut-off filter (Vis, $\lambda \geqslant 420$ nm).

**Photocatalytic activity for $H_2$ evolution.** The photocatalytic $H_2$ production experiments were performed in a 250 mL Pyrex top-irradiation reaction vessel. 50 mg of the as-prepared photocatalysts were suspended in 100 mL aqueous solution containing 10 vol% triethanolamine as sacrificial electron donor. 3 wt% Pt was photodeposited onto the catalysts using $H_2PtCl_6$ dissolved in the reactant solution. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xe lamp with a cut-off filter (Vis, $\lambda \geqslant 420$ nm). The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector with argon as the carrier gas.

**Apparent quantum efficiency calculations.** The apparent quantum efficiency (AQE) was measured in the same photocatalytic conditions except that a band-pass filter was used instead of the cut-off filter. In the following we describe the AQE determination at $\lambda_0$=420 nm for PTI/ZnO-QDs as an example. The catalyst suspension was irradiated by a 300 W Xe lamp applying a $\lambda_0$±15 nm band-pass filter for 5 hours. The average intensity of irradiation was determined to 4.51 $mW\cdot cm^{-2}$ by a Newport Oriel 91150V reference cell and the irradiation area was 27.3 $cm^2$. The number of incident photons ($N$) is as calculated by equation (1). The amount of $H_2$ molecules generated in

5 hours was 49.3 μmol. The AQE is calculated from equation (2).

$$N = \frac{E\lambda}{hc} = \frac{4.51\times10^{-3}\times27.3\times3600\times5\times420\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}} = 4.68\times10^{21} \qquad (1)$$

$$AQE = \frac{2\times number\ of\ evolved\ H_2\ molecules}{the\ number\ of\ incident\ photos}\times100\% = \frac{2\times6.02\times}{4}\times100\% = 1.27\% \qquad (2)$$

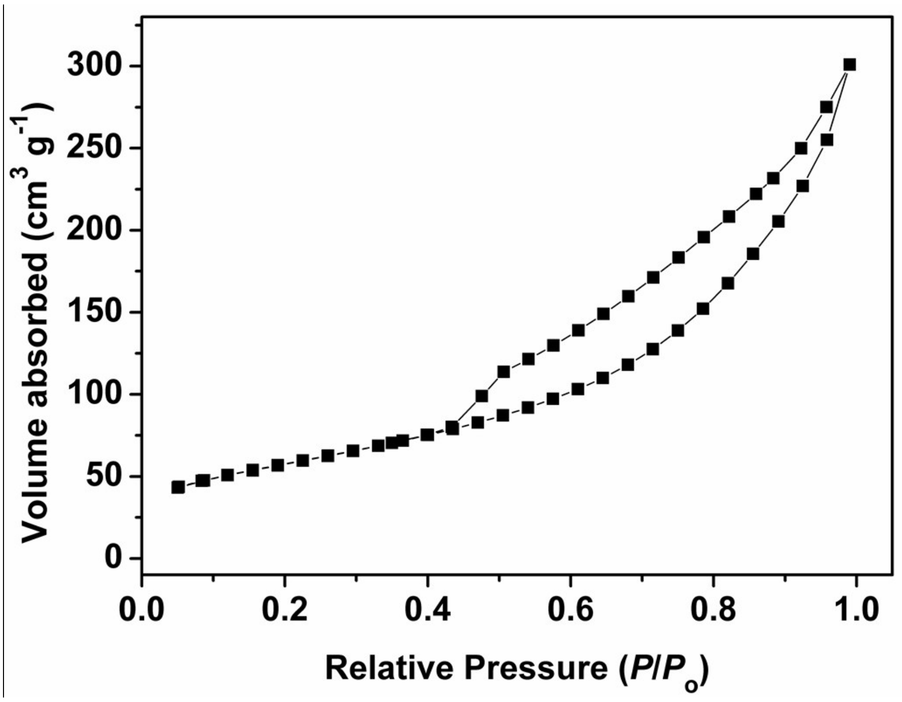

Fig. S1 $N_2$ adsorption–desorption isothermal curves of PTI/ZnO-QDs.

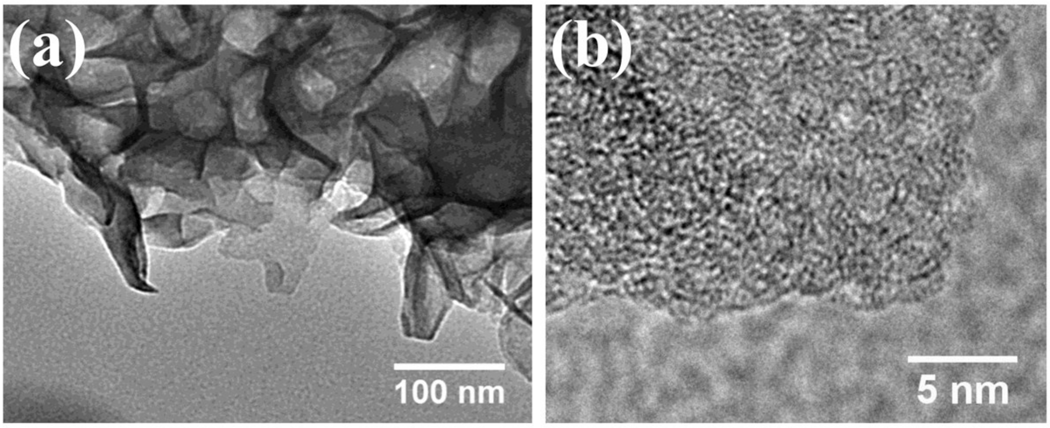

Fig. S2 TEM (a) and HRTEM (b) images of pure PTI.

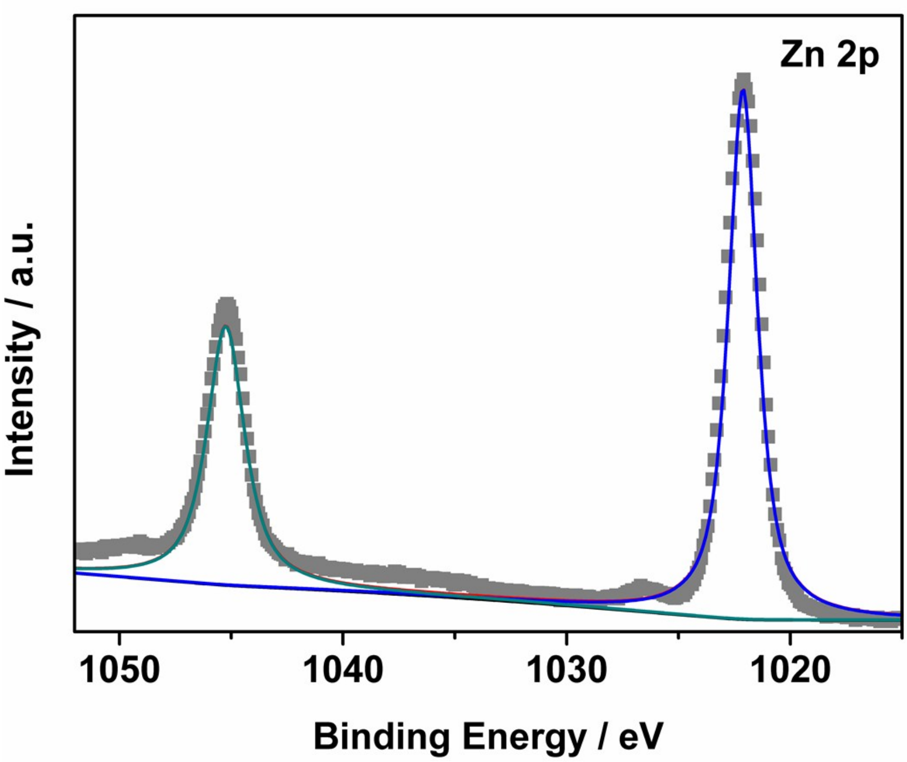

Fig. S3 XPS of Zn 2p spectrum of PTI/ZnO-QDs.

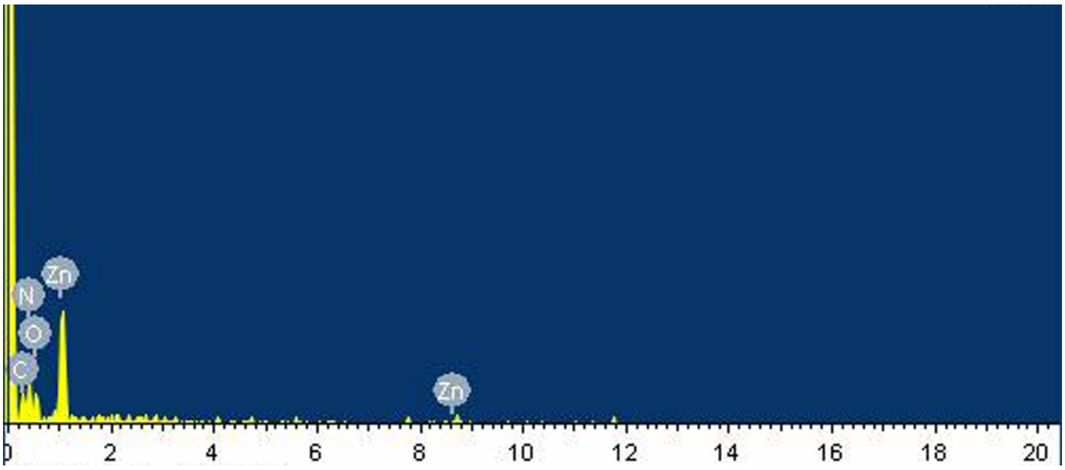

Fig. S4 EDS spectrum of PTI/ZnO-QDs

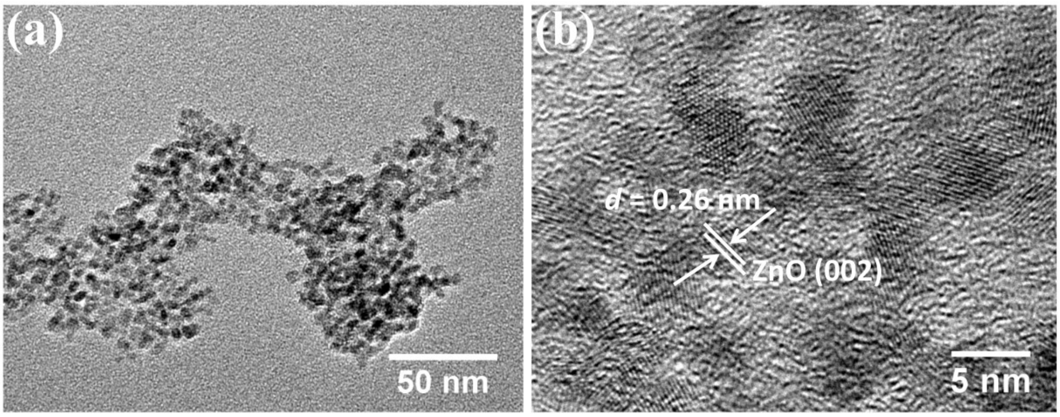

Fig. S5 TEM (a) and HRTEM (b) images of as-prepared Zn QDs.

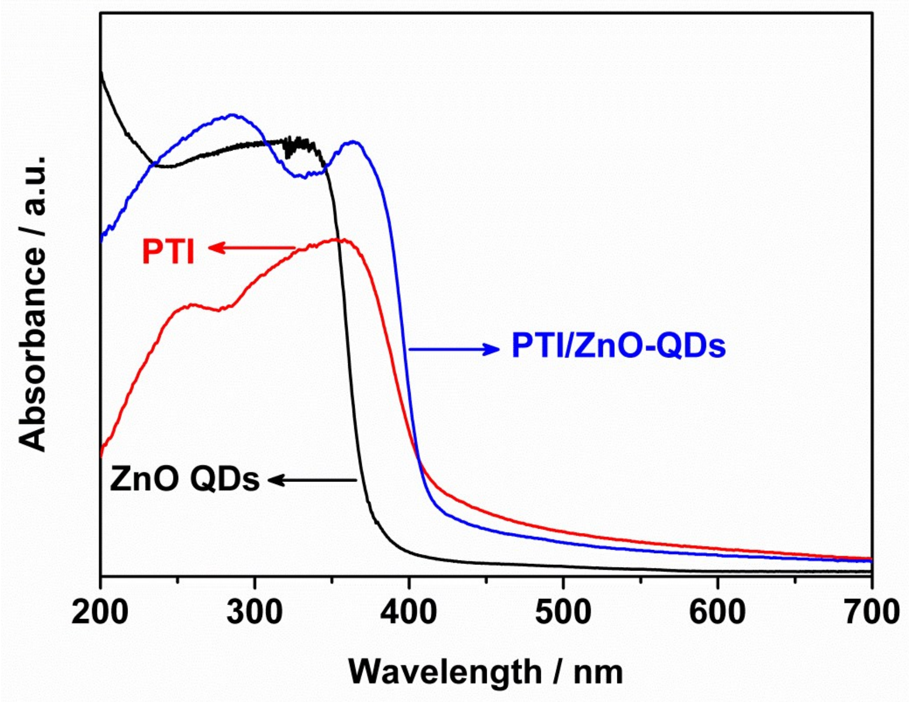

Fig. S6 UV-vis diffuse reflectance spectra of ZnO QDs, PTI and PTI/ZnO-QDs.

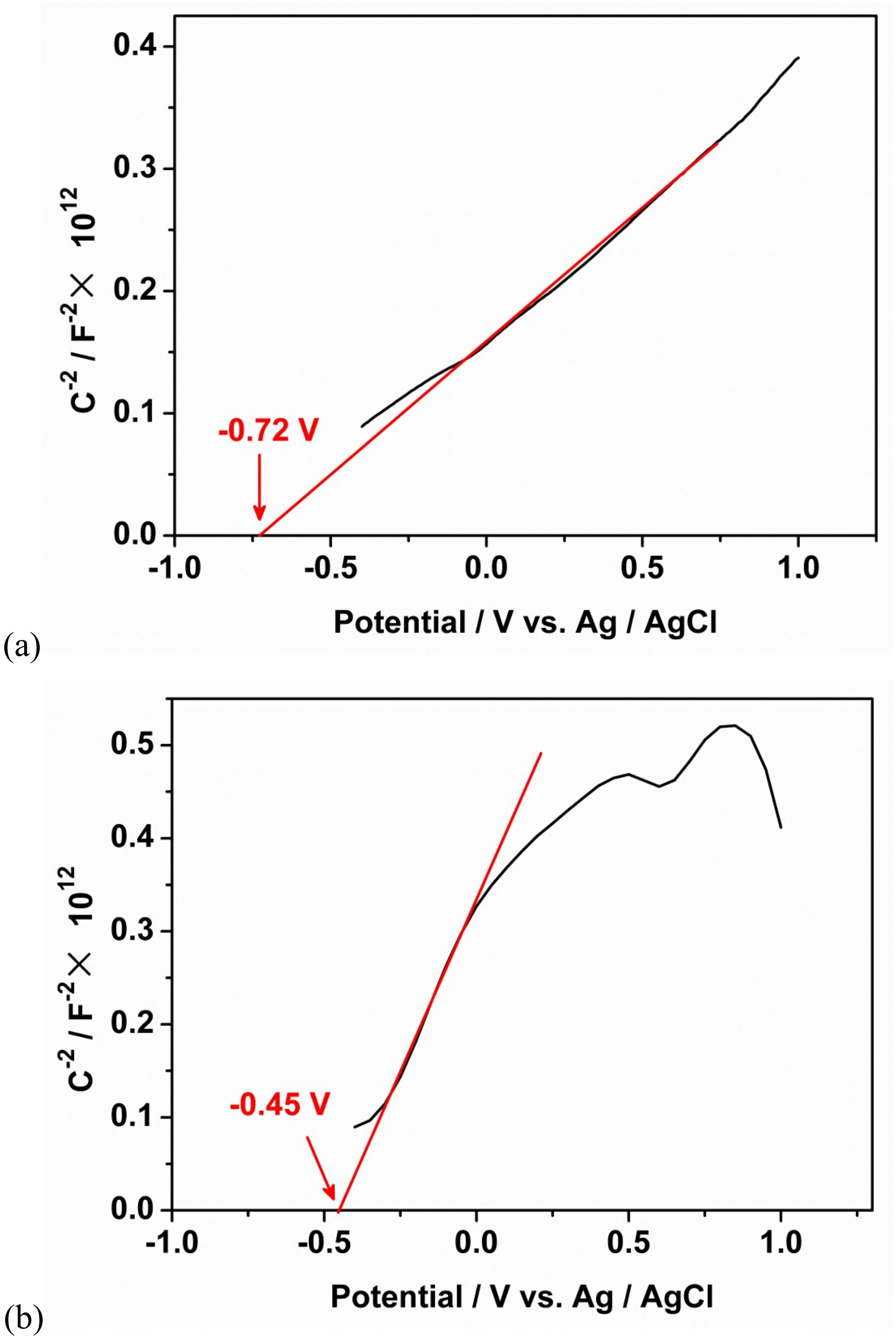

Fig. S7 Mott–Schottky plots of PTI(a) and ZnO QDs (b).

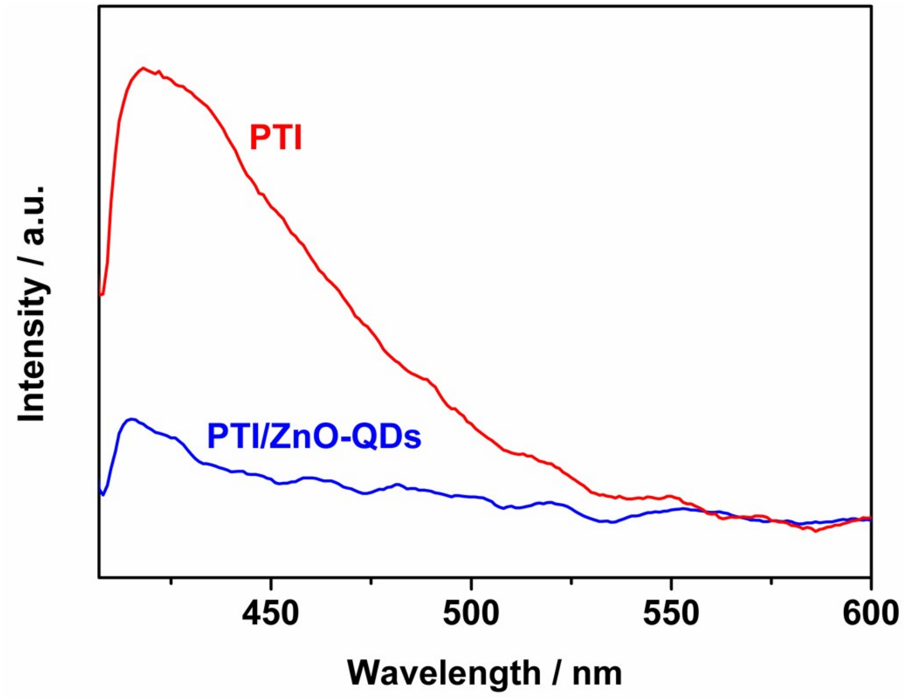

Fig. S8 Photoluminescence spectra of PTI and PTI/ZnO-QDs.

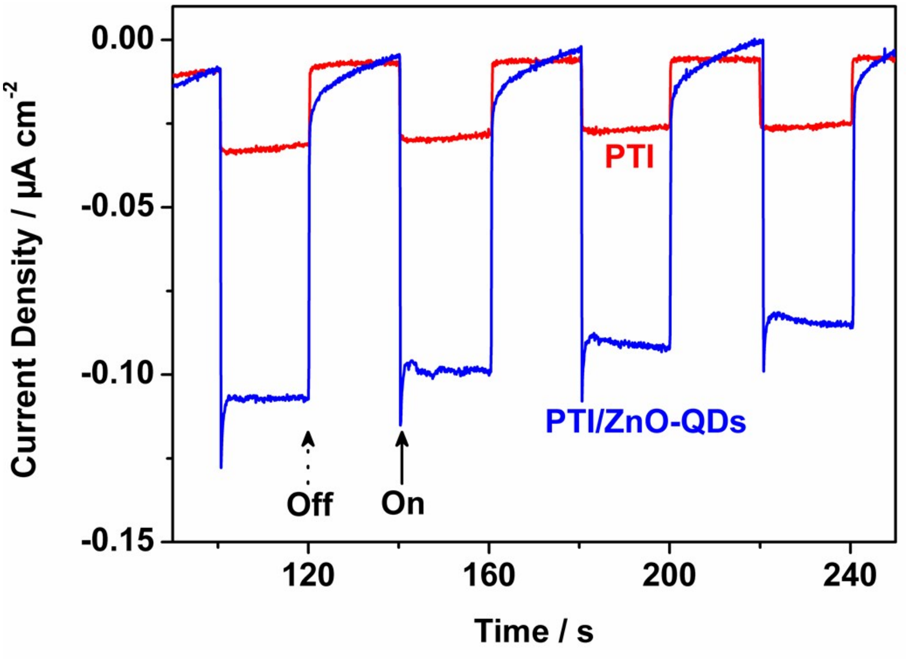

Fig. S9 Transient photocurrent responses of PTI and PTI/ZnO-QDs.

Table S1. Photocatalytic activity of different catalysts for hydrogen evolution under visible light and AQE at 420 nm.

| Catalyst | Hydrogen evolution rate / μmol $h^{-1}$ ($\lambda$>420 nm) | AQE / % ($\lambda_0$ = 420 nm) |
|---|---|---|
| PTI | 0.35 | 0.02 |
| PTI/ZnO-QDs | 22 | 1.27 |
| g-$C_3N_4$ | 6.5 | 0.55 |
| ZnO-QDs | 0.0 | 0.0 |

S1 L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge and G. K. L. Wong, *Appl. Phys. Lettt.*, 2000, **76**, 2901.