Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Preparation of P-doped CdS nanorods as efficient photocatalyst for the degradation of the emerging pollutant tetracycline antibiotic under blue LED light irradiation

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1. Materials

Cadmium chloride hemipentahydrate, sodium hypophosphite hydrate, tetracycline, ammonium oxalate, 1,4-benzoquione and tert-butanol (t-BA) obtained from Sigma Aldrich. Thiourea was purchased from Alfa Aesar. Ethylenediamine anhydrous and ethanol were obtained from Daejung chemicals, South Korea. All the chemicals were used as received without further purification.

1.1 Synthesis of CdS nanorods

CdS NRs was prepared by a typical solvothermal procedure according to our reported method. In this method, 4.9 mmol of $CdCl_2 \cdot 2.5H_2O$ and 15.2 mmol of NH_2CSNH_2 were dissolved in 26 mL of ethylene diamine. The mixture were homogenously stirred for 1h using magnetic stirrer to make clear solution. After string of the mixtures, the solutions were completely transferred into Teflon-lined stainless steel autoclave. The reaction solutions in an autoclave was placed inside a furnace and heated at 160 °C for 36 h. Finally, it was allowed to cool down to room temperature. Next, the yellow precipitate was obtained by centrifugation and washed with ethanol and deionized water for several times to remove any impurities. The obtained products were dried at 60 °C in vacuum overnight and abbreviated as CdS nanorods.

1.3 Characterization

The surface morphology of the synthesized materials was analyzed by a scanning electron microscopy (FEI QUANTA FEG 250) and transmission electron microscopy (TEM: FEI TECNAI G2 F20-ST) using an accelerating voltage of 200 kV after drop casting a drop of solution on a silicon wafer and a carbon coated copper grid, respectively. High resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDS) analyses were performed in the above mentioned TEM using an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were carried out on a RIGAKU MiniFlex II powder diffractometer using Cu Kα radiation in the 2θ range of 20°−60° with 35 kV beam voltage and 15 mA beam current. The UV-visible diffuse reflectance absorption spectrum of the CdS and CdS-$P_{0.8}$ nanorods were studied by the spectrophotometer (Shimadzu UV-2600) coupled with a diffuse reflectance auxiliary with a diffuse reflectance accessory. The photoluminescence (PL) emission of catalysts was carried out using a FLUORA MAX 4P spectrofluorometer at an excitation wavelength of 400 nm. X-ray photoelectron spectroscopy (XPS) was carried out using a monochromatized Al Kα (1486.6 eV) as X-ray source (PHI 5000 VersaProbe-II, Physical Electronics Inc., USA). The residual pressure of the analysis chamber was maintained to~10^{-8} mbar throughout the analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed using the PerkinElmer ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA). For ICP-OES analysis, CdS-P nanorods was dissolved in aqua regia and the supernatant was used to estimate the phosphorous concentration in the nanorods. Transient photocurrent responses experiments were performed on a CHI660E electrochemical workstation (CHI Instruments) in a three-electrode cell. A platinum wire and Ag/AgCl and FTO electrodes loaded with samples were used as the counter, reference

and working electrodes respectively. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range 0.1 Hz to 100 kHz with an AC amplitude of 0.005 V. Absorption spectra were carried out at room temperature using a UV-visible spectrometer (Optizen-pop, KLAB and South Korea) and taking the solutions in a 1 cm quartz cuvette.

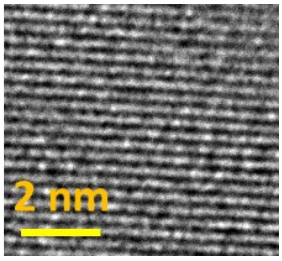

Fig. S1 HR-TEM images of CdS NRs, indicating the crystal structure of hexagonal CdS nanorods.

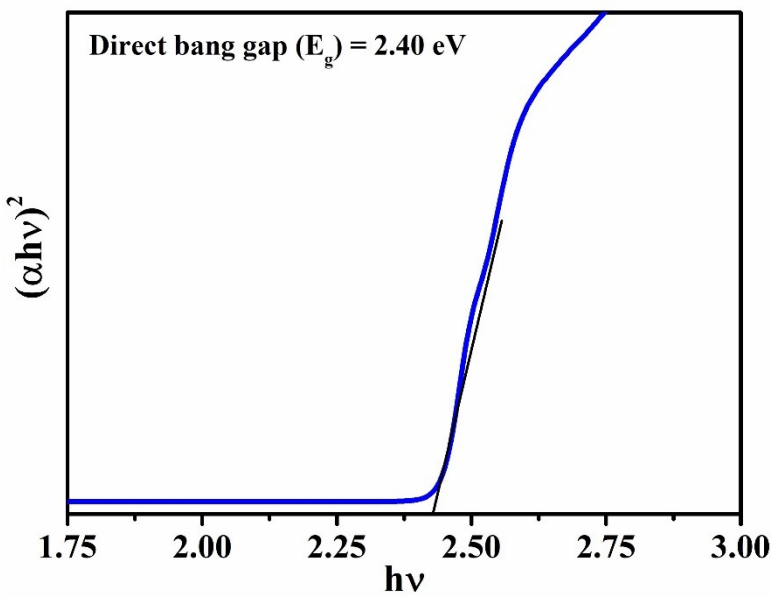

Fig. S2 Band gap energy plot from UV–Vis diffuse reflectance spectrum of the CdS NRs.

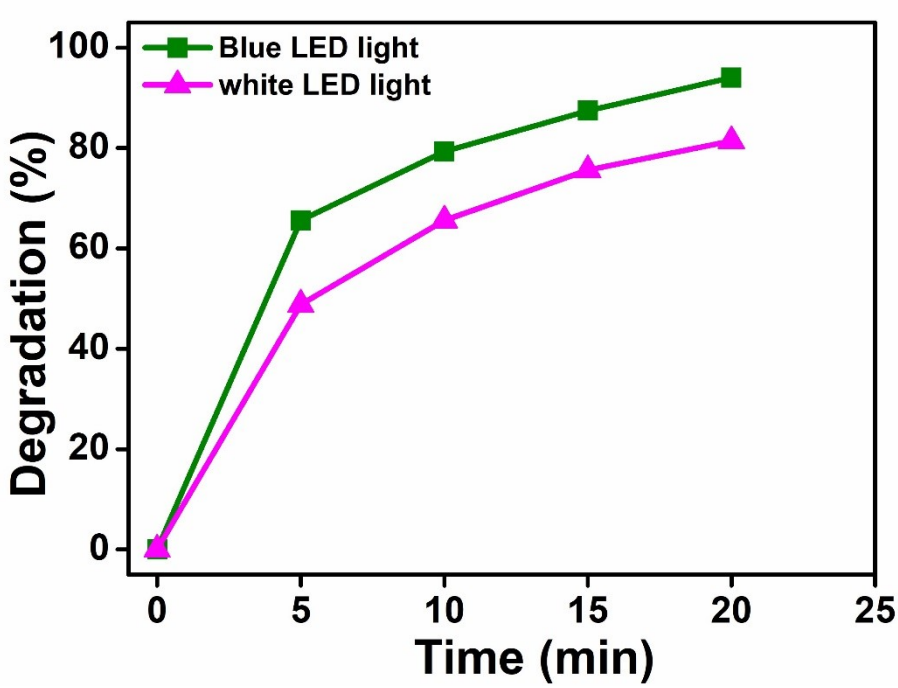

Fig. S3 Photocatalytic degradation efficiency of TC degradation at different light source. It indicates the faster degradation rate of tetracycline under blue light than white light irradiation. Condition of the reaction: catalyst: 10 mg and intensity of the light: 10 mW/cm^2.

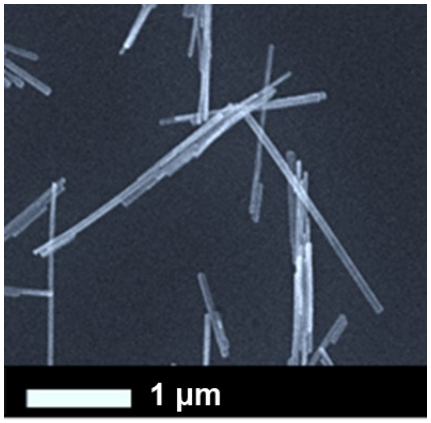

Fig. S4 SEM image of CdS-$P_{0.8}$ NRs after five cycles of the degradation reactions. It confirms the same as fresh photocatalyst before photocatalysis.