Electronic Supplementary Information (ESI)

Construction of Z-Scheme Carbon Nanodots/WO_3 with highly enhanced photocatalytic hydrogen production

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Experimental section:

Preparation of the CNDs

All chemicals were analytical-grade and used without further purification. Firstly, Glucose(3.6 g) was dissolved in deionized water(20 ml) to form a clear solution ,then HCl (20 ml,36-38 wt□) solution was dropped into the solution of glucose. Afterward, the mixture solution was transferred into a 50 ml Teflon liner followed by hydrothermal treatment at 180 ℃ for 6 h. After hydrothermal reaction, the black precipitates were centrifuged and get brown CNDs solution. CNDs solution was neutralized with NaOH and subsequently was further dialyzed through a dialysis membrane (molecular weight 3500) for 3 days to remove impurities. WO_3 was purchased directly from a supplier (Aladdin, China).

Measurement of photocatalytic performance of the CNDs and Z-scheme system

The water splitting reactions were performed using a closed system with an inner-irradiation-type Pyrex reactor. The CNDs solution (36 ml, 8 mg CNDs) was added into 174 ml methanol aqueous solution (30 ml methanol, 144 ml water). The mixed solution was degassed by Ar purging before reaction and irradiated with 300 W xenon lamp. As for the water splitting reactions of CNDs/WO_3 (Z-scheme system), the CNDs solution ((36 ml, 8 mg CNDs), appropriate WO_3 and NaI (2 mM) were added into photocatalytic reactor simultaneously, and then added 174 ml methanol aqueous solution (30 ml methanol, 144 ml water). The mixed solution was degassed by Ar purging before reaction and irradiated with 300 W xenon lamp. The temperature of the reaction

solution was maintained at 18-20 ℃ by a flow of cooling water. Platinum, acting as a cocatalyst, was deposited onto CNDs using an in situ photodeposition method (precursors, $H_2PtCl_6 \cdot (H_2O)_6$). The amount of hydrogen was measured by gas chromatography (Beifen-Ruili: SP-2100, MS-5Å column, TCD, Ar carrier).

Characterization:

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet Magna-IR 550-II spectrometer using KBr pallets. Raman spectra were recorded on a LABRAM-HR in plus laser Raman spectrometer with excitation wavelength 325 nm. UV-Visible absorption spectroscopy was carried out through placing the CNDs solution in a 1-cm quartz cuvette and analyzed using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at room temperature. Photoluminescence (PL) was measured on a Hitachi F-7000 FL spectrophotometer. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were carried out on a Thermo ESCALAB 250 XPS spectrometer. To eliminate the effect of sample surface charging the shift of the XPS peak of carbon (C1s whose binding energy is 284.8 eV) was used. X-ray powder diffraction pattern analysis was conducted on a D8 Advance Bruker X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) operating at 40 kV. The amounts of IO_3^- anions produced by the reactions were determined by ion chromatography (ICS-3000, Dionex Corporation).

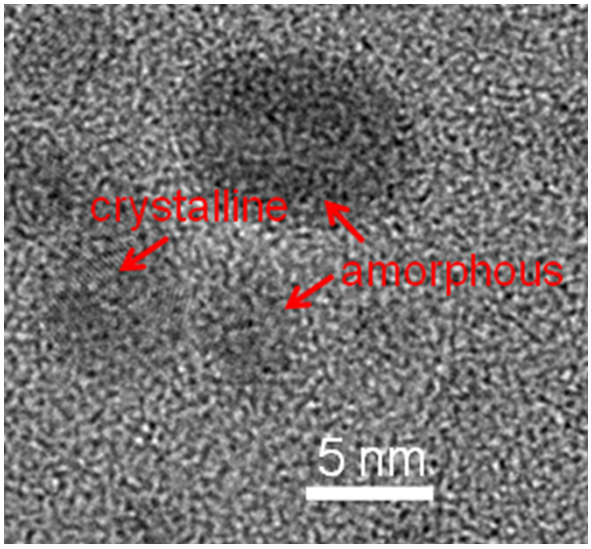

Fig S1 HRTEM image of CNDs

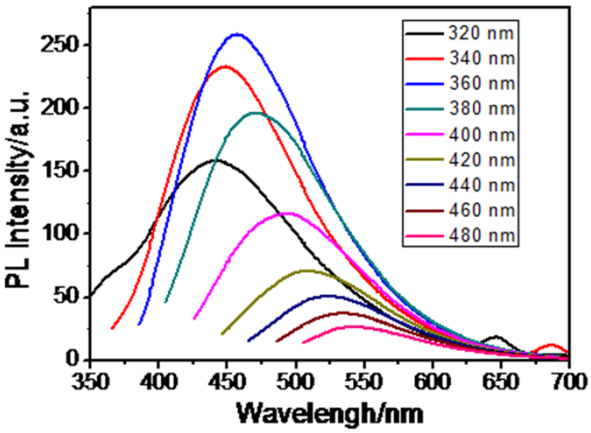

Fig S2 PL spectra of the CNDs at different excitation wavelengths

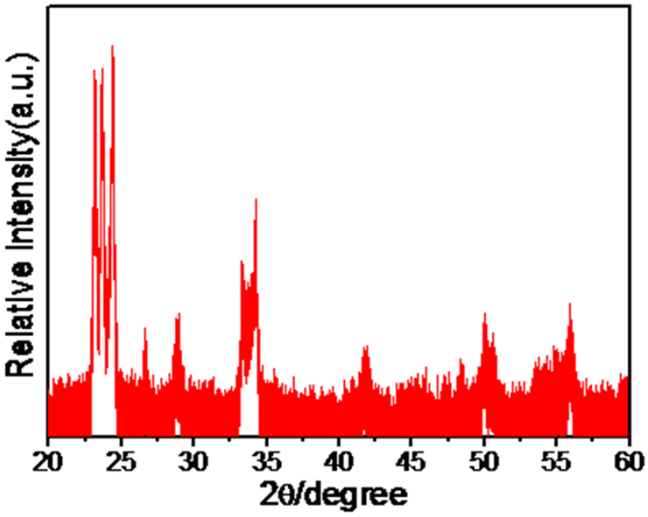

Fig S3 X-ray powder diffraction pattern of WO_3

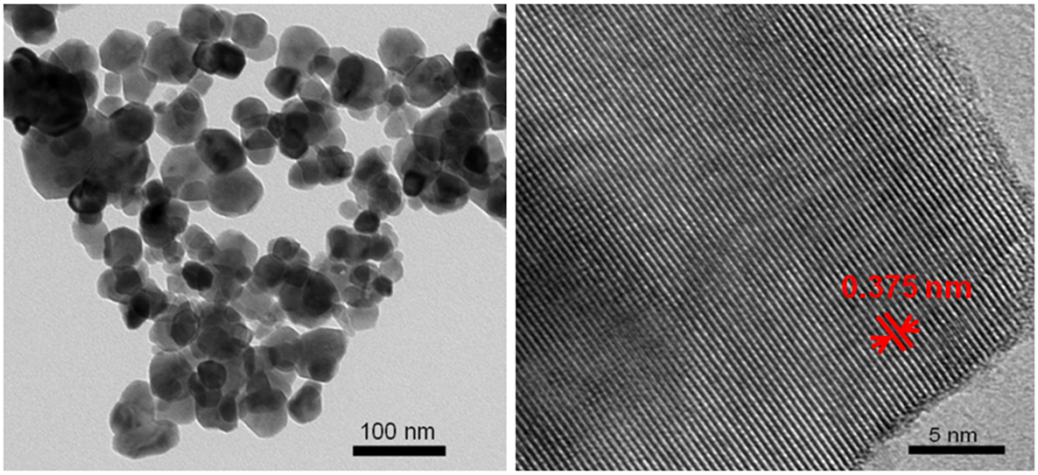

Fig S4 TEM and HRTEM images of WO_3

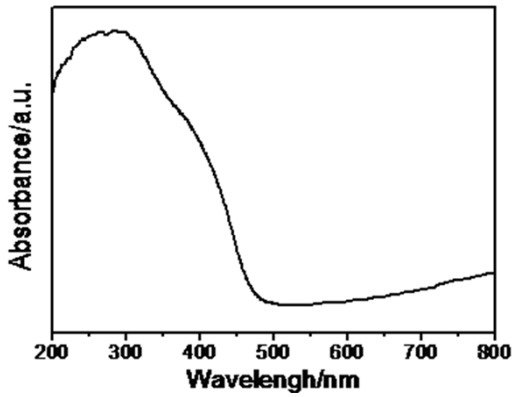

Fig S5 UV–vis adsorption spectrum of WO_3

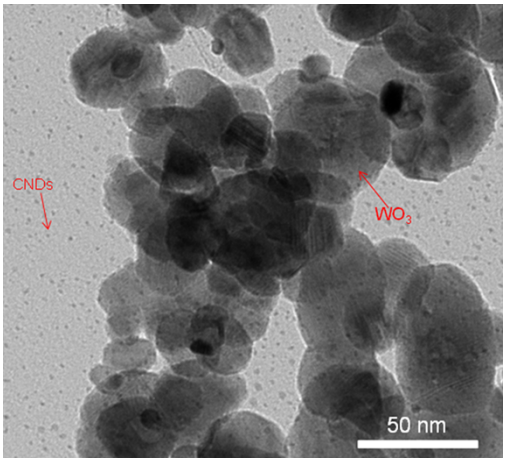

Fig S6 TEM image of CNDs/WO_3

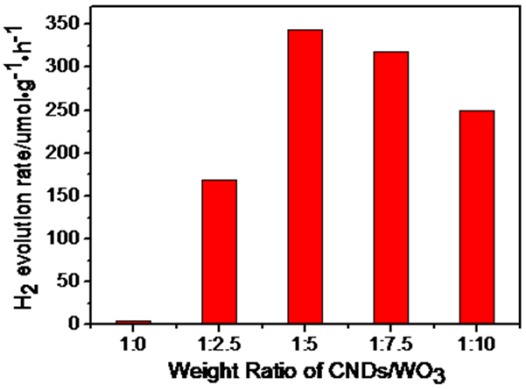

Fig S7 Dependence of the hydrogen evolution rate on the weight ratio of CNDs/WO_3(NaI concentration: 2 mM)

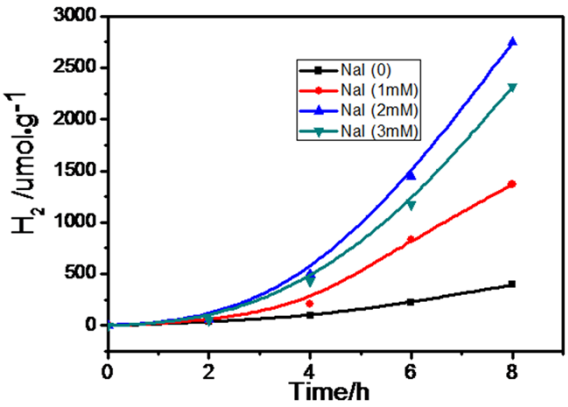

Fig S8 Dependence of the hydrogen evolution activity on the NaI concentration (weight ratio of CNDs/WO_3 is 1:5)

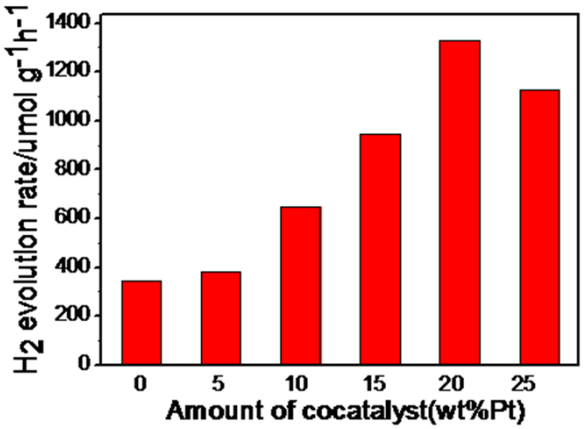

Fig S9 Dependence of the hydrogen evolution rate on the Pt load on the CNDs(NaI concentration: 2 mM)

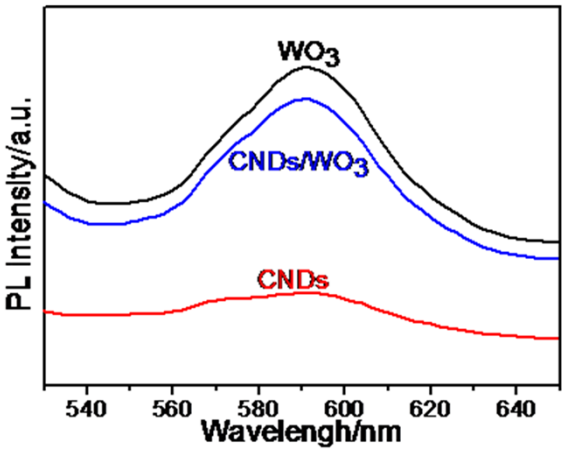

Fig S10 PL spectra of the WO_3,CNDs/WO_3 and CNDs at 450 nm excitation