Pure Carbon Nanodot for Excellent Photocatalytic Hydrogen Generation

Pengju Yang,[a,b] Jianghong Zhao,[a *] Jian Wang,[a,b] Huijuan Cui,[a,b] Li Li[a] and Zhenping Zhu[a *]

Experimental

Synthesis of CNDs

First, multi-wall carbon nanotubes were treated via Hummers' method to obtain multi-wall carbon nanotubes oxide (MWNTO).[1] MWNTO (0.4 g) was introduced into 200 mL of distilled water and was treated ultrasonically for 8 h to obtain a MWNTO aqueous solution. The MWNTO aqueous solution was then transferred into a Teflon-lined stainless-steel autoclave and was heated at 180 °C for 8 h. After reaction, the reactors were cooled to room temperature. Pale yellow transparent suspension product and black precipitates were obtained. This solution was then filtered through a 0.22-μm filter membrane to remove the large particles. CNDs were obtained through further high-speed centrifugation.

CNDs/P25: 50 mg P25 was dispersed into the CNDs aqueous solution (20ml) and kept stirring for 8 hours. Then the CNDs/P25 was filtered through a 0.22-μm filter membrane to remove the unabsorbed CNDs. The solid was dried at 60 °C.

Photocatalytic performance of the obtained CNDs

Water-splitting reactions were performed using a closed system with an inner irradiation-type Pyrex reactor. About 20 mL of the CND solution (2 mg CNDs, the CNDs' concentration: 0.1mg/mL) was added into 180 mL of distilled water (pH = 7). The mixed solution was degassed via Ar purging before the reaction and was irradiated at 300 W by using a high-pressure Hg lamp. The temperature of the solution was maintained at 18 °C to 20 °C by using cool, flowing water. The amounts of hydrogen were measured via gas chromatography (Beifen-Ruili: SP-2100, MS-5Å column, TCD, Ar carrier). Water-splitting reactions of Degussa P25 were performed at same reaction condition.

Characterization

To obtain the UV–vis absorption spectrum, the CND solutions were placed in a 1-cm quartz cuvette and analyzed using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at room temperature. TEM images were obtained using a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV. FTIR was performed using a Nicolet Magna-IR 550-II spectrometer with KBr pallets. PL emission spectra were obtained using a Hitachi F-7000 FL spectrophotometer. Raman spectra were recorded using a LABRAM-HR in plus laser Raman spectrometer with an excitation wavelength of 325 nm. XPS was carried out on a Thermo ESCALAB 250 XPS spectrometer with Al Kα ($h\nu$ = 1486.6 eV) radiation. 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. CND electrodes for electrochemical analysis were prepared by dropping the CND solution (about 10 mg of CNDs) onto an ITO glass and dried in air. We subjected the CND

electrodes to electrochemical analysis in 0.5 M Na_2SO_4 solution with a Pt sheet as the counter electrode and Ag/AgCl as the reference electrode on a CHI 760D electrochemical analyzer. Using Rhodamine B in ethanol (quantum yield = 0.65) as a reference, the PL quantum yield of CNDs (in water) was calculated according to:

$\phi = \phi_{st}(I_x/I_{st})(\eta_x/\eta_{st})^2(A_{st}/A_x)$ Where ϕ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index of the solvent, and A is the optical density. The subscript "st" refers to the reference with known quantum yield, and the subscript "x" refers to the sample.[2]

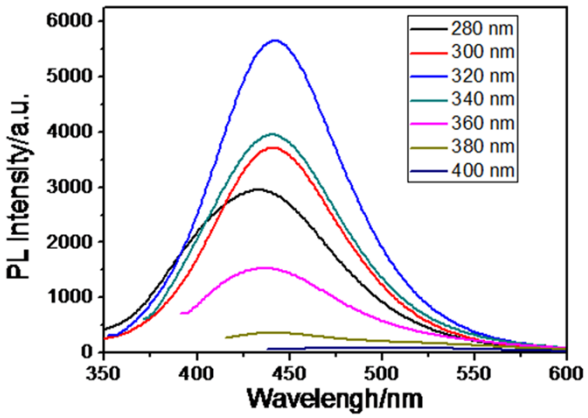

Fig S1 PL spectra of CNDs at different excitation wavelengh

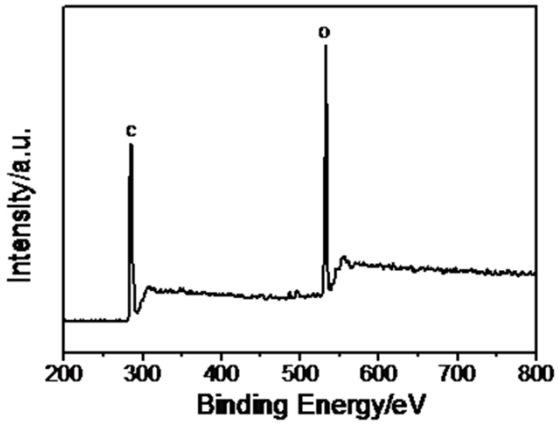

Fig S2 XPS spectrum of CNDs

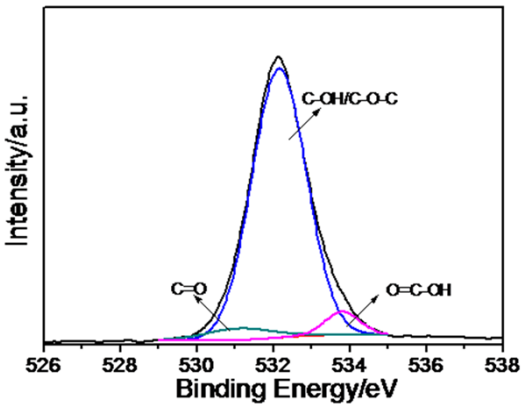

Fig S3 O1s XPS spectrum of CNDs

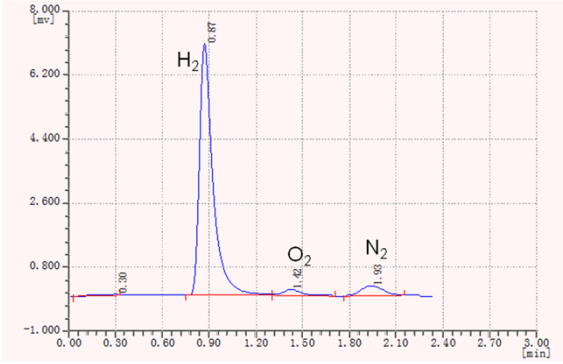

Fig S4 GC spectrum of gaseous product of CNDs after UV irradiation 4 h in pure water

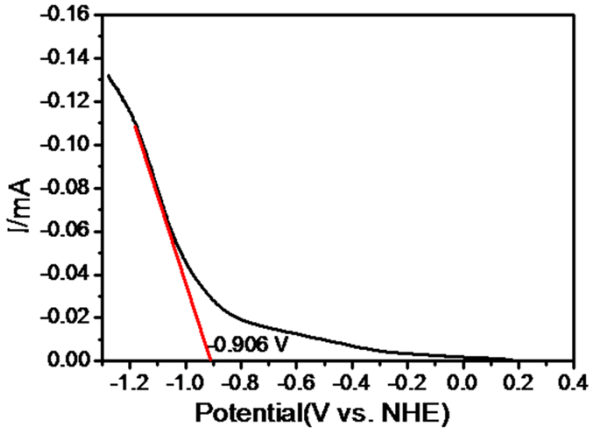

Fig S5 Cathodic scan for determining the conduction band of CNDs at 10 mV s^{-1}

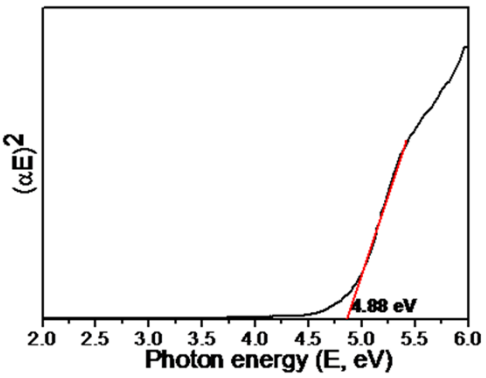

Fig S6 Plots of $(\alpha E)^2$ against photon energy (E) for the CNDs

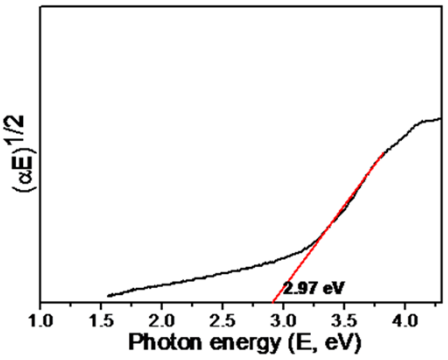

Fig S7 Plots of $(\alpha E)^{1/2}$ against photon energy (E) for the CNDs

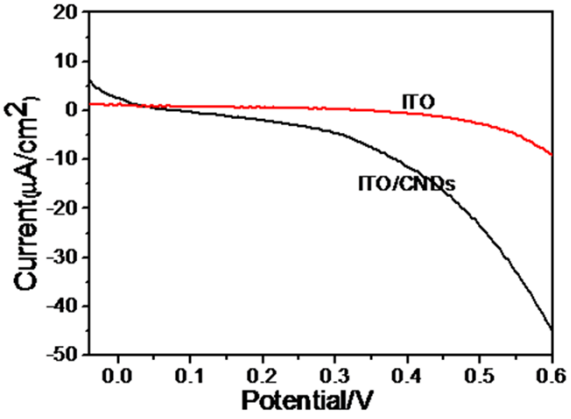

Fig S8 Photocurrent of CNDs at different bias voltages under UV irradiation

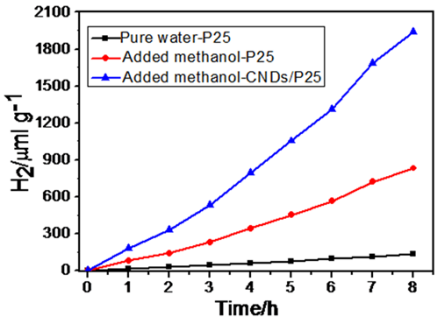

Fig S9 Photocatalytic hydrogen evolution of P25 and CNDs/P25 in pure water and in methanol aqueous solution (20 vol%)

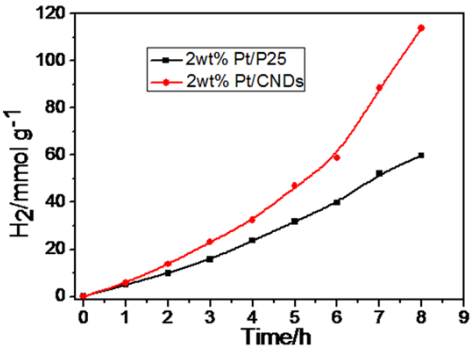

Fig S10 Photocatalytic hydrogen evolution of Pt/P25 and Pt/CNDs in methanol aqueous solution (20 vol%)

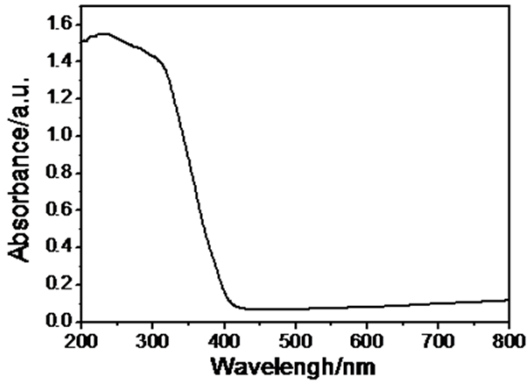

Fig S11 UV-vis adsorption spectrum of P25

1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958**, 80**, 1339.
2. R. F. Kubin and A. N. Fletcher, *J. Lumines.*, 1982**, 27**, 455.