

Electronic Supplementary Information

N-doped carbon nanodots/np⁺-Si photocathodes for efficient photoelectrochemical hydrogen generation

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S1: The light absorption of the CNDs.

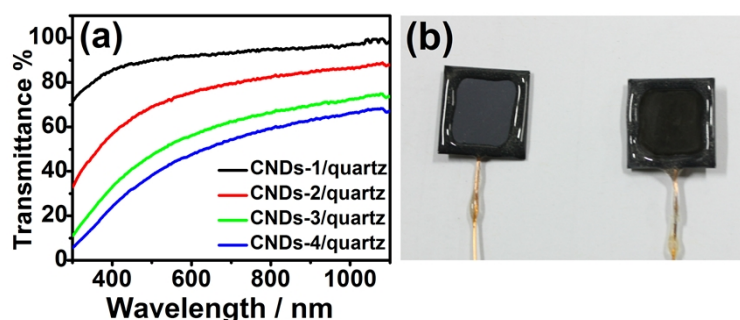


Fig. S1 (a) The light transmittance spectra of the different amounts of CNDs dropped on the quartz. (b) The pictures of the electrode surface without (left) and with (right) CNDs-3. More dark surface can be observed, indicating the visible light absorption of the CNDs. More the CNDs dropped, more the light is absorbed. Therefore, the accumulation of more CNDs at the top of Si electrode may inhibit the light absorption of Si, which decreases the photocurrent density.

S2: The stability of the CNDs/np⁺-Si photocathode.

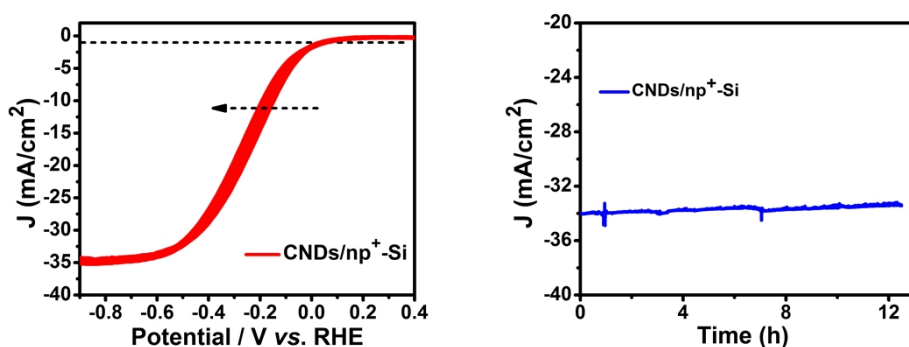


Fig. S2 Left: The stability test of the CNDs/np⁺-Si photocathode during 100 cycles with a scan rate of 0.05 V/s in an aqueous 1M perchloric acid solution (pH=0). The J - V curves left-shift slightly after 100-cycle measurements, indicating the catalytic ability of the CNDs is stable. **Right:** The chronoamperometry measurement during PEC water reduction under -0.6V vs. RHE. The photocurrent decreases slightly from 34 mA/cm² to 33 mA/cm² after 12 h continuous PEC reaction, again indicating the high stability of the CNDs/np⁺-Si photocathode.

S3: The open-circuit photovoltagages.

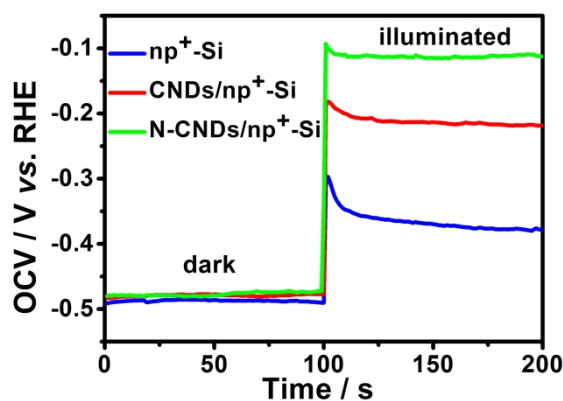


Fig. S3 The change in open-circuit voltage (OCV) in the dark and under illumination conditions for the three photocathodes. Higher E_{fb} usually corresponds to higher open-circuit photovoltage (V_{ph}). In the dark, all the configurations show an OCV of about -0.48 V vs. RHE, indicating the same equilibrium potential of the photocathodes in the electrolyte solution. Upon illumination, the OCV of the N-CNDs/Si, CNDs/Si and the bare Si increase to -0.12 V, -0.22 and -0.38 V vs. RHE, respectively. These changes in

OCV in the dark and under illumination demonstrate that the V_{ph} of the three photocathodes under open-circuit conditions are 0.36, 0.26 and 0.10 V, respectively.

S4: The electrodeposition of the Pt catalyst.

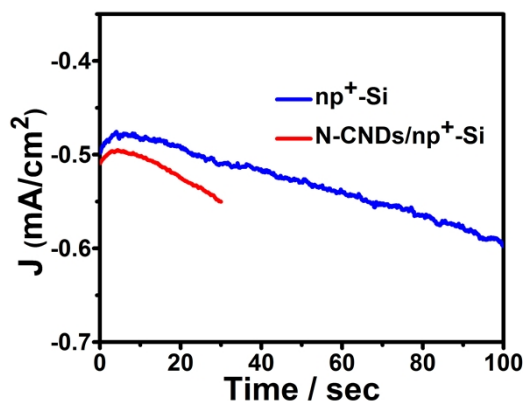


Fig. S4 The typical current density changing with the time during the electrodeposition of the Pt catalyst. Pt nanoparticles were fabricated onto electrode surface in the dark from a fresh solution containing H_2PtCl_6 (5mM) (Sigma-Aldrich, reagent grade) in deionized water. A potential of -0.1 V was applied to the working electrode reference to a Ag/AgCl (3M KCl) electrode for Pt deposition, and the current passed through the working electrode and counter Pt electrode was recorded. One period of deposition lasts for 10s to 20s. After one period of electrodeposition, the growth of Pt was interrupted and the sample was thoroughly rinsed with deionized water and dried in a nitrogen stream. Then the photocurrent was measured using an electrochemical workstation (CHI660D) with a 100 mW/cm² Xe lamp and 1M $HClO_4$ as electrolyte. During the measurement, the as-prepared sample served as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl (3M KCl) electrode as the reference electrode. After PEC measurements, the sample was again thoroughly rinsed with deionized water and dried in a nitrogen stream. Another period of Pt growth was performed repeatedly. One obvious advantage of this procedure is that we can know how many periods for the deposition of Pt particles is the best for the PEC performance of the photocathode.

Note that we can get the exact Pt amount on the electrode surface based on the

current and time during electrochemical deposition. Shortly, the total amount of electrons passing through the circuit during PEC reaction within a specific time (T) can be obtained through calculating the J-T square as shown in Fig. S4. Four electrons can reduce a Pt^{4+} ion into a Pt atom, and then the total Pt atoms and amount can be obtained.

S5: The effect of Pt electrodeposition time.

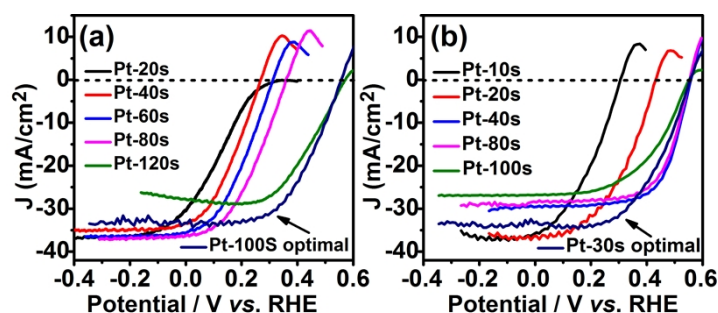


Fig. S5 Typical J-V curves for the bare $\text{np}^+\text{-Si}$ (a) and $\text{N-CNDs/np}^+\text{-Si}$ (b) loaded with different amount of Pt catalyst.

S6: The morphology of the Pt nanoparticles.

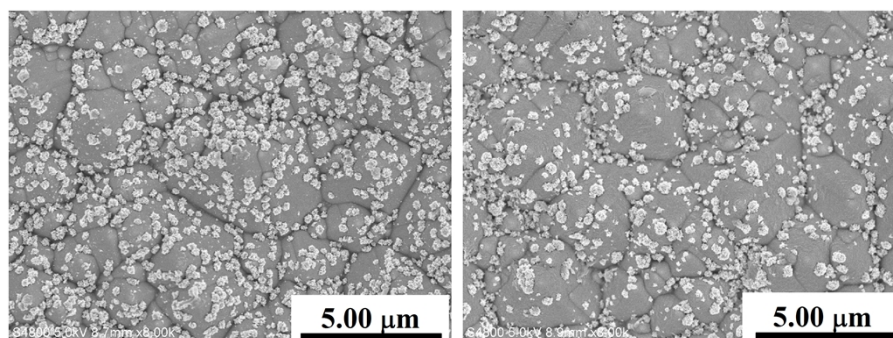


Fig. S6 The surface SEM images of the $\text{Pt}(7.8 \mu\text{g}/\text{cm}^2)/\text{N-CNDs/np}^+\text{-Si}$ (left) and $\text{Pt}(26.9 \mu\text{g}/\text{cm}^2)/\text{np}^+\text{-Si}$ (right) photocathodes.

Before the fabrication of np^+ junction, a pyramid-like surface nanostructure is formed on single-crystalline Si surface based on anisotropic alkali etching [H. Seidel, L. Csepregi, A. Heuberger and H. Baumgärtel, J. Electrochem. Soc. 137, 3626 (1990).] on a mass production line of crystalline-Si solar cells, in order to enhance the light

absorption. Therefore grain boundary-like features appear in both SEM images. CNDS and Pt particles were then deposited on the Si surface. The CNDs are too small to be observed and the white particles are Pt. They distribute uniformly on the sample surface with size of a few hundred nm.