SUPPORTING INFORMATION

Boosting Electrocatalytic Hydrogen Evolution by Plasmon-Driven Hot-Electron Excitation

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Experimental

General

All chemical reagents were used as purchased without further purification.

Preparation of ZIF-8 nanocrystals

ZIF-8 nanocrystals were prepared using a reported procedure with a slight modification.¹ In a typical synthesis, a solution of 0.3 g of $Zn(OAc)_2 \cdot 2H_2O$ in 5 mL of deionized (DI) water was added into a solution of 1.12 g of 2-methylimidazole in 5 mL of DI water, and the resulting mixture was stirred for a few seconds. Then, the mixture was left at room temperature for 24 h to form polyhedral ZIF-8 nanocrystals. The product was isolated as a white powder by centrifugation and washed several times with DI water and methanol, and finally dried overnight at 60 °C.

Preparation of N-doped porous carbon (PNC) and N-doped carbon (NC)

PNC was prepared using a reported procedure with slight modification by using ZIF-8 as both a precursor and a template and furfuryl alcohol (FA) as a second precursor.² The synthesized ZIF-8 (200 mg) was immersed in 4 mL of FA under ambient conditions for 24 h. After centrifugation and washing with ethanol, the FA/ZIF-8 composite was dried overnight at 60°C. The obtained mixture was placed into a temperature-programmed furnace under a N₂ flow heat-treated at 150°C for 2 h, then the temperature was elevated to 900 °C in 100 min and maintained at 900 °C for 5 h, to obtain the N-doped porous carbon.

For the preparation of NC, only ZIF-8 was used as a precursor and a template. The ZIF-8 powder was placed in a temperature-programmed furnace under a N_2 flow and heated at 900 °C for 5 h.

Preparation of Au nanoparticles

Au nanoparticles were synthesized by a reported procedure.³ 3 mL of ice-cold NaBH₄ solution (0.1 M) was added to 100 mL of 0.25 mM HAuCl₄ under vigorous stirring for 5 min. The color of the solution changed immediately from yellow to wine red, suggesting the formation of Au nanoparticles. Then, the Au colloid was aged in the dark over 12 h before used.

Preparation of PNC-Au and NC-Au

For the preparation of PNC-Au, 10 mg PNC powder was dispersed in 1 mL EtOH firstly, then added it to 40 mL of as prepared Au colloid solution under vigorous stirring. After stirring for 4 h, the resulting sample (PNC-Au) was centrifuged and washed with ethanol. The total Au content was 17.54% in PNC-Au by an inductively coupled plasma optical emission spectroscopy technique.

Similar method as described above was used for the preparation of NC-Au, except using NC instead of PNC.

Materials characterization

Scanning electron microscope (SEM) images were recorded on a JEOL JSM6700-F microscope. Field Emission Transmission Electron Microscope (FETEM) images were recorded by FEI Tecnai F20. PL spectra were measured using a fluorescent spectrophotometer (Edinburgh, FLS980). Particles size distribution was calculated by Laser Particle Size and Zeta Potential Analyzer (BROOKHAVEN, BI-200SM). Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å). A UV-visible spectrophotometer (Lambda 950, PerkinElmert) was used to measure the absorption spectra of the as-prepared samples. N₂ adsorption-desorption experiments were performed at 77 K to examine the Brunauer-Emmett-Teller surface area (Micromeritics, ASAP 2020). Surface chemical analyses were performed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250Xi).

Electrochemical Measurements.

2 mg of catalyst were dispersed in 1 mL ethanol mixed with 20 μ L of Nafion solution (5 wt%) then by sonication to form a homogeneous ink. 7.5 μ L catalyst ink was loaded onto a glassy carbon electrode of 3 mm in diameter as working electrode. Linear sweep voltammetry and cyclic voltammetry curves were measured in three-electrode system using a CHI760E instrument at room temperature.



Figure S1. XRD patterns (a) and SEM images (b) of ZIF-8.



Figure S2. N₂ adsorption-desorption isotherms of the N-doped (NC) thermolysis at different temperature (700 °C, 800 °C, 900 °C and 1000 °C).



Figure S3. The pore size distributions of the N-doped carbon (NC) thermolysis at different temperature (700 °C, 800 °C, 900 °C and 1000 °C).



Figure S4. (a) N₂ adsorption-desorption isotherms and (b) the corresponding pore size distributions of the N-doped porous carbon (PNC) and N-doped carbon (NC). As shown in figure, PNC exhibits higher BET surface area and bigger pore distribution.

ZIF-8 (ZIF = zeolite imidazolate frameworks), among a well-known subfamily of MOFs formed through the coordination interaction between the metal ions and the imidazole, was selected as one

of the most ideal candidate owing to its merits including abundant nitrogen component and intersecting three-dimensional structural feature. By calcining ZIF-8 precursor at different temperature (700 °C, 800 °C, 900 °C and 1000 °C), N-doped carbon with different surface area and pore size distribution were obtained (Figure S2). NC900 and NC1000 have the similar BET surface area, 690 m²g⁻¹ and 723 m²g⁻¹, respectively. According the pore size distribution (Figure S3), the bigger size channels in NC900 accounts for a larger proportion than it in NC1000. This is due to that Zn metal vaporizes and escapes from the material at 900°C. So, 900 °C is suitable temperature for thermolysis. To further increase the porosity, the second precursor furfuryl alcohol (FA) was added to ZIF-8 via thermolysis at 900°C in N₂ atmosphere. The resulting porous N-doped carbon (PNC) exhibits higher BET surface area and bigger pore distribution, which was chosen as substrate used in the following electrocatalytic experiments (Figure S4).



Figure S5. TEM images of Au nanoparticles.



Figure S6. Au nanoparticles size distribution provided by laser particle size analyzer

Elapsed Time	00:03:00	100 1		
Mean Diam.	543.6 nm	1.000000		
Rel. Var.	0.000	, 75		
Skew	0.017	90 50 25		
		50.0		5000.0
			Diameter (nm)	

Multimodal Size Distribution

Figure S7. N-dope carbon from ZIF-8 particles size distribution provided by laser particle size analyzer.



Figure S8. (a) TEM images and (b) EDS spectrum of of PNC-Au hybrids.



Figure S9. HER polarization curves obtained on several catalysts as indicated in 0.5 M H_2SO_4 electrolyte.



Figure S10. HER activity of PNC-Au with different laser intensity and wavelength irradiation.



Figure S11. EIS Nyquist plots of PNC-Au hybrids measured with and without 532 nm light irradiation and the corresponding equivalent circuit and impedance parameters obtained by fitting the experimental data. R_s , R_{ct} , R_{mt} and CPE indicated a series resistor (representing the resistivity of the electrolyte between the working and reference electrodes), charge transfer resistance, mass transfer resistance and constant phase element, respectively. It is interesting that laser irradiation considerably reduces the charge transfer resistance in the PNC-Au electrode. This could be attributed to the irradiation-induced LSPR excitation of Au nanoparticles which might significantly accelerate the electron transport from PNC-Au to the GC electrode, as illustrated in Figure 5 in the manuscript.



Figure S12. HER polarization curves obtained on PNC-Au and NC-Au.

In addition, to evaluate the effect of the carbon substrate on the electron transport rate, another N-doped carbon (NC) with smaller surface area (Figure S2) was obtained from ZIF-8 by controlling the calcination conditions. By comparing the HER activity of NC-Au and PNC-Au (Figure S8), we found that the catalytic efficiency of NC-Au is much lower than that of PNC-Au. This result suggested that the porous structure are expected to maximize the number of exposed active sites for electrochemical reactions, facilitating the diffusion of reactants in the electrolyte and the electron transfer.

Three possible reaction steps suggested for the HER in acidic media:

 $\begin{array}{ll} H_{3}O^{+}+e-\rightarrow H_{ads}+H_{2}O & \mbox{Volmer reaction} & (S1) \\ H_{3}O^{+}+H_{ads}+e-\rightarrow H_{2}+H_{2}O & \mbox{Heyrovsky reaction} & (S2) \\ H_{ads}+H_{ads}\rightarrow H_{2} & \mbox{Tafel reaction} & (S3) \end{array}$



Figure S13. Photoluminescence (PL) spectra recorded under the excitation of a 385 nm laser for Au NPs and PNC-Au.



Figure S14. Decay curve of PNC-Au recorded under the excitation of a 375 nm laser.

References

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