# **Energy Materials**

Supplementary Material: Photo-coupled Electrocatalytic Oxygen Reduction to Hydrogen Peroxide by Metal-Free CNTs-threaded Oxidized g-C<sub>3</sub>N<sub>4</sub>

## **EXPERIMENTAL SECTION**

## **Preparation of electrode**

The electrode was prepared by electrophoresis. Firstly, 10 mg of catalyst and 20 mg of iodine were dissolved in 25 mL of acetone solution and ultrasonicated for 30 minutes to obtain a uniformly dispersed suspension. Fixed the conductive glass composed of fluorine-containing tin oxide (FTO) on the cathode and anode respectively, put them in the solution and ensure the working area was  $2*2 \text{ cm}^2$ . Electrodeposition was conducted for 3 minutes under the condition of a DC power supply of 10V, and the catalyst was tightly electrodeposited on the cathode FTO due to the positive charge on the catalyst surface. Put the prepared electrode in a muffle furnace and dry at 200 °C for 2 h at 5 °C/min to remove excessive iodine. Finally, the dried electrode was weighed. The mass of this sample except OCN-200/CNTs-12 h was 1.3 mg due to its special electrophoresis conditions (30 V, 3 min), the mass of other samples was controlled at 0.8 mg.

## **Instruments and Characterization**

X-ray diffraction (XRD) patterns were collected in parallel mode (20 from 10° to 80°) with a commercial instrument (Rigacu Dmax-3C with Cu K  $\alpha$  radiation). X-ray photoelectron spectroscopy (XPS) measurements were analyzed on a Perkin-Elmer PHI 5000C with an Al K  $\alpha$  source. The morphology of the products was studied by field-emission scanning electron microscope (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL, 2010F). The UV–vis diffuse



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reflectance spectroscopies were collected from 200-800 by an MC-2530 spectrometer (BaSO<sub>4</sub> as a reference). Fourier transform infrared (FT-IR) spectra were measured using a Nicolet 6700 spectrometer on samples embedded in KBr pellets. Raman spectra were measured using the SuperlabRamll. The NOVA 4000e automatic physical adsorption instrument (Quantachrome) was used to measure the adsorption and desorption isotherm of N<sub>2</sub> at a liquid-nitrogen temperature of 77 K to obtained the BET of the catalyst. Wherein the specific surface of the catalyst was calculated by BET equation. For temperature programmed desorption (TPD) of O<sub>2</sub> measurement<sup>[1]</sup>, after 1 h at 300 °C helium as a carrier gas pretreatment, in He atmosphere was removed by isothermal physical adsorption of 2 % O<sub>2</sub> for 30 minutes. At an O<sub>2</sub> gas flow rate of 50 mL min<sup>-1</sup>, the temperature is continuously increased to 500 °C at 10 °C/min.

#### Photoelectrochemical activity measurements

All photoelectrochemical performance measurements were performed on an electrochemical workstation (CHI660E) with that an SCE electrode as the reference electrode, a Pt wire electrode as the counter electrode, the prepared electrode as the working electrode and 60 mL 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte. The photocurrent measurement was a cycle of illumination and darkness in 20s or 40s at 60 mL 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. Similarly, the EIS and LSV measurements were carried out under illumination and darkness and Ar and O<sub>2</sub> atmosphere of the electrodes. The photoelectrochemical H<sub>2</sub>O<sub>2</sub> production activity measurements were carried out with a bias of -0.50 V, under the 300 W Xe lamp illumination with a 400 nm cutoff filter. At this process, the solution was continuously purged by oxygen bubbling during the irradiation.

## Rotating disk electrode (RDE) measurements

The measurements were performed on a Pine Durham, NC 27705 electrochemical system with a three-electrode cell using an Ag/AgCl electrode and a graphite rod electrode as the reference and counter electrode, respectively<sup>[2]</sup>. 5 mg catalysts were dispersed in 1 mL EtOH containing 25  $\mu$ L Nafion by ultrasonication to prepare the working electrode suspension. The prepared solution (10  $\mu$ L) was dropped on a Pt disk

electrode and dried at room temperature. The linear sweep voltammogram (LSV) was obtained in an O<sub>2</sub>-saturated 0.05 M Na<sub>2</sub>SO<sub>4</sub> (pH = 3) with a scan rate of 10 mV/s after O<sub>2</sub> bubbling for 30 min. The current response of the same voltage range in N<sub>2</sub> was also collected to deduct the background value. The average number of electrons (n) involved in the overall O<sub>2</sub> reduction was determined by the slopes of the Koutecky-Levich plots with the following equation:

$$j^{-1} = j_k^{-1} + B^{-1} \omega^{-1/2} \tag{1}$$

$$B = 0.2 \mathrm{nF} v^{-1/6} \mathrm{C} D^{2/3} = \mathrm{A} * n \tag{2}$$

j is the current density,  $j_k$  is the kinetic current density,  $\omega$  is the rotating speed (rpm), F is the Faraday constant, v is the kinetic viscosity of water, C is the bulk concentration of O<sub>2</sub> in water, and D is the diffusion coefficient of O<sub>2</sub>, respectively. The contribution of all parameters (denoted as A= 0.032 mC S<sup>-1/2</sup>) to **Equation (2)** in solution of 0.05 M Na<sub>2</sub>SO<sub>4</sub>.

#### Detection of H<sub>2</sub>O<sub>2</sub> concentration

The concentration of hydrogen peroxide was detected by the DPD method<sup>[3-5]</sup>. In order to avoid exceeding the detection limit of the standard concentration curve of the DPD method, samples with an excessive H<sub>2</sub>O<sub>2</sub> concentration was measured by dilution of 5 times. The stock solutions of N,N-diethyl-1,4-phenylene-diamine sulfate (DPD, 97%, Aldrich) and peroxidase (POD, horseradish, Aldrich) were the reagent, the sodium phosphate buffer was used to adjust pH to neutral. The POD, DPD and sodium phosphate buffer were prepared as follow. 0.1 g of DPD was dissolved in 10 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> solution and 5 mg of POD was dissolved in 5 mL of purified water. The POD solution was kept in 3-5 °C for five days. Sodium phosphate buffer solution was made by mixing 99.7 mL of purified water, 87.7 mL of 1 M sodium dihydrogen phosphate anhydrous solution, and 12.6 mL of 1 M sodium phosphate dibasic dihydrate solution. Adding 0.4 mL phosphate buffer, 1.12 mL water, 0.05 mL DPD and 0.05 mL POD into 1mL sample and shaking vigorously for 90 seconds for measurement. The calibration curves of the concentration of H<sub>2</sub>O<sub>2</sub> were also obtained relying on the different range of  $H_2O_2$  concentration. The absorbance was measured at 551 nm by UV/visible spectrophotometer.

#### The measurement of electrochemical surface area (ECSA)

The ECSA values were estimated by determining the double-layer capacitance of the system from CV measurement. Firstly, a non-Faradaic region was identified from CV in quiescent solution. And all the measured currents in this region were assumed to be from the double-layer charging. Based on this assumption, the charging current (ic) was equal to the product of electrochemical double layer capacitance,  $C_{dl}$  and the scan rate (v), as show in **Equation (3)**<sup>[6]</sup>.

$$I_c = v * C_{dl} \tag{3}$$

Linear fit ic with different scanning speeds (v), the slope of the straight line obtained was  $C_{dl}$ . So, the ESCA of the photoelectrode can be calculated through dividing  $C_{dl}$  by the specific capacitance of the sample as shown in **Equation** (4)<sup>[7, 8]</sup>.

$$ESCA = C_{dl} / C_s \tag{4}$$

Here we used a general specific capacitance of  $0.015 \text{ mF cm}^{-2}$  for the carbon materials.

#### **DFT computational details**

All the spin theoretical simulations in our work were carried out on the Vienna ab initio Simulation Package (VASP) with the version 5.4.1<sup>[9]</sup>. The Generalized gradient approximation (GGA) with the Perdew-Burke-Emzerhof (PBE) functional form was employed to evaluate the electron-electron exchange and correlation interactions while the projector augmented-wave (PAW) methods were implanted to represent the core-electron (valence electron) interactions. Plane-Wave basis function was set with a kinetic cut-off energy of 550 eV. The ground-state atomic geometries were optimized by relaxing the force below 0.02 eV/Å and the convergence criteria for energy was set with the value of  $1.0 \times 10^{-5}$  eV/cell. A Monkhorst-Pack meshes<sup>[10]</sup> with the size of  $3 \times$  $3 \times 1$  were employed to sample bulk Brillouin zone for the electronic properties. Tetrahedron method with Blächl corrections<sup>[11]</sup> was employed for the electronic structures and total energy of our models while the Gaussian smearing was for stress/force relaxations. In order to better describe the interactions between molecules, van der Waal (vdw) interactions are included descripting by DFT-D3 method of Grimme.



**Supplementary Figure 1.** SEM image of different sample A: pristine g-C<sub>3</sub>N<sub>4</sub>, B: OCN, C-D: GCN-NRs, E-F: OCN-NPs.



**Supplementary Figure 2.** A: XRD patterns and B: Raman spectra of OCN-200/CNTs with different acidification times.



**Supplementary Figure 3.** A: FTIR spectra of OCN NPs and OCN/CNTs with different weight ratios of OCN-NPs and CNTs and B: FTIR spectra of OCN NPs and OCN/CNTs with different acidification times.



Supplementary Figure 4. XPS spectra of OCN-200/CNTs-y (y = 6, 12, 18 and 24 h).



Supplementary Figure 5. The UV-Visible spectra of OCN-NPs and OCN/CNTs.



Supplementary Figure 6. H<sub>2</sub>O<sub>2</sub> production of OCN-200/CNTs-y (y=0, 6, 12, 18 and 24) ( $\lambda \ge 400$  nm, - 0.5 V *vs.* SCE).



**Supplementary Figure 7.** H<sub>2</sub>O<sub>2</sub> production of OCN-NPs, OCNTs and OCN-200/CNTs-18h ( $\lambda \ge 400$  nm, - 0.5 V *vs.* SCE).



**Supplementary Figure 8.** H<sub>2</sub>O<sub>2</sub> production of mechanical mixing, OCN-Bulk/CNTs and OCN-NPs/CNTs ( $\lambda \ge 400$  nm, - 0.5 V *vs.* SCE).



**Supplementary Figure 9.** A: electrocatalysis H<sub>2</sub>O<sub>2</sub> production at different bias; B: the 1 h current diagram of the reaction under different systems.



**Supplementary Figure 10.** A: the  $H_2O_2$  production and Faradaic efficiency for the electrodes at -0.5 V *vs.* SCE; B: The cycle experiment of  $H_2O_2$  production and FE of the OCN-200/CNTs-18h.



**Supplementary Figure 11.** A: XRD pattern of the FTO, FTO-OCN/CNTs-fresh and FTO-OCN/CNTs-used; B: SEM of OCN/CNTs-fresh and OCN/CNTs-used.



**Supplementary Figure 12.** Electrochemical Mott–Schottky curves of OCN-NPs and OCN/CNTs.



Supplementary Figure 13. Gap energies of OCN-NPs and OCN/CNTs.



**Supplementary Figure 14.** IPCE of OCN-200/CNTs-18h, OCN-200/CNTs-12h and OCN-NPs.



**Supplementary Figure 15.** Porter curve converted from impedance spectrum of OCN-NPs.



**Supplementary Figure 16.** Porter curve converted from impedance spectrum of OCN/CNTs.



Supplementary Figure 17. ECSA of different weight ratio of OCN-NPs and CNTs



Supplementary Figure 18. ECSA of different acidification time of OCN/CNTs.



Supplementary Figure 19. N<sub>2</sub> adsorption-desorption isotherms of different samples.



Supplementary Figure 20. H<sub>2</sub>O<sub>2</sub> production under Ar and O<sub>2</sub> atmosphere.



**Supplementary Figure 21.** The comparison of TPD-O<sub>2</sub> among different weight ratio of OCN-NPs and CNTs.



**Supplementary Figure 22.** The comparison of TPD-O<sub>2</sub> among different acidification time of OCN/CNTs.

**Supplementary Table 1.** The oxygen content (%) of OCN-200/CNTs-y (y=6, 12, 18 and 24 h).

Samples	OCN-200/CNTs-6h	OCN-200/CNTs-12h	OCN-200/CNTs-18h	OCN-200/CNTs-24h
O Content (%)	3.63	4.09	4.41	4.62

**Supplementary Table 2.** The comparison of  $H_2O_2$  production for OCN/CNTs with other previously reported catalysts.

Samples	System	Potential (V.vs.RHE)	Sacrificial agent	H <sub>2</sub> O <sub>2</sub> in acid	H <sub>2</sub> O <sub>2</sub> in alkali	Authors
AKCN	PC	/	10% EtOH	3.00	2.40	12
OCN-500	PC	/	10% IPA	0.0053	/	2
AKMT	PC	/	10 vol% EtOH	3.50	2.20	1
Co <sub>1</sub> /AQ/C <sub>3</sub> N <sub>4</sub>	PC	/	10% MeOH	0.12	/	13
PCN-NaCA	PC		3.5 wt% glycerol	18.7	/	14
Ni MOF NSs	EC	0.5 V	No	/	80.00	15
FeCN@C	EC	-0.6 V	No	2.20	1.20 (pH=7)	16
EPI	PEC	0.26 V	No	2.76	/	17
pTTh	PEC	0.65 V	No	/	74.07	3
OCN-NPs/CNTs	PEC	-0.083 V	No	30.7	5.51	This work

PC: Photocatalytic system; EC: Electrocatalytic system; PEC: Photo-coupled electrocatalytic system; The  $H_2O_2$  concentration unit is mmol/h/g<sub>cat.</sub>

# 1 Supplementary Table 3. The electronic life of the Porter curve for OCN-NPs and

2 OCN-200/CNTs-18h.

Samples	f <sub>max</sub>	τ (s)
OCN-NPs	0.316	0.503
200:1,18 h	0.121	1.313

# 4 Supplementary Table 4. The BET surface areas, pore volume and average pore size

5 of all samples.

Samula	<b>DET</b> surface $prop(m^2/s)$	Pore	Average pore	
Sample	DET surface area(m <sup>-</sup> /g)	volume(cm <sup>3</sup> /g)	size(nm)	
GCN	6.49	0.06	34.11	
GCN-NRs	25.19	0.09	14.88	
OCN-NPs	68.61	0.15	8.49	
OCN-200/CNTs	28.94	0.28	38.55	

<sup>3</sup> 

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