## **Supplementary Information**

# N-Doped Carbon Dots as Electrolytes to Boost Photoelectrochemical Water Oxidation for Photo-assisted Zinc-Air Batteries

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#### **1. Experimental Procedures**

**Experimental section.** Citric acid, urea, nitric acid (HNO<sub>3</sub>), p-benzoquinone, vanadyl acetylacetonate, sodium hydroxide (NaOH), dimethyl sulfoxide (DMF) were purchased from Energy Chemical. Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) was purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without any further purification. FTO conductive glass plate was purchased from Luoyang Tengchang Xukun Biotechnology Co., Ltd.

**Preparation of BiVO**<sub>4</sub> and carbon dots (CDs). The fabrication of BiVO<sub>4</sub>-modified FTO photoanode was based on the reported method without further development.<sup>[1]</sup> The hydrothermal method was employed to synthesize citric acid and urea derived-carbon dots (CA-N-CDs).<sup>[2]</sup> Specifically, 0.3842 g of citric acid was dissolved in 10 mL of deionized water to form an aqueous solution, which was subsequently maintained in an autoclave at 220 °C for 5 h. The resulting mixture was filtered through a membrane with a pore diameter of 0.22 µm. Following this, the resultant solution underwent dialysis using a cellulose dialysis membrane with a molecular weight cut-off (MWCO) of 500 Da in 1 L of deionized water under continuous stirring conditions. Fresh deionized water was added every 2 h, and the entire dialysis process continued for one day. Finally, 58 mg CA-N-CDs were obtained as pale yellow powders after freeze-drying. For comparison, CA-CDs was prepared in the same way but without the addition of urea. Noted that both of CA-N-CDs and CA-CDs are very hygroscopic, which was changed into light brown very quickly in the room condition. Therefore, the yields and amounts of CA-N-CDs and CA-CDs after preparation are not very accurate.

**Material Characterization.** Zeta potentials of the synthesized CDs solutions were measured using a Malvern Nano ZS90 Particle Size Potentiometer. The pH of the aqueous solution was determined with an Orion Star A211 pH meter from Thermo

Fisher, while the conductivity of the CDs solution was assessed using a DDSJ-319L conductivity meter. High-resolution transmission electron microscopy (HR-TEM) imaging was conducted using a Tecnai G2 F20 field emission electron microscope operated at 200 kV acceleration voltage. A Bruker D8 Advance X-ray powder diffractometer (XRD) was used to characterize the structures of materials. Raman spectra were measured on a Renishaw in Via with 532 nm laser source. X-ray photoelectron spectroscopy (XPS) analysis of the CDs was carried out on a Kratos AXIS ULTRA DLD XPS instrument. The C 1s peak at 284.6 eV was chosen as the calibration for binding energy. UV-vis absorption spectra were recorded on a Hitachi F-7000 fluorescence spectrometer. Zeta potential measurements were conducted on a Malvern Nano ZS90 Particle Size Potentiometer, in which the pH and conductivity of **CA-CDs** and **CA-N-CDs** were kept identical as shown in Table S1.

**Photoelectrochemical (PEC) and Electrochemical Characterization.** Since strong electrolyte can complete ionization in aqueous solution, it is easy to identify the charged particle concentration by controlling the concentration of electrolyte. However, **CA-N-CDs** is a kind of weak electrolyte, which is difficult to identify the accurate concentration. Based on the Kohlausch's law of independent ion movement,<sup>[3]</sup> the concentration of charged particles is proportional to the electro-conductibility of system. Therefore, in order to compare the activity of CDs solution with H<sub>2</sub>SO<sub>4</sub> under similar conditions, the conductivity and pH for **CA-N-CDs**, **CA-CDs** and H<sub>2</sub>SO<sub>4</sub> is adjusted around the identical pH and electro-conductibility (Table S1).

All the electrochemical and photoelectrochemical measurements were carried out by a CHI 660e workstation (CH instrument, Shanghai, China) in a three-electrode system, where BiVO<sub>4</sub>, Ag/AgCl electrode and platinum wire were used as the working electrode, reference electrode and counter electrode, respectively. Electrochemical impedance spectroscopy (EIS) were collected in a frequency range from 0.1 Hz to 10 kHz. And measurements were carried out under Ar saturation conditions and 420 nm

LED lamp (the input optical power is 8.87 mW cm<sup>-2</sup>).

The measurement of Mott-Schottky (M-S) plots. The purified CDs were dissolved in water, giving a concentrated CDs aqueous solution, respectively, which was further drop-cast onto an FTO plate and then air-dried at room temperature. The modified FTO plates were then dried in a vacuum oven at 100 °C for 1 h. M-S measurements were conducted in a three-electrode system, in which the working electrode was the CDs/FTO plate, the counter electrode was a graphite rod, the reference electrode was the Ag/AgCl, and 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH = 2.8) was the electrolyte. The CHI 660E electrochemical workstation was used for M-S tests. The flat-band potentials ( $V_{\rm fn}$  and  $V_{\rm fp}$ ) of n-type **CA-CDs** and p-type **CA-N-CDs** were determined using M-S plots at potentials varying from -1.2 to 1.7 V vs. RHE with a frequency of 1 kHz. Based on the M-S equation shown in equation 1, a plot of  $\frac{1/C_{\rm SC}^2}{2}$  against *E* yields a straight line. The values of  $V_{\rm fn}$  and  $V_{\rm fp}$  were determined from the intercept on the E axis.

$$\frac{1}{C_{\rm SC}^2} = -\frac{2}{\varepsilon \varepsilon_0 E N_{\rm d}} (E - E_{\rm fb} - \frac{k_{\rm B}T}{e})$$
(1)

Here,  $C_{SC}$  is the interfacial capacitance,  $\varepsilon$  is the dielectric constant of the semiconductor,  $\varepsilon_0$  is the permittivity of free space,  $N_d$  is the number of donors, E is the applied voltage,  $E_{fb}$  is the flat-band potential of semiconductor, e is the electronic charge,  $k_B$  is Boltzmann's constant and T is the absolute temperature. The flat-band potential can be approximated as the Fermi level ( $V_f$ ) in the semiconductor. A positive slope indicates an n-type semiconductor, while a negative slope indicates a p-type semiconductor.

**Photo-assisted Zinc-air battery test.**  $2 \times 2 \text{ cm}^2 \text{BiVO}_4$  was modified on the FTO plate. The photo-assisted zinc-air battery (ZAB) was assembled by the BiVO<sub>4</sub>-modified FTO plate as the working electrode and a Zn plate as the counter/reference electrode. CDs solution was used as the electrolyte (pH = 2.8), in which the pH and conductivity were kept identical as Table S1. Charging/discharging profiles of photo-assisted ZABs operated at 0.1 mA cm<sup>-2</sup> under 420 nm illumination with the input optical power of 8.87 mW cm<sup>-2</sup>. The long-term cycling stability of the cell was assessed under 420 nm light irradiation at a current density of 0.1 mA cm<sup>-2</sup>, with alternating cathodic (oxygen reduction reaction, ORR) and anodic (oxygen evolution reaction, OER) phases over 150 consecutive charge-discharge cycles, in which each half-cycle maintains for 120 s.

The test potential was converted to a reversible hydrogen electrode (RHE) by the following equation:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.197 + 0.059 \times \rm pH$$
(2)

 $E_{\text{RHE}}$  represents the converted potential versus RHE, while  $E_{\text{Ag/AgCl}}$  refers to the obtained potential versus Ag/AgCl electrode.

#### The determination of the incident photon-to-current conversion efficiency (IPCE).

IPCE is determined by measuring photocurrent densities generated under monochromatic light irradiation at specific wavelengths (equation 3).<sup>[4]</sup>

IPCE (%) = 
$$\frac{1240 \times J}{\lambda \times P_{\text{light}}}$$
 (3)

In which,  $\lambda$  is the irradiation wavelength,  $P_{\text{light}}$  and J represent the input optical power and photocurrent density at each irradiation wavelength, respectively.

### 2. Figures and Tables



Figure S1. XRD spectra of (a) BiVO<sub>4</sub> and (b) CA-CDs and CA-N-CDs, respectively.



Figure S2. The TEM image of CA-N-CDs.



Figure S3. Fourier transform infrared (FTIR) spectra of CA-CDs and CA-N-CDs respectively.



**Figure S4.** Emission fluorescence plots of (a) **CA-CDs** solution and (b) **CA-N-CDs** solution at the different excitation wavelength, respectively.



**Figure S5.** (a) UV-vis absorption spectra of **CA-CDs** and **CA-N-CDs** respectively. (b) The corresponding Tauc plots of **CA-CDs** and **CA-N-CDs** based on Figure S5a.

The bandgaps ( $E_g$ ) of **CA-CDs** and **CA-N-CDs** were calculated to be 2.40 eV and 2.58 eV, respectively, using the Kubelka-Munk function and Tauc plot,<sup>[5]</sup> as shown in equation 4:

$$(\alpha h v)^2 = A(h v - E_g) \tag{4}$$

in which  $\alpha$ , h, v and A represent the absorption coefficient, Planck constant, light frequency and the constant.



**Figure S6.** Anodic scan for determining the lowest unoccupied molecular orbital (LUMO) level of (a) **CA-CDs** and (c) **CA-N-CDs** at 5 mV s<sup>-1</sup>. Cathodic scan for determining the highest occupied molecular orbital (HOMO) level of (b) **CA-CDs** and (d) **CA-N-CDs** at 5 mV s<sup>-1</sup> respectively.



**Figure S7.** LSV curves of BiVO<sub>4</sub> photoanode in **CA-N-CDs**, **CA-CDs** and H<sub>2</sub>SO<sub>4</sub> electrolytes under the dark conditions, respectively.



Figure S8. Chopped LSV curves of  $BiVO_4$  under 420 nm illumination in CA-CDs, CA-N-CDs and  $H_2SO_4$ , respectively.



Figure S9. PEC stability of BiVO<sub>4</sub> under 420 nm illumination in CA-CDs, CA-N-CDs and H<sub>2</sub>SO<sub>4</sub>, respectively.



**Figure S10.** SEM images of (a) pristine BiVO<sub>4</sub>, (b) BiVO<sub>4</sub> photoanode in **CA-N-CDs**, and (c) BiVO<sub>4</sub> photoanode in H<sub>2</sub>SO<sub>4</sub> after continuous photo-electrolysis at a constant photocurrent density 5 mA·cm<sup>-2</sup> under 420 LED illumination for 4 h.

In order to check the stability of BiVO<sub>4</sub> in the acidic **CA-N-CDs** solution, SEM characterization was performed before and after long-time photo-electrolysis. Figure S10 shows the SEM images of BiVO<sub>4</sub> photoanodes in **CA-N-CDs** or H<sub>2</sub>SO<sub>4</sub> electrolytes respectively after long-time electrolysis under a constant photocurrent density of 5 mA·cm<sup>-2</sup> for 4 h, in which the pH and electroconductivity of two solutions are kept in Table S1. Clearly, in **CA-N-CDs** electrolyte (Figure S10b), the corrosion of BiVO<sub>4</sub> surface is dramatically suppressed, while the H<sub>2</sub>SO<sub>4</sub> solution induces the significant surface corrosion and structural collapse of BiVO<sub>4</sub> in the acidic CA-N-CDs is stable.



Figure S11. Incident photon-to-current conversion efficiency (IPCE) of  $BiVO_4$  in CA-CDs, CA-N-CDs and  $H_2SO_4$ , respectively.



**Figure S12.** Device diagram of photo-assisted ZAB under the room condition (left) and under the LED illumination (right).

Working principle of the photo-assisted ZAB:<sup>[6]</sup>

$$BiVO_4 \xrightarrow{hv} e^- + h^+$$

Charging process:

| Zn electrode:        | $Zn^{2^+} + 2e^- \rightarrow Zn$      |
|----------------------|---------------------------------------|
| Air electrode:       | $2H_2O + h^+ \rightarrow O_2 + 4H^+$  |
| Discharging process: |                                       |
| Zn electrode:        | $Zn + 2h^+ \rightarrow Zn^{2+}$       |
| Air electrode:       | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ |

Figure S12 is the device diagram of photo-assisted ZAB at room condition or under the illumination respectively. Under the LED illumination, BiVO<sub>4</sub> is triggered to generate holes and electrons. In the CA-N-CDs solution, the "semiconductor electrolyte" feature of such the CDs serve as both semiconductors and electrolytes. The surface-charged CA-N-CDs was abstracted via the electronic interaction with the BiVO<sub>4</sub> during the PEC proceeding, which act as the electrolytes. After approaching to the BiVO<sub>4</sub>, the semiconductor feature of CA-N-CDs facilitate for the charge separation by assembling into p-n heterojunctions with BiVO<sub>4</sub>. In the charging process, the reduction reaction occurs at Zn electrode, while the WOR happens in the system with BiOV<sub>4</sub> and CA-N-CDs solution (here called as the air electrode). In the discharging process, ORR occurs on the air electrode, accompanied by the oxidation process at Zn electrode. Clearly, the

 $BiVO_4$  in the CA-N-CDs facilitates the separation of charge carriers under the irradiation, which can efficiently decrease the voltage gap of the ZAB.



Figure S13. Charge curves at  $0.1 \text{ mA} \cdot \text{cm}^{-2}$  under the LED irradiation with different optical power.

In order to investigate the influence of light intensity on the performance of ZAB, we carried out the measurement of ZAB under the LED lights irradiation with different output power (the input optical power is 8.87, 6.69 and 1.60 mW cm<sup>-2</sup>, respectively). Note that the effect of illumination on the discharging curves is negligible (Figure 3b), indicating that the interaction of BiVO<sub>4</sub> and CA-N-CDs can dramatically affect the WOR process rather than the ORR process. Therefore, the charging curves under the LEDs illumination with different light intensity were measured. As depicted in Figure S13, the charging voltage increases with the decreasing light intensity, indicating that the enhancement in light intensity can improve the performance of the ZAB.



**Figure S14.** (a) UV-vis DRS spectrum and (b) band gap  $(E_g)$  value estimated by the Tauc plot of BiVO<sub>4</sub>.



Figure S15. The M-S plots of BiVO<sub>4</sub> in CA-CDs and CA-N-CDs solutions, respectively.

As shown in Figure S15, the positive slope of the tangent indicates that BiVO<sub>4</sub> is an ntype semiconductor. The intercept represents the conduction band (CB) position of the semiconductor. Given that an n-type semiconductor has negligible gap between flat band potential and the CB, which for BiVO<sub>4</sub> is -0.31 V vs. RHE and 0.02 V vs. RHE in **CA-CDs** and **CA-N-CDs**, respectively.<sup>[7]</sup> By means of the  $E_g = E_{VB} - E_{CB}$  equation, the valence band (VB) can be calculated as 1.93 V vs. RHE and 2.26 V vs. RHE in **CA-CDs** and **CA-N-CDs**, respectively.



Figure S16. The absorption of in-situ UV-vis spectroelectrochemical spectra at 400 nm for the PEC water oxidation system on  $BiVO_4$  photoanode in CA-N-CDs solution at 1.23 V.

|           | рН  | к (mS·cm⁻¹) |
|-----------|-----|-------------|
| CA-CDs    | 2.6 | 1.2         |
| CA-N-CDs  | 2.6 | 1.2         |
| $H_2SO_4$ | 2.6 | 1.7         |

Table S1. pH and conductivity for CA-CDs, CA-N-CDs and  $H_2SO_4$  solutions.

#### 3. Reference

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