

## Supplementary Information

### **Carbon dots induce abundant oxygen vacancies in CeVO<sub>4</sub> for promoting photocatalytic selective hydrogenation of functionalized nitroarenes**

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# 1. Experimental Section

## 1.1 Materials and reagents

All the reagents were of analytical grade and directly used without any further purification. All of chemicals including 4-nitrostyrene (4-NS), 4-aminostyrene (4-AS), 4-nitroethylbenzene (4-NE), 4-ethylbenzenamine (4-EA), ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), formic acid (88 v/v%),  $\text{H}_2\text{O}_2$  (30 v/v%), ammonium hydroxide and  $\text{NaBH}_4$  were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. All aqueous solutions in the experiment were prepared using ultrapure water.

## 1.2 Preparation of samples

The CDs were obtained from coal pitch according to our method as reported previously<sup>1</sup>. Subsequently, 59 mg of  $\text{NH}_4\text{VO}_3$  were dissolved into 60 mL of aqueous solution containing 54 mg of CDs under stirring. The resultant homogeneous brown solution was transferred into a Teflon-lined autoclave and then heated at 120 °C for 12 h. After that, the reactor was cooled down to room temperature naturally to achieve Solution A, i.e. the targeting solution of amine-modified CDs (NCDs). Meanwhile, 0.217 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved into 60 mL of water for obtaining Solution B. Next, Solution B was dropped into Solution A. The pH of the obtained solution was then adjusted to 9 with  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . After reacting for 4h in room temperature, the precipitates were collected by centrifugation. The collected precipitates were washed for several times with ethanol and water respectively, and finally dried in a vacuum oven at 60 °C to obtain  $\text{CDs@CeVO}_4$ .

### 1.3 Sample characterization

Absorption spectra of samples were determined with a Shimadzu UV-2550 UV-Vis spectrometer. X-ray diffraction (XRD) patterns of samples were obtained using a Bruker D8 ADVANCE powder diffractometer at Cu K $\alpha$  with a scanning rate of 2°min<sup>-1</sup> in the 2 $\theta$  range of 5–90°. TEM and HRTEM were performed on a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. XPS data of all samples were collected using a Kratos AXIS 165 multitechnique electron spectrometer with an Al K $\alpha$  X-ray source for determining the composition and chemical bonding configurations. Zeta potential measurement was conducted on a model Zetasizer Nano manufactured by Malvern Panalytical. The sample (3 mg) was uniformly dispersed in 20 mL of water by ultrasound and then taking a certain volume was pipetted into a Malvern potential cuvette for testing. Fluorescence lifetime spectra were collected on a Hamamatsu C11367 transient State Fluorescence Spectrometer. FTIR spectra were obtained by a Bruker Vertex 70 FTIR with a range of 400-4000 cm<sup>-1</sup>. Low-temperature electron paramagnetic resonance (EPR) spectra were acquired on a Bruker EMXPLUS10/12 spectrometer (140 K, 9.062 GHz).

Experiment of radical scavengers was performed by the same reaction conditions with photocatalytic performance test expect for adding proper h<sup>+</sup>, ·O<sub>2</sub><sup>-</sup> and e<sup>-</sup> radical scavengers. Typically, 500  $\mu$ L triethanolamine (TEOA), 4 mg p-benzoquinone (BQ) and 4 mg AgNO<sub>3</sub> as h<sup>+</sup>, ·O<sub>2</sub><sup>-</sup> and e<sup>-</sup> radical scavengers were added to the photocatalytic reaction system upon illumination, respectively. The evolution of 4-NS reduction over time was recorded to determine the conversion ratio of 4-NS to 4-AS.

Hydrogen release of  $\text{NaBH}_4$  hydrolysis was conducted on a photocatalytic activity evaluation online analysis system model CEL-SPH2N manufactured by Beijing China Education Au-light Technology Co., Ltd. First of all, 10 mg of catalyst was dispersed in 15 mL water, then transferred into a container and evacuated. Next, 10 mg of  $\text{NaBH}_4$  was dispersed in 5 mL water and then injected into the above solution. The reaction temperature was set to 25 °C. The hydrogen release from  $\text{NaBH}_4$  hydrolysis under dark condition and visible light irradiation was pumped through the pipe to the gas chromatograph for volume analysis.

Electrochemical measurements were performed in a Bio-Logic (SP 120) electrochemical workstation with a three-electrode electrochemical cell system. All working electrodes were fabricated through coating ethanol suspension of the samples onto indium tin oxide (ITO) glass electrodes, then the suspensions were evaporated in vacuum at 60 °C. The electrolyte solution was made using 0.5 M  $\text{Na}_2\text{SO}_4$ . A Platinum plate and Ag/AgCl reference electrode acted as the counter electrode and reference electrode.

#### **1.4 Photocatalysis measurement**

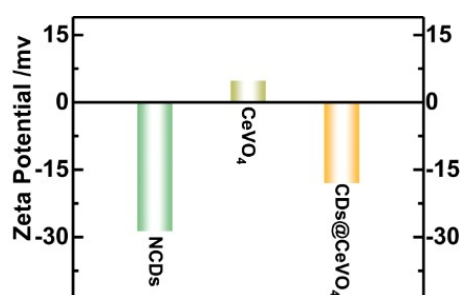
Typically, 3 mg of sample powder and 20 mL of aqueous solution of the 4-NS (0.168 mM) were added into a quartz reactor placed on a magnetic stirrer and thermostatted at 25 °C. After dissolving the powder completely, 10 mg of  $\text{NaBH}_4$  as a reducing reagent was then put into the reactor. The sealed reactor was irradiated under a Xe lamp with a cut 420 filter attached ( $\lambda \geq 420$  nm, light intensity of  $100 \text{ mW} \cdot \text{cm}^{-2}$ ). The characteristic absorption of the products was monitored using UV-Vis

spectrophotometry by taking aliquots at regular intervals. The concentrations of the product ( $C$ ) were determined using the Lambert beer's law:

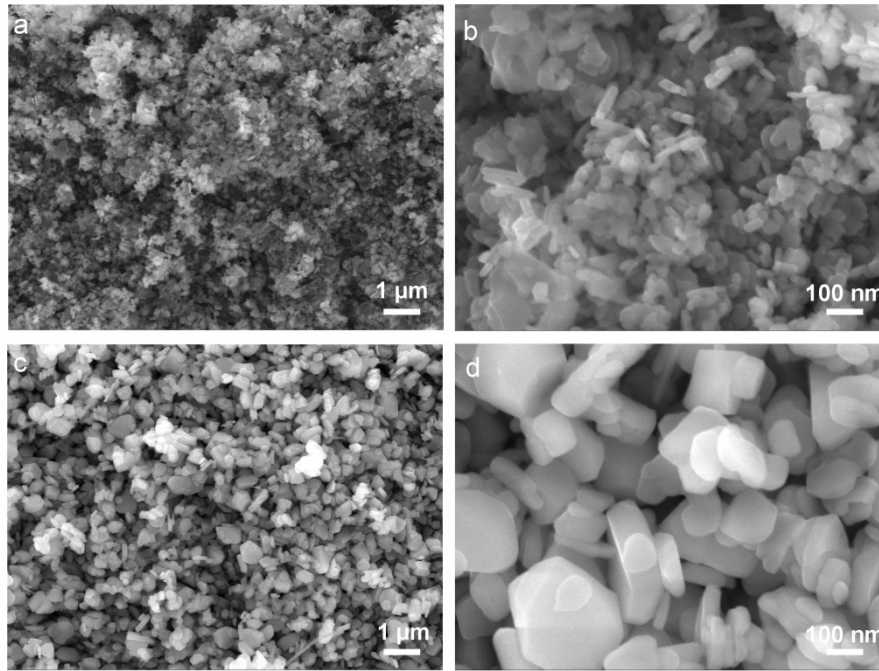
$$A = \varepsilon \times b \times C \quad (1)$$

where  $\varepsilon$  is the molar absorbance coefficient of the products;  $A$  is the absorbance which can be measured;  $b$  is the path length of light ( $b=1$  cm). At last, the product contents were further confirmed by GC-MS (gas chromatography with a Thermo Finnigan chromatograph equipped with a flame ionization detector and a DB-WAX capillary column with nitrogen as the carrier gas).

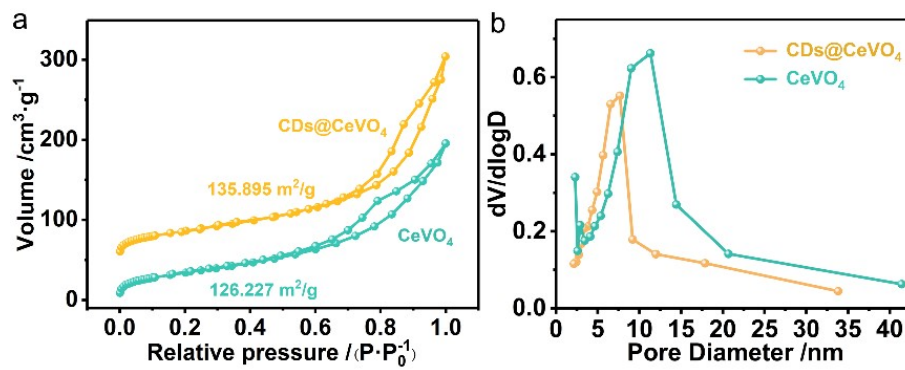
## 2. Supporting results



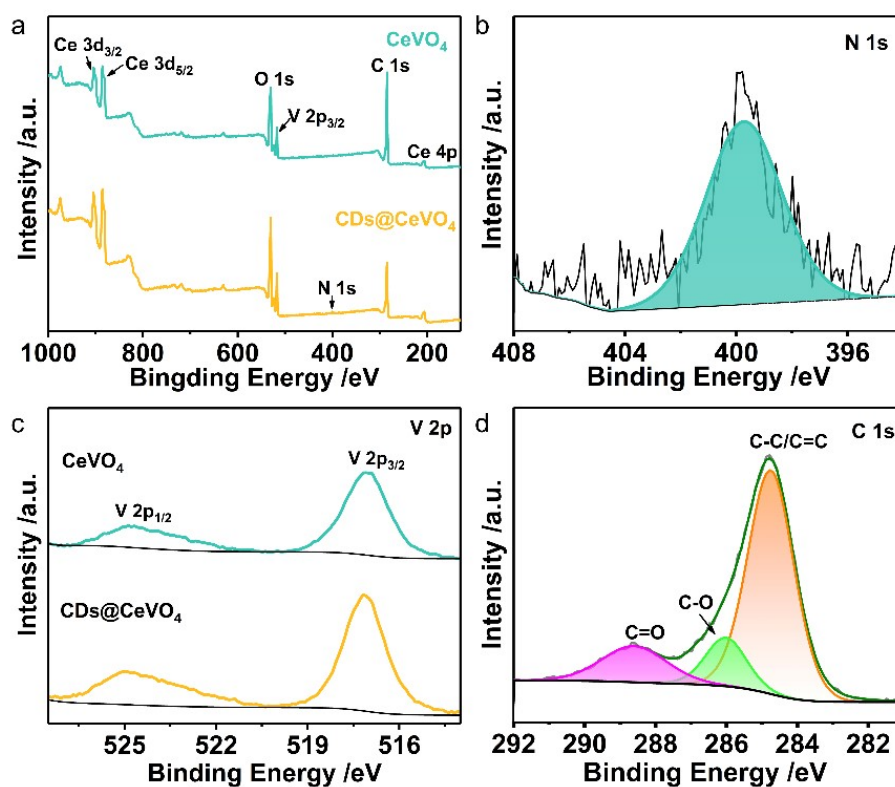
**Figure S1.** Zeta potentials of NCDs, CeVO<sub>4</sub> and CDs@CeVO<sub>4</sub>



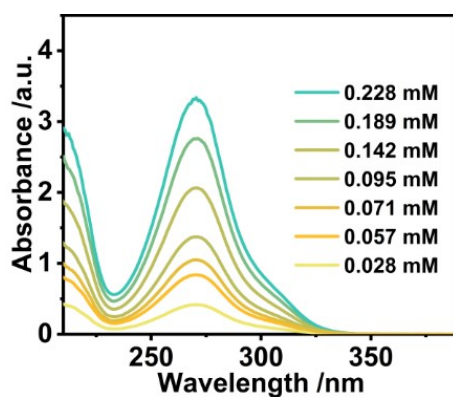
**Figure S2.** SEM images of CDs@CeVO<sub>4</sub> (a and b) and CeVO<sub>4</sub> (c and d) with different magnification



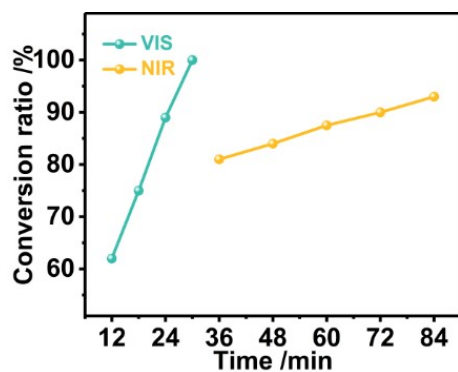
**Figure S3.** N<sub>2</sub> adsorption-desorption isotherms (a) and pore size distributions (b) of CDs@CeVO<sub>4</sub> and CeVO<sub>4</sub>



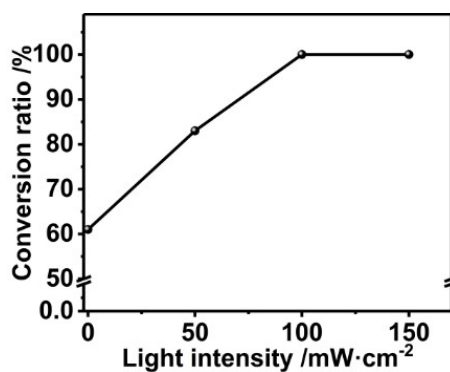
**Figure S4.** XPS results: (a) full survey of CDs@CeVO<sub>4</sub> and CeVO<sub>4</sub>; (b) N1s XPS spectrum of CDs@CeVO<sub>4</sub>; (c) V 2p XPS spectra of CDs@CeVO<sub>4</sub> and CeVO<sub>4</sub>; (d) C1s spectrum of CDs@CeVO<sub>4</sub>



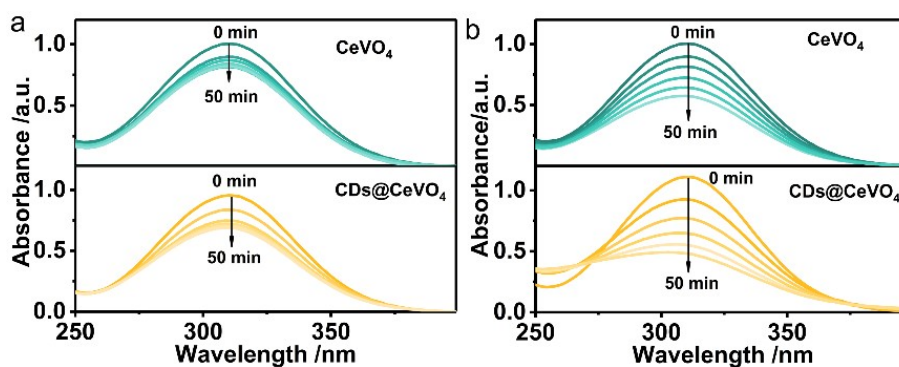
**Figure S5.** UV-Vis absorption spectra of 4-AS solution at different concentrations



**Figure S6.** The time dependence of conversion rate with visible light and near-infrared light irradiation (Light intensity:  $100 \text{ mW}\cdot\text{cm}^{-2}$ )

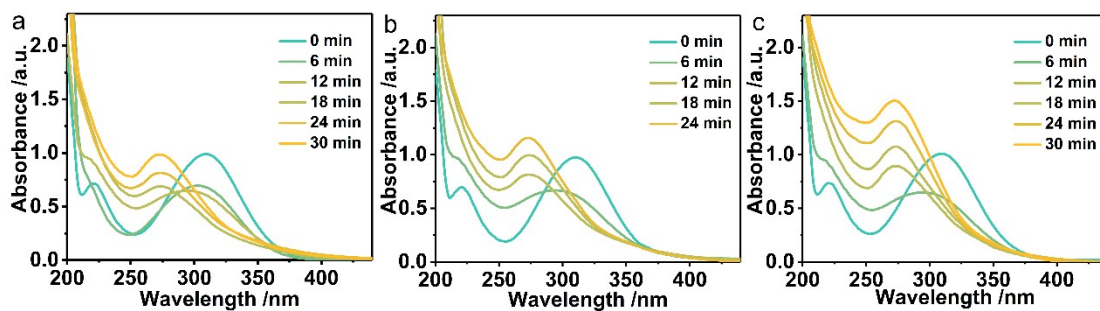


**Figure S7.** The effect of visible light intensities on conversion rate of 4-NS to 4-AS

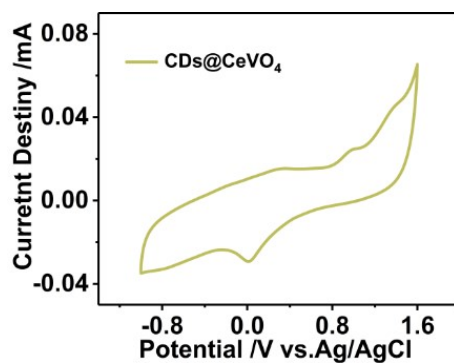


**Figure S8.** The evolution of 4-NS reduction over time without sodium borohydride upon (a) dark and (b) illumination conditions

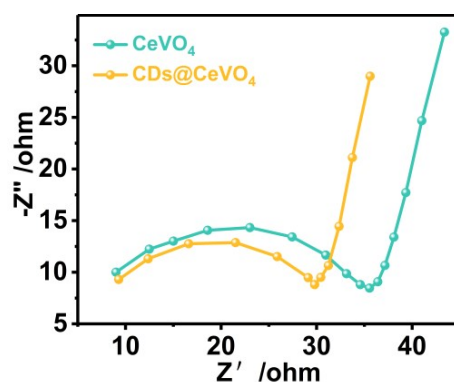




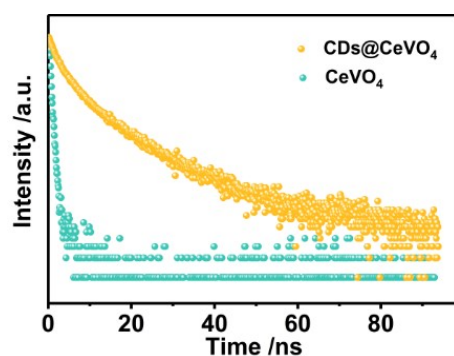
**Figure S9.** The evolution of 4-Ns reduction over time for CDs@CeVO<sub>4</sub> (10 mg) with adding different amounts of NaBH<sub>4</sub> (2.5 mg (a), 5 mg (b), 15 mg (c)) under visible light irradiation.



**Figure S10.** CV curve of CDs@CeVO<sub>4</sub>



**Figure S11.** The electrochemical impedance spectra of CDs@CeVO<sub>4</sub> and CeVO<sub>4</sub>



**Figure S12.** Fluorescence lifetime of CDs@CeVO<sub>4</sub> and CeVO<sub>4</sub>

**Table S1.** Influence of CDs contents in CDs@CeVO<sub>4</sub> on the conversion rate of 4-NS to 4-AS under the same catalytic conditions

Catalyst	CDs (g)	Ce(NO <sub>3</sub> ) <sub>3</sub> (g)	NH <sub>4</sub> VO <sub>3</sub> (g)	Yield (%)	Selectivity (%)	
CDs@CeVO <sub>4</sub> -1	0.0135	0.271	0.059	-	-	
CDs@CeVO <sub>4</sub> -2	0.027	0.271	0.059	43	100	
CDs@CeVO <sub>4</sub> -4	0.054	0.271	0.059	100	100	This work
CDs@CeVO <sub>4</sub> -8	0.108	0.271	0.059	72	100	

Reaction conditions: 10 mg of catalyst, 10 mg of NaBH<sub>4</sub>, 100 mW cm<sup>-2</sup> of visible light intensity, 25 °C of reaction temperature, 30 min of irradiation time

## References

1. X. Meng, Q. Chang, C.-R. Xue, J.-L. Yang and S.-L. Hu, Full-colour carbon dots: from energy-efficient synthesis to concentration-dependent photoluminescence properties, *Chem. Commun.*, 2017, **53**, 3074-3077.