Electronic Supplementary Information (ESI)

A new Ni-diaminoglyoxime-g-C_3N_4 complex towards efficient photocatalytic ethanol splitting *via* ligand-to-metal charge transfer (LMCT) mechanism

Yanqi Xu,[a] Cui Du,[a] Chen Zhou[b]* and Shengyang Yang[a]*

[a]School of Chemistry and Chemical Engineering, Yangzhou University, 180 Siwangting Road, Yangzhou, Jiangsu, 225002, P. R. China.

[b]School of Natural Sciences, University of Central Missouri, Warrensburg, Missouri 64093, USA.

**Corresponding author*

E-mail address: syyang@yzu.edu.cn, zhou@ucmo.edu

Tel: +86 51487978843.

1. Materials and experiments

1.1 Materials

Sodium hydroxide (NaOH, ≥99.0%), glyoxal ($C_2H_2O_2$, 40%), sodium nitrite ($NaNO_2$, ≥99.0%), acetic acid (CH_3COOH, 99.8%), ethyl acetate ($C_4H_8O_2$, 99.8%), *N*, *N*-dimethylformamide (DMF, 99.5%), sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 65.0%-68.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, 98%) was purchased from Energy Chemical. Dicyandiamide ($C_2H_4N_4$, 99.0%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Ethanol (CH_3CH_2OH, ≥99.7%), sodium hydrogen sulfite ($NaHSO_3+Na_2S_2O_5$, ≥58.5%) was purchased from Yonghua Chemical Technology Co., Ltd (Jiangsu). Nickel acetate tetrahydrate ($Ni(OAc)_2{\cdot}4H_2O$, 98%) was purchased from Nanjing Chemical Reagent Co., Ltd. Basic fuchsin ($C_{20}H_{20}ClN_3$, 99.0%) was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used as received without further purification. Deionized (DI) water with the resistivity of ≥18.2 MΩ·cm was used in all experiments.

1.2 Synthesis of diaminoglyoxime (DAG)

18 g sodium hydroxide, 24.1 g hydroxylamine hydrochloride, and 100 mL deionized (DI) water were mixed in a 150 mL three-necked flask and vigorously stirred at 0-5 °C for 15 min for homogenous suspension. Then, 9.4 mL glyoxal was added to the three-necked flask equipped with an air condenser and heated at 95 °C in an oil bath for 5 h with vigorous stirring. After being cooled to 20 °C naturally, the solution was stored in the refrigerator at 0-5 °C for 24 h to obtain precipitates. Finally, the precipitates were washed several times with deionized water and collected by centrifuge and freeze-drying. ^1H NMR (400M, dimethyl-d6 sulfoxide): δ (ppm)= 9.75 (s, 2H), 5.12 (s, 4H).

1.3 Synthesis of diaminoglyoxime-g-C_3N_4 complex (DAG-CN)

The bulk g-C_3N_4 (denoted as CN) was synthesized by heating 5 g dicyandiamide from room temperature to 550 °C in Ar flow with a ramp rate of 1 °C/min and stayed for 4 h, then cooled to room temperature. For x wt% DAG-CN in which x refers to the weight percentage of DAG (x=0.5 wt%, 1 wt%, 2 wt%, and 3 wt%), 300 mg CN was weighed and put into a 100 mL three-necked flask and dispersed in 30 mL of acetic acid under a nitrogen atmosphere. The suspension was sonicated and then stirred for 1 h at ambient temperature, respectively, to achieve better dispersion. After that, a certain amount of DAG and sodium nitrite (mole ratio of DAG: $NaNO_2$ =1: 1.4) was added to the suspension and mixed with vigorous stirring. The mixture was stirred for 1 h at 25 °C under a nitrogen atmosphere. Then, 20 ml of DMF was added to the suspension and vigorously stirred for 10 min. Finally, the precipitates obtained with a centrifuge were washed several times with ethyl acetate and ethanol and freeze-dried for further use. Details of reagents and amounts for preparation of DAG-CN were listed as follows

Table S1. Details of reagents and corresponding amounts for preparation of DAG-CN

x wt% DAG-CN	CN	DAG	$NaNO_2$	acetic acid	DMF
0.5 wt% DAG-CN	300 mg	1.5 mg	1.3 mg	30 mL	20 mL
1 wt% DAG-CN	300 mg	3.0 mg	2.5 mg	30 mL	20 mL
2 wt% DAG-CN	300 mg	6.0 mg	5.0 mg	30 mL	20 mL
3 wt% DAG-CN	300 mg	9.0 mg	7.5 mg	30 mL	20 mL

1.4 Synthesis of Ni-diaminoglyoxime-g-C_3N_4 complex (Ni-DAG-CN)

For the fabrication of x wt% Ni-DAG-CN in which x refers to the mass loading of Ni on DAG-CN (x=0.5 wt%, 1 wt%, 2 wt%, and 3 wt%), 100 mg corresponding x wt% DAG-CN was added into a 50 mL flask and dispersed in 20 mL DMF via sonication. Then, a certain amount of $Ni(OAc)_2·4H_2O$ was added to the suspension of x wt% DAG-CN in DMF and vigorously stirred for 24 h. Finally, the precipitates were repeatedly washed with ethyl acetate and ethanol. After that, samples were collected by centrifuge and freeze-drying. Details of reagents and amounts for preparation of Ni-DAG-CN were shown as follows

Table S2. Details of reagents and corresponding amounts for preparation of Ni-DAG-CN

x wt% Ni-DAG-CN	**x wt% DAG-CN**	**$Ni(OAc)_2 \cdot 4H_2O$**	**DMF**
0.5 wt% Ni-DAG-CN	0.5 wt% DAG-CN 100mg	2.5 mg	20 mL
1 wt% Ni-DAG-CN	1 wt% DAG-CN 100mg	5.1 mg	20 mL
2 wt% Ni-DAG-CN	2 wt% DAG-CN 100mg	10.2 mg	20 mL
3 wt% Ni-DAG-CN	3 wt% DAG-CN 100mg	15.3 mg	20 mL

For comparison, Ni(0)/CN and NiO_x/CN were fabricated according to previous reported literatures.[1,2] Specifically, 1 wt% Ni(0)/CN was prepared by a photo-deposited method; briefly, 160 mg C_3N_4 was mixed with 12 mL triethanolamine (TEOA), 800 μL of 0.1 M $NiCl_2$ aqueous solution, 5.6 mL of 0.1 M NaH_2PO_2 aqueous solution and 22 mL water. Then, the suspension was irradiated with UV-Vis light for 30 min under vacuum by 300 W xenon-lamp. Finally. The precipitate was collected and washed by DI water several times. For 1 wt% NiO_x/CN, 1.0 g C_3N_4 was dispersed in 10 mL of 15 mM $Ni(NO_3)_2$ aqueous solution and impregnated for 12 h by continuously stirring. After that, the mixture was dried under 80 °C and calcined at 250 °C for 3 h in air atmosphere.

1.5 ICP-AES measurement of Ni content

Ni-DAG-CN samples were dissolved in 2 mL of nitric acid in screw-capped glass bottles (10 mL) under sonication for 2 hours. The solution was then diluted to 5 mL with DI water in a volumetric flask and centrifuged to remove all precipitates. The supernatant solutions were used for the measurement. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement indicated practical mass loading of Ni were 0.12 wt%, 0.22 wt%, 0.34 wt%, and 0.41 wt%, respectively.

1.6 Material characterization

Powder XRD measurements were completed using an X-ray diffractometer (D8

Advance, BRUKER-AXS) with Cu Kα radiation. Fourier transform infrared spectra (FTIR) of the samples were recorded from 400 to 4000 cm^{-1} on a Bruker spectrometer (Tensor 27) using KBr pellets. Sample was placed on a copper mesh for the transmission electron microscopy (TEM) observation, which was conducted on a field emission transmission electron microscope (Tecnai G2F30 S-TWIN, FEI) at an acceleration voltage of 300 kV. UV-vis DRS was conducted on a UV-Vis-NIR spectrophotometer (Cary-5000, Varian) using $BaSO_4$ as a reference. Surface electronic states and compositions of the samples were analyzed by X-ray photoelectron spectroscopy (ESCALAB250 Xi, Thermo Scientific). The specific surface area (S_{BET}) was analyzed by the Brunauer-Emmett-Teller (BET) method on an Autosorb IQ3; samples were degassed at 100 °C before measurements. The photoluminescence (PL) spectrum was investigated using a spectrofluorometer (F-4500, Hitachi). The time-resolved fluorescence (TRFL) spectrum was conducted on Edinburgh Instruments F980. ICP-AES measurements were completed using a PerkinElmer Optima 7300 DV DRC Emission Spectrometer. ^1H NMR spectrum of diaminoglyoxime (DAG) was performed on Agilent nuclear magnetic resonance (NMR) spectrometer (400M) using a solvent of dimethyl-d6 sulfoxide. The analysis of acetaldehyde concentration in solution after photocatalysis was carried out on a UV-vis spectrophotometer (i5, Hanon). Electrochemical Impedance Spectroscopy (EIS) was carried out in 0.1 M Na_2SO_4 using an electrochemical instrument (Gamry Interface 1010) with a three-electrode configuration under light irradiation (300 W Xe-lamp, λ>350 nm). Nyquist plots and were measured at a frequency range of 10^6-0.05 Hz. Mott-Schottky plots were measured at a fixed frequency of 1000 Hz, 3000 Hz and 5000 Hz, using Ag/AgCl and platinum electrodes as the reference electrode and counter electrode, respectively. The working electrodes were the FTO separately coated with CN and Ni-DAG-CN solutions and dried in air.

1.7 Photocatalytic activity measurement

Photocatalytic H_2 evolution reactions were carried out in a Pyrex reactor under a vacuum. The temperature of the reactant solution was maintained at 6 °C by cyclic water. Ni-DAG-CN complex (10 mg) was dispersed in 40 mL ethanol with vigorous stirring. The resulting suspension was irradiated by a 300 W xenon-lamp (CEL-HXF 300). Photocatalytic H_2 evolution activities of CN were measured for comparison under the same conditions. The evolved gases were analyzed by a gas chromatograph (CEAULIGHT, GC-7920) equipped with a thermal conductivity detector (TCD) using N_2 as a carrier gas. In addition, a flame ionization detector (FID) was also employed to analyze whether the evolved gases included CO or CO_2.

Photocatalytic benzyl alcohol oxidation reaction was performed in a photochemical reaction system (Beijing Perfect Light, PCX50B). The catalyst (25 mg), benzyl alcohol (0.2 mmol), H_2O_2 (0.2 mmol) were suspended in reaction bottle with 2.5 mL acetonitrile as solvent, and then reaction bottles were fixed in this photochemical reaction system. The reaction was carried out under the bottom irradiation by an LED lamp at 365 nm at room temperature under magnetic stirring for 24 h. The conversion and selectivity of this reaction were tested by GC (CEAULIGHT, GC-7920) and calculated by peak area normalization method. The results of photocatalytic benzyl alcohol oxidation were summarized in Table S3.

1.8 Analysis of acetaldehyde concentration

The concentration of acetaldehyde was analyzed by a spectrophotometric method. In the first step, the basic fuchsin solution was prepared for the chromogenic agent. 15.0 mg basic fuchsin was added to 15 mL DI water at 80 °C. After that, 10.6 g $NaHSO_3$, 1.50 mL H_2SO_4 and 20 mL DI water were added to the above solution, and transferred to a 100 mL volumetric flask and diluted to mark with DI water. The solution above was stored in a refrigerator at 0-5 °C for 12 h. Secondly, the standard curve of acetaldehyde was established. Specifically, 0.2, 0.4, 0.6, 0.8 and 1.0 mL standard aqueous solutions of acetaldehyde (1 g/L) were added to 100 mL volumetric flask and diluted to mark with DI water, respectively. Then, 1 mL of the above solutions was added to different 10 mL volumetric flasks and diluted to mark with DI water, respectively. 2 mL chromogenic agent was added to 3 mL of acetaldehyde standard solutions above and kept at 20 °C for 20 min. The acetaldehyde concentration of the solutions was analyzed by measuring the UV-vis absorbance at 520 nm to obtain the standard concentration curve of acetaldehyde. The measurement process of acetaldehyde concentration in photocatalytic solution was the same as the above spectrophotometric method. The acetaldehyde concentration of the photocatalytic solution can be calculated by interpolating the absorbance in the standard curve.

1.9 Theoretical calculations

Gaussian 09 software package was utilized for theoretical calculations based on density functional theory. All calculations were achieved at b3lyp including a 6-31g(d) basis set for H, C, O, N atoms and a Lanl2dz basis set for Ni atom.

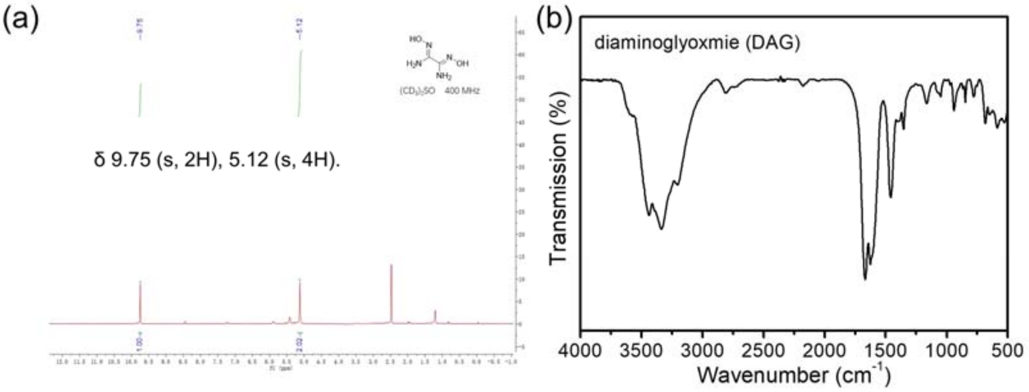

Fig. S1 (a) ^{1}H NMR and (b) FT-IR spectra of diaminoglyoxmie (DAG).

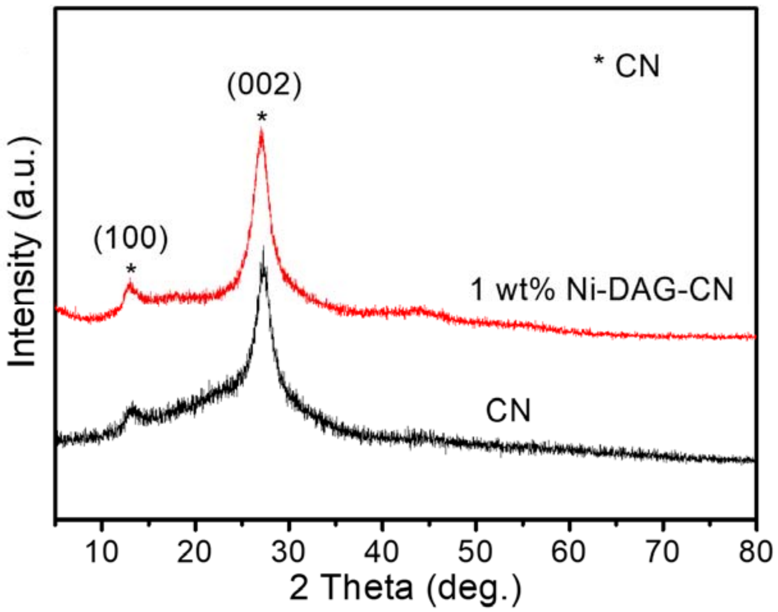

Fig. S2 XRD patterns of CN and 1 wt% Ni-DAG-CN.

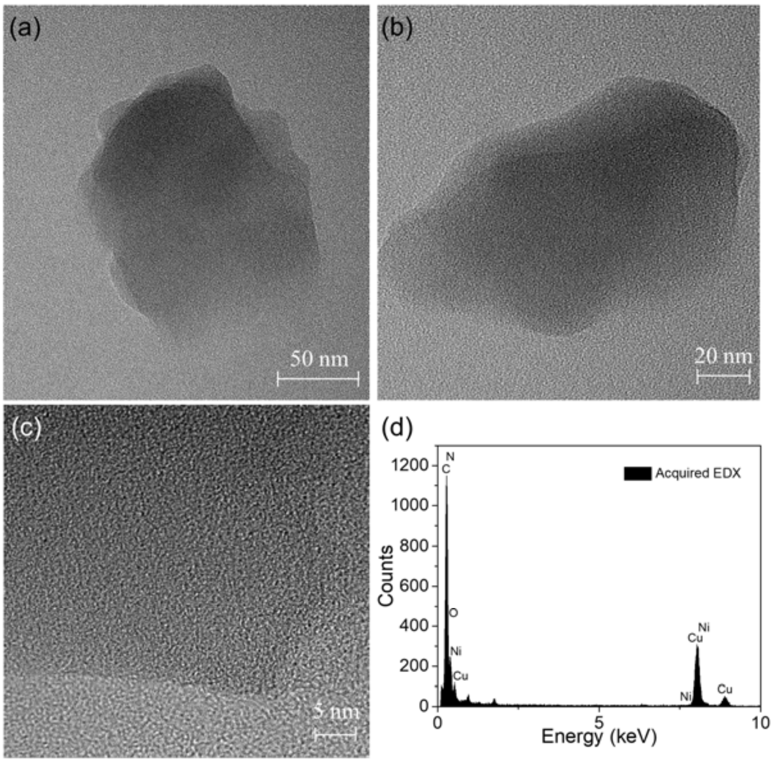

Fig. S3 (a, b) TEM images of 1 wt% Ni-DAG-CN and (c, d) HRTEM image of 1 wt% Ni-DAG-CN and corresponding energy dispersive X-ray (EDX) images. Note: Cu signal was attributed to the Cu mesh for loading sample.

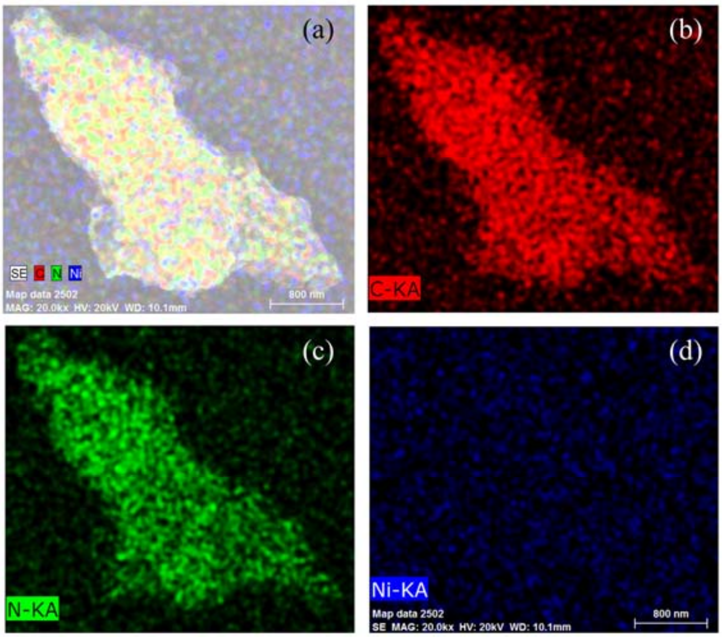

Fig. S4 Energy dispersive X-ray elemental mapping images of 1 wt% Ni-DAG-CN complex (a) all elements, (b) C, (c) N and (d) Ni. Scale bar = 800 nm.

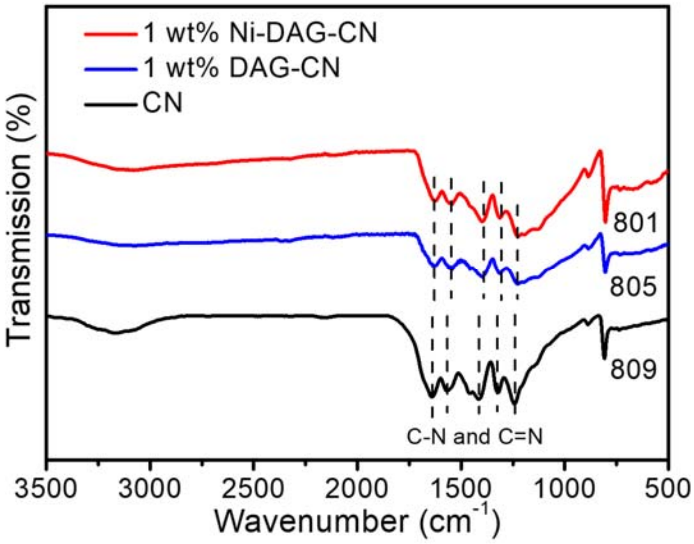

Fig. S5 FT-IR spectra of CN, 1 wt% DAG-CN and 1 wt% Ni-DAG-CN

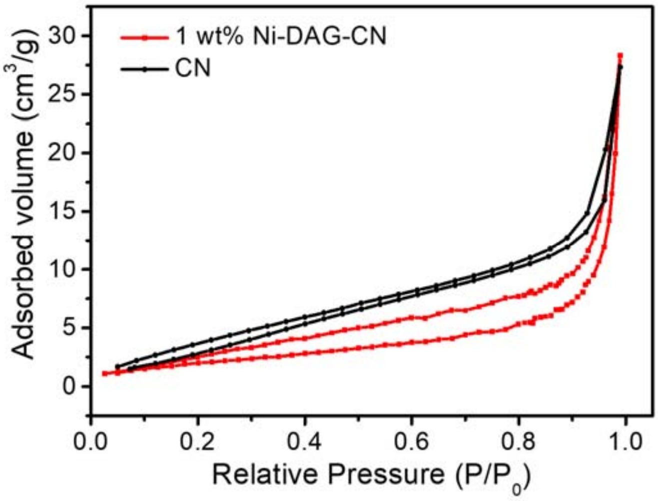

Fig. S6 Nitrogen adsorption-desorption isotherms of CN and 1 wt% Ni-DAG-CN. Specific surface areas of CN and 1 wt% Ni-DAG-CN are 13.1 and 10.3 $m^2 \cdot g^{-1}$, respectively.

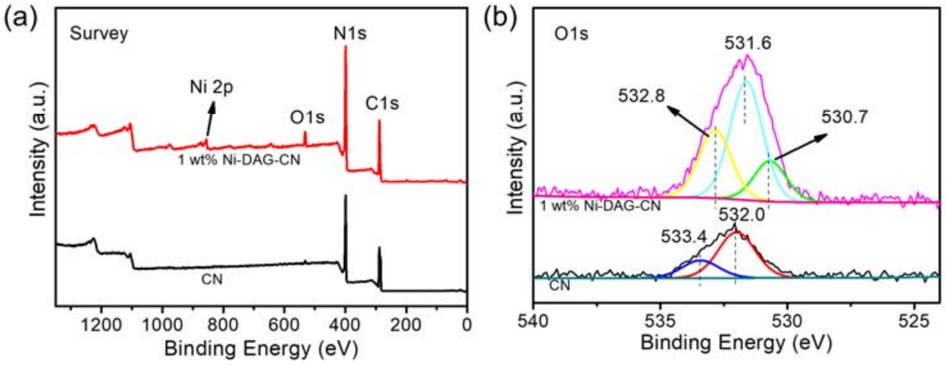

Fig. S7 XPS spectra of CN and 1 wt% Ni-DAG-CN complex: (a) survey and (b) O 1s.

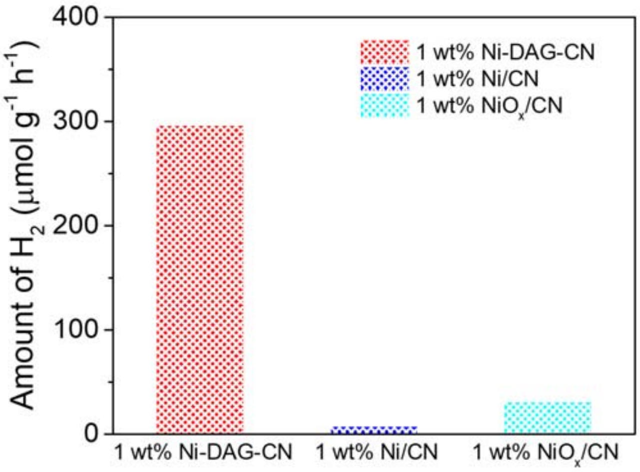

Fig. S8 Photocatalytic H_2 evolution rates of 1 wt% Ni-DAG-CN, 1 wt% Ni/CN and 1 wt% NiO_x/CN (λ > 350 nm).

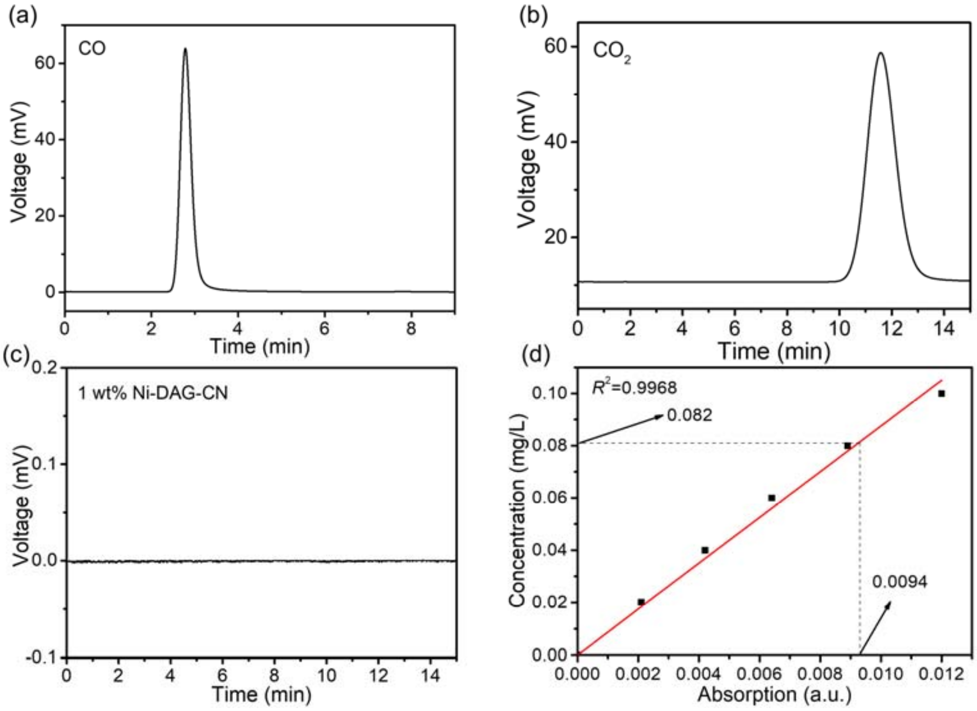

Fig. S9 (a, b, c) GC-FID results of CO, CO_2 and evolved gas from 1 wt% Ni-DAG-CN during photocatalysis. (d) The concentration of acetaldehyde in the solution after photocatalysis obtained by the standard curve.

Table S3. Results of photocatalytic selective oxidation of benzyl alcohol.

Entry	Catalyst [a]	Solvent	Temperature	Conv. (%)	Sel. (%)
1	CN	acetonitrile	RT	28.5	> 99
2	0.5 wt% Ni-DAG-CN	acetonitrile	RT	55.4	> 99
3	1 wt% Ni-DAG-CN	acetonitrile	RT	74.1	> 99
4	2 wt% Ni-DAG-CN	acetonitrile	RT	37.2	> 99
5	3 wt% Ni-DAG-CN	acetonitrile	RT	29.1	> 99
6	1 wt% Ni-DAG-CN [b]	acetonitrile	RT	-	-
7	- [c]	acetonitrile	RT	-	-

[a] Reaction conditions: Photocatalysts: 25 mg, acetonitrile (MeCN): 2.5 ml, benzyl alcohol: 0.2 mmol. H_2O_2: 1 equiv (0.2 mmol). All suspensions were irradiated by LED lamp at 365 nm for 24 h at room temperature (RT) except other specific statement. [b] The reaction was under the dark condition with 1 equiv. H_2O_2. [c] The reaction was under the light condition with 1 equiv. H_2O_2 in the absence of photocatalyst. Conv. denotes conversion. Sel. denotes selectivity.

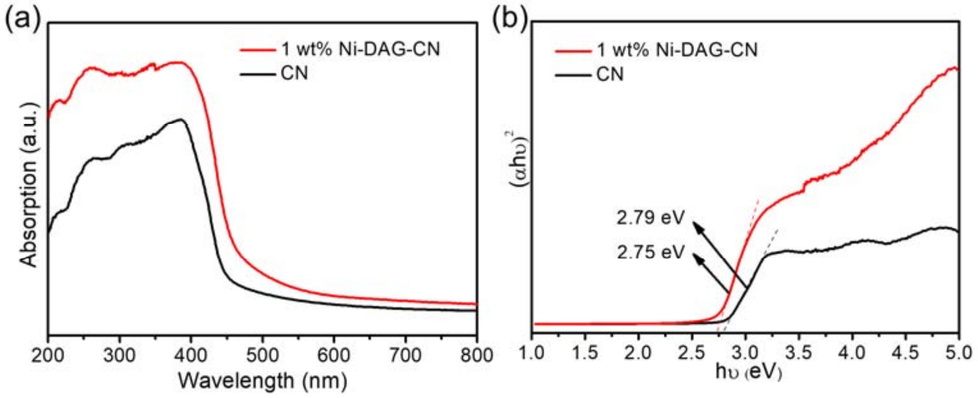

Fig. S10 (a) UV-vis diffuse reflectance spectra and (b) Bandgap calculated by Kubelka-Munk Method.

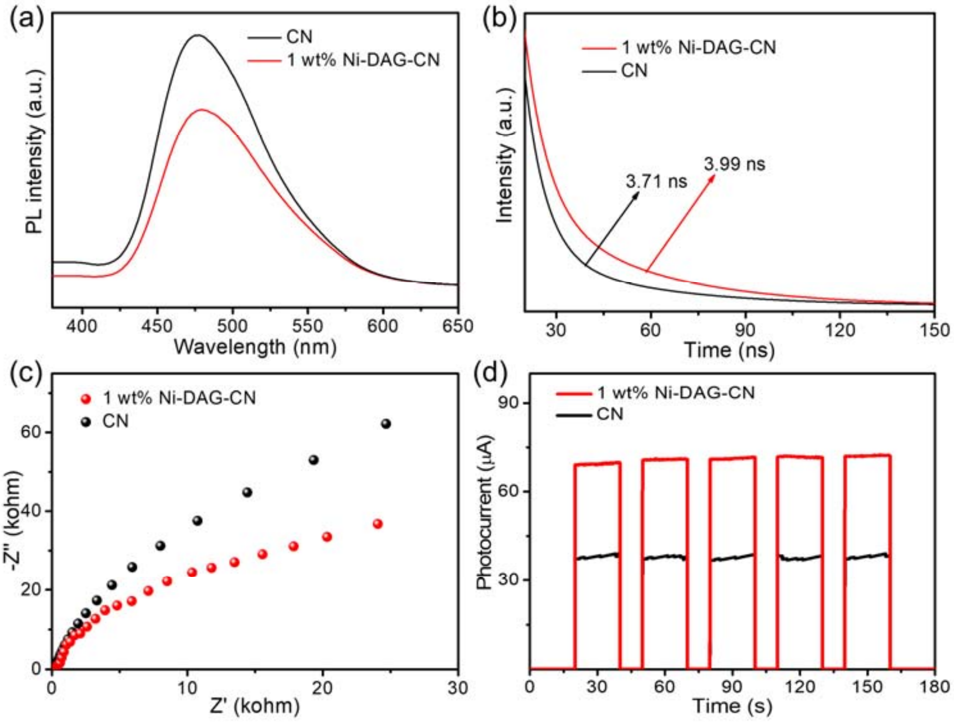

Fig. S11 (a) PL spectra, (b) TRFL spectra, (c) Nyquist plots from EIS, and (d) photocurrent responses of pure CN and 1 wt% Ni-DAG-CN.

Table S4. Theoretical bandgap, HOMO and LUMO of CN and Ni-DAG-CN according to calculation results of constructed models.

Model	HOMO (eV)	LUMO (eV)	Bandgap (eV)
CN	-6.10379	-3.40279	2.70100
Ni-DAG-CN	-5.81181	-3.95518	1.85663

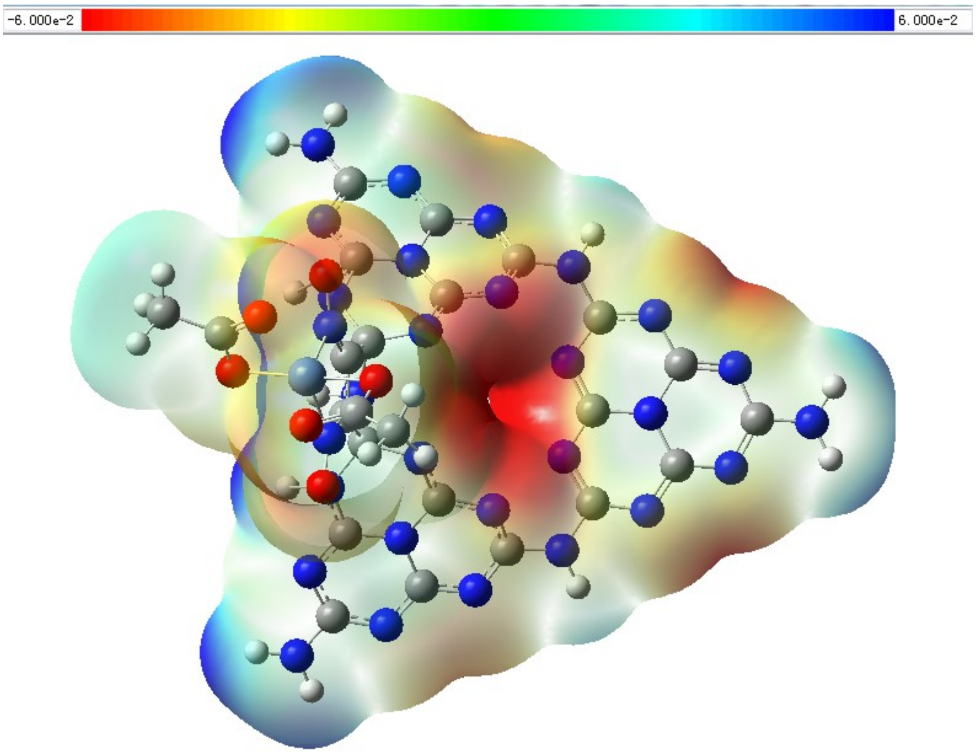

Fig. S12 Electrostatic potential (ESP) map of Ni-DAG-CN model. The red surface corresponds to a region of the lower potential, whereas the blue color corresponds to the higher potential.

Reference

1. L. Kong, Y. Dong, P. Jiang, G. Wang, H. Zhang and N. Zhao, *J. Mater. Chem. A*, 2016, **4**, 9998.

2. R. Liu, H. Yoshida, S.-i. Fujita and M. Arai, *Appl. Catal., B*, 2014, **144**, 41.