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A new Ni-diaminoglyoxime-g-C₃N₄ complex towards efficient photocatalytic ethanol splitting *via* ligand-to-metal charge transfer (LMCT) mechanism

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We report a novel Ni-diaminoglyoxime-g-C₃N₄ (Ni-DAG-CN) complex for photocatalytic H₂ evolution through ethanol splitting. Compare to that of pristine g-C₃N₄, Ni-DAG-CN exhibits a 21-fold enhancement on photocatalytic activity (296.1 μ mol h⁻¹ g⁻¹) under irradiation with excellent stability. The enhanced photocatalytic activity can be attributed to a proposed ligand-to-metal charge transfer (LMCT) mechanism, which is illustrated both experimentally and theoretically. This work provides great potentials to the future design of low-cost, high-performance photocatalysts for alcohol splitting H₂ evolution.

Hydrogen (H_2) is emerging as clean energy to address the urgent energy demand and associated environmental pollution by conventional fossil fuel.¹ While the transportation and storage of H₂ remain a great challenge due to its physical properties,² recent studies revealed promising approaches to tackle this issue by utilizing small molecular alcohols from biomass fermentation as H_2 storage media.³ One main route is to produce H_2 through ethanol reforming, which, however, requires high temperature and pressure, and often includes side reactions with carbonic by-products (CO₂, CH₄ and etc.).^{3a,} ⁴ In this context, alternative explorations on ethanol dehydrogenation to aldehyde via photocatalysis began to attract significant attention due to its high selectivity, mild reaction conditions, and most importantly, the utilization of inexhaustible solar energy.⁵

Graphitic carbon nitride $(g-C_3N_4)$ is a low-cost, stable and toxic-free photocatalyst that has been demonstrated for photocatalytic H₂ evolution.⁶ To enhance its photocatalytic activity, different strategies including heteroatom doping, microstructure modification, and cocatalyst coupling have been explored.⁷ Recently, a unique engineering concept through the metal-to-ligand charge



Scheme 1 Schematic illustration of the synthesis of Ni-DAG-CN complex.

transfer (MLCT) mechanism draws more consideration because the internal low energy electron pathway created through MLCT can significantly expand its photocatalytic potential.⁸ Nevertheless, limitations on cost and catalytic performance still severely hinder its application on photocatalysis.

In this work, we propose a ligand-to-metal charge transfer (LMCT) mechanism with a novel Ni-diaminoglyoxime-g-C₃N₄ complex (denoted as Ni-DAG-CN) for enhanced photocatalytic H₂ evolution from ethanol splitting. Compare to that of pristine g-C₃N₄, the Ni-DAG-CN exhibits a 21-fold enhancement on photocatalytic activity (296.1 µmol h⁻¹ g⁻¹) with excellent photostability. The direct splitting of ethanol into H₂ and aldehyde at room temperature with no CO_x formation is highly desired for future green energy advancement.⁹

The design of the novel Ni-DAG-CN complex was displayed in Scheme 1 and the synthesis details were summarized in ESI. ¹H NMR and FT-IR spectra confirmed the successful fabrication of DAG (Fig. S1).¹⁰ Diffraction peaks at 13.1° and 27.1° in XRD patterns of g-C₃N₄ and 1 wt% Ni-DAG-CN can be attributed to (100) and (002) crystal planes of graphitic materials (JCPDS-87-1526), respectively (Fig. S2).¹¹ Notably, the diffraction peaks of Ni and NiO_x were not presented in the XRD patterns (Fig. S2), suggesting no Ni and NiO_x species in the

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synthesized Ni-DAG-CN complex. TEM and EDX were employed to further verify the state of Ni. The results showed no lattice spacing of Ni or NiO_x nanoparticles in TEM images (Fig. S3a-c), while the corresponding EDX image revealed the existence of Ni element (Fig. S3d). The elemental mapping images demonstrate C, N, Ni, and O elements were uniformly distributed (Fig. S4). In addition, the interaction between the Ni and DAG-CN was revealed by the FT-IR spectra (Fig. S5). Negative shifts were observed from the representative tri-striazine peaks at 809 cm⁻¹ and between 1100 and 1700 cm⁻¹, indicating the coordination bonds formation between the Ni(II) and DAG-CN.¹² The successful incorporation of DAG and Ni in the as-prepared 1 wt% Ni-DAG-CN also resulted in slightly decreased surface area compared to that of g-C₃N₄ (Fig. S6).¹³

To provide insights on the electronic states of Ni-DAG-CN complex, X-ray photoelectron spectroscopy (XPS) was employed. The survey spectrum of 1 wt% Ni-DAG-CN confirmed the existence of C, N, Ni and O elements (Fig. S7a). Two strong peaks of Ni $2p_{3/2}$, Ni $2p_{1/2}$ at 856.4 eV and 873.9 eV and their corresponding satellite peaks confirmed the Ni(II) state in the 1 wt% Ni-DAG-CN sample.¹⁴ The absence of Ni⁰ signals from XPS further indicated the lack of Ni particles in the Ni-DAG-CN.¹⁵ In the O 1s spectrum of 1 wt% Ni-DAG-CN, two peaks at 532.8 eV and 531.6 eV shifted to lower binding energy and a new peak appeared at 530.7 eV, implying a $g-C_3N_4$ structural change after the introduction of DAG and Ni(II) (Fig. S7b). Similarly, no binding energy peaks that can be attributed to NiOx were observed in Ni-DAG-CN complex.¹⁶ In addition, compared to the 288.5 eV found from C 1s spectrum of g-C₃N₄, lower binding energy of C 1S at 288.2 eV was shown in 1 wt% Ni-DAG-CN. The N 1s peaks of 1 wt% Ni- DAG-CN were also shifted to lower



Fig. 1 XPS spectra of CN and 1 wt% Ni-DAG-CN complex: (a) Ni 2p (b) C 1s, (c) N 1s, and (d) photocatalytic H₂ evolution rates of CN and Ni-DAG-CN irradiated by a 300 W Xenon-lamp (λ > 350 nm), (e) H₂ production over 6 h for CN and 1 wt% Ni-DAG-CN (λ > 350 nm), (f) Cyclic H₂ production of 1 wt% Ni-DAG-CN complex.

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binding energy (Fig. 1b, c). These energy shifts not only indicated strong interactions amongoint, 10AG and 10N through complexation, but also suggested a higher electron concentration environment in 1 wt% Ni-DAG-CN according to "electron screening effect".¹⁷ As a result, the promotion of charge separation from g-C₃N₄ to Ni(II) could improve the photocatalytic activity of Ni-DAG-CN.

The Ni-DAG-CN displayed significantly enhanced photocatalytic H₂ evolution from ethanol. The highest hydrogen evolution rate of 296.1 µmol h⁻¹ g⁻¹, which is 21 times higher than that of pristine $g-C_3N_4$, was observed from 1 wt% Ni-DAG-CN (Fig. 1d). Further increment of Ni wt% in Ni-DAG-CN resulted in decrease in H₂ evolution rate, which can be explained by the light shield effect caused by the amount of Ni.¹⁸ Additionally, H₂-evolution performances of 1 wt% Ni/CN and 1 wt% NiO_x/CN were both tested for comparison (Figure S8). The 1 wt% Ni-DAG-CN exhibited much higher H₂-evolution rate than those of 1 wt% Ni/CN and 1 wt% NiO_x/CN. Timedependent H₂ production test showed almost a linear increase in 6 h period (Fig. 1e), and no obvious decline was observed from the 18 h cyclic test (Fig. 1f), suggesting excellent photocatalytic stability of Ni-DAG-CN complex. No CO_x was generated during photocatalysis based on the monitor from an online gas chromatography flame ionization detector (GC-FID) system (Fig. S9a-c). In addition, acetaldehyde was also produced and its concentration in the solution after photocatalysis was determined to be up to 0.082 mg/L (Fig. S9d). Besides fatty alcohol (ethanol), the Ni-DAG-CN complex can be also employed to photocatalytic aromatic alcohol oxidation. Surprisingly, the optimum conversion and selectivity of benzyl alcohol for 1 wt% Ni-DAG-CN reached 74.1% and 99% when irradiated for 24 h, respectively (Table S3). These results suggested that the complexation of Ni and DAG into CN was fundamentally beneficial to alcohol splitting photocatalytic activity and stability.

This significantly enhanced photocatalytic activity from Ni-DAG-CN was further investigated with diverse spectroscopic characterizations for fundamental understandings. Light absorption is a vital factor for photocatalytic reactions. Compared with pristine g-C₃N₄, the increased light absorption of Ni-DAG-CN can contribute to higher photocatalytic H₂ evolution activity (Fig. S10a). The bandgaps of g-C₃N₄ and 1 wt% Ni-DAG-CN were estimated to be 2.79 and 2.75 eV, respectively (Fig. S10b). A significantly decreased slope of Mott-Schottky plots further indicated a contribution to photocatalytic activity enhancement through increased donor densities (Fig. 2a).¹⁹ The band structures of CN and 1 wt% Ni-DAG-CN were illustrated based on the Mott- Schottky plots and valence band (VB)-XPS spectra (Fig. 2b-d), which were consistent with the UV-vis results. Charge separation efficiency is also crucial to photocatalysis apart from light absorption and band structure. Compare to that of pristine g-C₃N₄, 1 wt% Ni-DAG-CN displayed a

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(a) (b) 20 1 wt% Ni-DAG-CN CN 1000 Hz 3000 Hz 5000 Hz /C²(10¹⁵F⁻²cm⁴) 1/C²(10¹² -0.5 0.0 Potential (V) vs NHE -0.5 0.0 Potential (V) vs NHE (d) (c) Ni-DAG-CN 1.23 (Va) Intensity (a.u.) • CN Band Binding Energy (eV)

Fig. 2 (a) Mott-Schottky plots of CN and 1 wt% Ni-DAG-CN at 1000 Hz. (b) Mott-Schottky plots of 1 wt% Ni-DAG-CN at 1000, 3000 and 5000 Hz. (c) VB-XPS of CN and 1 wt% Ni-DAG-CN. (d) Band energy position of CN and 1 wt% Ni-DAG-CN.

lower fluorescence intensity in the photoluminescence (PL) spectra. This observation suggested improved efficiencies of charge separation from 1 wt% Ni-DAG-CN (Fig. S11a).²⁰ In addition, the enhanced charge separation of 1 wt% Ni-DAG-CN can be also verified from timeresolved fluorescence (TRFL), in which a longer lifetime of fluorescence decay was observed (Fig. S11b).²¹ Moreover, the smaller radius of Nyquist plot from electrochemical impedance spectroscopy (EIS) tests (Fig. S11c) and larger photocurrent response (Fig. S11d) both also implied that 1 wt% Ni-DAG-CN possessed better separation of charge carriers compared to that of g-C₃N₄.²²

The above results strongly support that the charge transfer from g-C₃N₄ to Ni(II) could enhance the photocatalytic activity of Ni-DAG-CN complex. Therefore, simulations at the density functional theory (DFT) level were carried out to propose the fundamental mechanism (Fig. 3). As illustrated in this calculation, the charge on the highest occupied molecular orbital (HOMO) of 1 wt% Ni-DAG-CN was mainly distributed on g-C₃N₄, while the charge distribution on its lowest unoccupied molecular orbital (LUMO) was concentrated on Ni(II). Previous studies have demonstrated that the incorporation of Cu(II) and 1,2,4,5-benzenetetracarboxylic acid (BTEC) could lead to narrower bandgaps;¹⁹ similarly, Ni(II) and DAG also played an essential role in reduced bandgaps of Ni-DAG-CN. As shown in Table S4, the calculated theoretical bandgaps of g-C₃N₄ and Ni-DAG-CN were 2.70



Fig. 3 Diagram of charge excitation pathway in the unit model of Ni-DAG-CN.



Fig. 4 Diagram of photocatalytic mechanism for enhanced ethanol splitting according to theoretical calculations and (b) proposed reaction process in details.

and 1.86 eV, respectively. This result confirmed the indispensable role of introduced DAG and Ni(II) for narrowed bandgaps. Moreover, electrostatic potential (ESP) map of Ni-DAG-CN model (Figure S12) was applied to analyze charges of the elements. According to the ESP map result, electron density of metal (Ni) was considerably higher than that of C_3N_4 . This result suggested the electron transfer from CN to Ni(II) via LMCT mechanism. Based on the above analysis, a feasible LMCT mechanism is proposed in Fig. 4. The reduced bandgap and the lower theoretical LUMO of Ni-DAG-CN than that of C₃N₄ are ideal for photocatalytic ethanol splitting for H₂ evolution. Specifically, the Ni-DAG-CN complex can be treated as a heterojunction composed of g-C₃N₄ and Ni-DAG-CN units. Under light irradiation, electrons (e⁻) and holes (h⁺) were generated on the conduction band (CB) and valence band (VB) of CN. Afterward, e⁻ on CB of g-C₃N₄ transferred onto CB of Ni-DAG-CN via LMCT mechanism for enhanced H_2 evolution from ethanol splitting (Fig. 4a). A possible reaction process was illustrated in Fig. 4b. Firstly, h⁺ on VB activated ethanol, forming ethoxy species (•CH₂CH₂OH) and proton (H⁺).²³ •CH₂CH₂OH then interacted with Ni-DAG-CN to provide metastable CH₂CH₂O-Ni-DAG-CN. Afterwards, the formed CH₂CH₂O-Ni-DAG-CN further interacted with Ni-DAG-CN to generate a metastable intermediate which then and H-Ni-DAG-CN.24 dissociated to acetaldehyde Meanwhile, e⁻ on CB can easily transfer to the Ni(II) via the LMCT mechanism, which further reacted with H-Ni-DAG-CN and H⁺ to produce H₂.²⁵

The free energy profiles for the overall reactions were calculated to provide further evidence for on the proposed process (Fig. 5). Step M1 to M2 was an endothermic process. Photons can provide energy to allow this photocatalytic reaction, promoting the interaction between •CH₂CH₂OH and Ni-DAG-CN to form metastable CH₂CH₂O-Ni-DAG-CN. Step M3 to M4 was an exothermic reaction, which provide the reasonability for the further interactions between Ni-DAG-CN and CH₂CH₂O-Ni-DAG-CN. Afterwards, the metastable intermediate generated in the previous step reacted with H• to form acetaldehyde and H-Ni-DAG-CN in the step M5 and M6. Finally, the reaction among H-Ni-DAG-CN, H⁺ and e⁻ transferred via the LMCT mechanism could easily

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Fig. 5 Free energy profiles for the proposed photocatalytic process.

proceed to achieve the H_2 production (step M7 to M8). It is worth to note that the exothermic reactions in previous steps provide the energy required for the latter endothermic reactions in this mechanism; consequently, the calculation results on free energy confirmed the feasibility of the proposed process.

In conclusion, a novel, low-cost Ni-DAG-CN complex was synthesized and displayed a 21-time enhancement of the H₂ evolution rate from ethanol splitting than that of pure g-C₃N₄. The significantly increased photocatalytic activity can be attributed to the proposed LMCT mechanism via the complexation of Ni into g-C₃N₄ with DAG, which was confirmed by both characterizations and theoretical calculations. This work provides great potential to the future design of low-cost, high-performance photocatalysts for alcohol splitting H₂ evolution.

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Conflicts of interest

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There are no conflicts to declare

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A Ni-diaminoglyoxime-g- C_3N_4 complex is developed for photocatalytic ethanol splitting H_2 evolution via a ligand-to-metal charge transfer mechanism.