Integration of Bio-Inspired Lanthanide-Transition Metal Cluster and P-doped Carbon Nitride for Efficient Photocatalytic Overall Water Splitting

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Abstract
Photosynthesis in nature uses the Mn₄CaO₅ cluster as the oxygen-evolving center to catalyze the water oxidation efficiently in photosystem II (PS II). Herein, we demonstrate a bio-inspired heterometallic cluster LnCo₃ (Ln = Nd, Eu and Ce) clusters, which can be viewed as synthetic analogs of CaMn₄O₅ cluster. Anchoring LnCo₃ on phosphorus-doped graphitic carbon nitrides (PCN) shows efficient overall water splitting without any sacrificial reagents. The NdCo₃/PCN-c photocatalyst
exhibits excellent water splitting activity and a quantum efficiency of 2.0 % at 350 nm. Ultrafast transient absorption (TA) spectroscopy revealed the transfer of photoexcited electron and hole into the PCN and LnCo$_3$ for hydrogen and oxygen evolution reactions, respectively. DFT calculation showed the cooperative water activation on lanthanide and O-O bond formation on transition metal for water oxidation. This work not only prepares a synthetic model of bio-inspired oxygen-evolving center but also provides an effective strategy to realize light-driven overall water splitting.

Keywords: bio-inspired, lanthanide-transition metal cluster, photocatalytic overall water splitting, synergistic effects, oxygen-evolving center

INTRODUCTION

Green plants used a cubane-type \{CaMn$_4$O$_5$\} cluster for catalyzing water oxidation reaction in the oxygen evolution center (OEC) of photosystem II (PSII) [1-4], which is a critical half reaction for converting sunlight energy into chemical energies stored in ATP and NADPH. Synergistic effect among the multi-metal centers of OEC plays a key role for the high catalytic activity of PSII [5, 6]. Ca$^{2+}$ serves to adsorb and activate H$_2$O molecule, while Mn with variable oxidation states in the cluster provides the oxidative equivalents. Nature chooses Ca and Mn as the elements to build the cluster, partly because of the availability of the two elements in environment. To mimic nature, we can use any elements available to us. Lanthanide ions can be better Lewis acid than Ca$^{2+}$ and Co is found to be a common element in water oxidation catalysts. As a result, a lanthanide-cobalt cluster may be a good biomimetic water oxidation catalyst [7]. Mimicking the natural photosynthesis, light-driven overall water splitting to produce H$_2$ and O$_2$ including both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is a promising pathway for artificial conversion and storage of solar energy [8-10]. The OER side is usually the rate-determining step. Inspired by the structure model of the PSII, some interesting heterometallic cubane-like clusters have been designed and synthesized to act as bio-inspired water oxidation catalysts [11-16]. Sacrificial agents are used to test
the performance of these catalysts. However, the natural OEC functions in an integrated system to optimize overall efficiency of a sequential of events including charge separation, charge transfer, and catalytical reaction, which diminishes charge recombination. We envisioned that the synthetic biomimetic OECs should also be studied in an integrated system to reveal their true potentials and provide better understanding of the synergistic effect in catalysis on atomic level.

Various approaches have been put forward to build integrated systems for improving the separation and transportation of photo-generated electron-hole pairs [17-21]. For example, close connection between the catalytic center and the photosensitive center can effectively reduce charge recombination rates [22-25]. Assembling bio-inspired OECs on surface of two-dimensional (2D) layered semiconductor materials may enhance photocatalytic overall water splitting, which uses connection between the OEC and the 2D materials as a junction to improve charge separation and fine tune surface electronic structure. Herein, we synthesized a heterometallic cluster LnCo$^{II}$Co$^{III}$$_2$ (LnCo$_3$), which is a structural analog to the CaMn$_4$O$_5$ of PSII. By anchoring the bio-inspired LnCo$_3$ as OEC on phosphorus-doped graphitic carbon nitrides (PCN), we realized light-driven spontaneous overall water splitting to efficiently produce O$_2$ and H$_2$. The NdCo$_3$/PCN-c exhibited remarkable water-splitting activity with high H$_2$ production rate of $\sim$297.7 μmol h$^{-1}$ g$^{-1}$ and O$_2$ evolution rate of 148.9 μmol h$^{-1}$ g$^{-1}$ under light irradiation. The photoexcited electron-hole pairs would be easily dissociated and transferred into the PCN and LnCo$_3$ to participate in HER and OER, respectively.

RESULTS AND DISCUSSION

LnCo$_3$ was synthesized by reacting Ln(NO$_3$)$_3$, Co(Ac)$_2$ and bis-tris-propane (btp) in methanol solution. The LnCo$_3$’s are isostructural. Here we only describe structure of NdCo$_3$ as a representative in detail. Single X-crystal structural analysis showed that NdCo$_3$ crystallizes in monoclinic P2(1)/n space group and contains one [NdCo$^{II}$Co$^{III}$_2(btp-3H)$_2$(Ac)$_2$(NO$_3$)$_2$]$^+$ cation core, one nitrate ions and two guest water molecules. In the metal core, each Co$^{3+}$ is chelated by two N and three O atoms from
one deprotonated bis-tris-propane (btp-3H) ligand, to form one stable [Co$^{III}$](btp-3H)] unit (Supplementary Fig. 1). One Co$^{2+}$ and one Nd$^{3+}$ ion connect two [Co$^{III}$](btp-3H)] units by coordinating to the six bridging-O and two bridging-COO$^{-}$ from two btp-3H ligands, generating the heterometallic tetranuclear structure [NdCo$^{II}$Co$^{III}$O$_2$(btp-3H)$_2$]$.^{5+}$ (Fig. 1a). In addition, two Ac$^{-}$ ligands bridge the Nd$^{3+}$ and its neighboring Co$^{3+}$. There are two NO$_3^{-}$ anions coordinated to one Nd$^{3+}$ in chelated bidentate (μ$_2$) mode. The adjacent Nd$^{3+}$, Co$^{2+}$, Co$^{3+}$ and three bridging O’s from one btp-3H ligand form a defective cubane [NdCo$^{II}$Co$^{III}$O$_3$] motif. Two [NdCo$^{II}$Co$^{III}$O$_3$] connect by sharing faces, resulting in [NdCo$^{II}$Co$^{III}$] core (Fig. 1b). The distances of Co$^{II}$-O range from 1.988 to 2.147 Å, and the distances of Co$^{III}$-O/Co$^{III}$-N range from 1.870 to 1.966 Å, both of which are consistent with the reported values of other cobalt structures [26-28]. According to the theoretical calculation formula of valence bond, BVS = exp ((R$_0$-R)/B), the states of the metal ions and the pronation states of each oxygen and nitrogen atom of the organic ligand were calculated. As shown in Supplementary Table 11 and 12, the calculated results show that the oxidation states of all the lanthanide ions are +3 and the oxidation states of Co1 and Co2 are +2 and +3; the O7, O9 and O10 in btp-3H ligands show the O$^{2-}$ state, while the O6, O5 and O8 atoms exhibit OH$^{-}$ states.

Interestingly, the heterometallic cluster [NdCo$^{II}$Co$^{III}$] mimics the structure of CaMn$_4$O$_5$ of PSII. Considering the monotonic change in radius and chemical properties of the lanthanides, it was an attractive choice for investigating the physical characteristics of the clusters [29]. In addition, due to the similarities in their ionic radii and high coordination numbers of lanthanide ions and Ca$^{2+}$, they can be exchanged in biological systems [30, 31]. As shown in Fig. 1, topologically, the NdCo$_3$ cluster can be viewed as the CaMn$_4$O$_5$ missing one metal vertex from the cubane and adding one bridging-O atom between Nd$^{3+}$ and Co$^{3+}$. In addition, the coordination mode of bridging-O in NdCo$_3$ cluster is also very similar to that in CaMn$_4$O$_5$ of PSII, except for the five bridging-O atoms are O$^{2-}$ in biological CaMn$_4$O$_5$-cluster, while six bridging-O atoms are come from the -OH groups of two btp-3H ligands in NdCo$_3$. Notably, the mixed oxidation states of the cobalt ions (+2
and +3) in NdCo$_3$ cluster are similar to the mixed oxidation states of manganese ions in CaMn$_4$ (+3 and +4), suggesting that the NdCo$_3$ cluster can be viewed as a synthetic model of the OEC [32-35]. Compared with the CaMn$_4$O$_5$, the NdCo$_3$ cluster shows high stability because of the presence of a chelating btp-3H ligand. High-resolution electro-spray ionization mass spectrometry (HRESI-MS) of NdCo$_3$ in methanol shows main peaks in the range from 1242 to 1252, which correspond to the $\{[\text{NdCo}_3(\text{btp-3H})_2(\text{Ac})_2(\text{NO}_3)_2](\text{NO}_3)_2]^{-}\}$ and the dimer structure $\{[\text{NdCo}_3(\text{btp-3H})_2(\text{Ac})_2(\text{NO}_3)_2](\text{NO}_3)_2\}_2^{2-}$ (Supplementary Fig. 3). This result indicates that the NdCo$_3$ cluster remains intact in methanol solution. The EuCo$_3$ and CeCo$_3$ clusters show the same crystal structure as NdCo$_3$ (Supplementary Fig. 4).

Based on the stability of the cluster in methanol solution, anchoring NdCo$_3$ clusters on phosphorus-doped graphitic carbon nitrides (PCN) was prepared as shown in Fig. 2a. 45 mg of prepared PCN was dispersed in methanol solution (3 mg/mL) with sonication and then transferred to flask with stirring. 1 mL of NdCo$_3$ methanol solution (1, 2, 3, 5 and 7 mg mL$^{-1}$) was dripped into the PCN suspension and refluxed for 12 h. The resultant precipitates were collected by filtration and dried at 70 °C overnight, resulting in NdCo$_3$/PCN samples with different loading amounts of the clusters (as measured by inductively coupled plasma mass spectrometry [ICP-MS]) are denoted NdCo$_3$/PCN-a (0.36 wt%), NdCo$_3$/PCN-b (0.61 wt%), NdCo$_3$/PCN-c (1.05 wt%), NdCo$_3$/PCN-d (1.55 wt%), and NdCo$_3$/PCN-e (2.03 wt%) (Supplementary Table 6).

Transmission electron microscopy (TEM) shows that the obtained NdCo$_3$/PCN exhibits the morphology of nanosheets (Fig. 2b). To determine the distribution of the NdCo$_3$ clusters, atomic-resolution high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) measurement was performed. The isolated bright dots in Fig. 2d can be assigned to NdCo$_3$ clusters. Elemental mapping analysis of the STEM images revealed that the Nd, Co and P atoms are uniformly distributed throughout the nanosheets (Fig. 2e), demonstrating good dispersion of NdCo$_3$ clusters on the PCN support.
Extended X-ray absorption fine structure (EXAFS) of NdCo$_3$ and NdCo$_3$/PCN-c were performed to probe the first coordination sphere of Co$^{3+}$/Co$^{2+}$ metal centers. As displayed in Fig. 3a, the Co K-edge X-ray absorption near edge spectroscopy (XANES) of NdCo$_3$ cluster gives a rising edge between that of CoO and Co$_2$O$_3$, indicating that Co centers in NdCo$_3$ have mixed oxidation states of +2 and +3, which is consistent with the crystal structure analysis. The XANES spectrum of Co centers in NdCo$_3$/PCN is very similar to that of isolated NdCo$_3$ cluster, suggesting that the Co oxidation states in NdCo$_3$ remain the same during the assembly on PCN. The pre-edge of the NdCo$_3$ and NdCo$_3$/PCN-c manifested that Co ions are maintaining an octahedral coordination [36]. As shown in Fig. 3b, the Fourier transform (FT) peak of the extended region of the spectrum (EXAFS) at 1.43 Å contain both Co-O and Co-N coordination. An emerging peak at 1.59 Å after anchoring the cluster on PCN could be ascribed to Co-P coordination with P from PCN. The EXAFS also confirm that no Co nanoparticles were formed in the reaction. A peak at a high R value (ca. 2.60 Å) corresponds to the distance of Co…Co path, which is also present in the as-prepared cluster. As shown in Supplementary Fig. 6, the experimental and fitting FT-EXAFS curve of Nd$^{3+}$ (Nd L$_{III}$ Edge) in NdCo$_3$/PCN-c can be perfectly matched, which indicating that Nd$^{3+}$ in NdCo$_3$/PCN-c and the sample after reaction have the same coordination environment. The X-ray photoelectron spectroscopy (XPS) of NdCo$_3$/PCN-c shows characteristic peaks of Nd 3d and Co 3d (Supplementary Fig. 7). Co 2p XPS spectra show different oxidation states of Co ions in NdCo$_3$ cluster on PCN nanosheets (Fig. 3c). The P 2p XPS spectra for the NdCo$_3$/PCN-c sample displayed two peaks at 129.5 and 133.1 eV, which can be attributed to P with and without Co-P connections, respectively (Fig. 3d), and no peak related to Co-P showed up in the PCN spectra [36-38]. This XPS result suggests that P atoms coordinated with Co ion in NdCo$_3$ cluster. According to the EXAFS and XPS results, the NdCo$_3$ cluster was anchored on the PCN through Co-P bonds and remained intact during the assembling process. The linker model of NdCo$_3$/PCN-c was shown in Fig. 2a.

The photocatalytic overall water splitting performance of NdCo$_3$/PCN-c catalysts were evaluated in pure water without any sacrificial reagents under
simulated solar illumination (see details in Supporting Information). As shown in Fig. 4a, \( \text{NdCo}_3/\text{PCN-c} \) with different cluster loadings on PCN display different photocatalytic activities under light (\( \lambda > 300 \) nm) irradiation. With increasing loading from 0.31 to 1.05 wt\%, the photocatalytic activity of \( \text{NdCo}_3/\text{PCN-c} \) improved because of increased number of active sites for OER. The \( \text{NdCo}_3/\text{PCN-c} \) with the loading of 1.05 wt\% \( \text{NdCo}_3 \) shows the highest photocatlytic H\(_2\) production rate of 297.7 μmol h\(^{-1}\) g\(^{-1}\) and O\(_2\) production rate of 148.9 μmol h\(^{-1}\) g\(^{-1}\), which is approximately 7.2 times than that of PCN without loading clusters. Further increasing the loading of \( \text{NdCo}_3 \) to 1.55 and 2.03 wt\% leads to slightly reduced H\(_2\) and O\(_2\) production rates, possibly due to competitive transfer of holes to adjacent clusters, which decreases the chance of transferring four electrons to the same OEC to complete the whole OER process. As shown in Fig. 4b, the time course of simultaneous evolution of H\(_2\) and O\(_2\) gases of \( \text{NdCo}_3/\text{PCN-c} \) display a constant H\(_2\)/O\(_2\) stoichiometric ratio of 2:1, suggesting the occurrence of overall water splitting. The \( \text{NdCo}_3/\text{PCN-c} \) catalyst was recovered and reused four times without significant decrease in photocatalytic activity. A time course of H\(_2\) and O\(_2\) production of \( \text{NdCo}_3/\text{PCN-c} \) under visible light irradiation (\( \lambda > 420 \) nm) was also studied. As displayed in Supplementary Fig. 9 and 10, \( \text{NdCo}_3/\text{PCN-c} \) shows about 210.4 μmol g\(^{-1}\) of H\(_2\) production rate and 105.7 μmol g\(^{-1}\) of O\(_2\) production rate in 12 hours under visible light irradiation. The quantum efficiency closely followed that of ultraviolet-visible (UV-vis) absorbance trend, revealing that the reaction was driven by light absorption by the catalyst (Fig. 4c). Specifically, the \( \text{NdCo}_3/\text{PCN-c} \) achieves a photocatalytic quantum efficiency of 2.0 % at 350 nm and retains a quantum efficiency of 1.2% at the visible-light wavelength of 420 nm. To study the catalytic activity of \( \text{NdCo}_3 \) itself, the CV and LSV measurements were performed in the cell equipped with three electrodes, working electrode, counter electrode (Pt plate) and reference electrode (Ag/AgCl) in 0.5 M NaAc/HAc buffer solution (pH = 6). As shown in Supplementary Fig. 11, the \( \text{NdCo}_3 \) cluster has obviously water oxidation catalytic activity. The overpotential for \( \text{NdCo}_3 \) is 325 mV to reach 1 mA cm\(^{-2}\). The photocatalytic OER activity of \( \text{NdCo}_3 \) cluster itself was also studied in 20 mL 0.5 M NaAc/HAc (pH = 8) buffer solution using 1
mM [Ru(bpy)$_3$]Cl$_2$ as photosensitizer, 5 mM Na$_2$S$_2$O$_8$ as sacrificial reagent. Under $\lambda \geq 420$ nm light irradiation, the NdCo$_3$ cluster shows the photocatalytic O$_2$ production rate of 9.5 μmol h$^{-1}$ g$^{-1}$, which is close to the 11.5 μmol h$^{-1}$ g$^{-1}$ O$_2$ evolutions of NdCo$_3$/PCN-c (Supplementary Fig. 12). The close values of photocatalytic O$_2$ production rate of NdCo$_3$ and NdCo$_3$/PCN-c suggest that the OER rate is still the rate-determining step for the overall water splitting of NdCo$_3$/PCN-c.

The TEM image and HAADF-STEM image of NdCo$_3$/PCN-c after photocatalysis show that the morphology of NdCo$_3$/PCN remained unchanged after the photocatalytic reaction (Supplementary Fig. 13). ICP-MS studies revealed that less than 0.3% clusters leached into the solution after reaction of 12 h, indicating the stability of NdCo$_3$/PCN-c. The stability of clusters is not only due to the chelating effect of the bis-tris-propane ligand but also due to the Ln$^{3+}$ ions that stabilize the 3d-4f cubane structure [39, 40]. To verify the role of the lanthanide on the photocatalytic activities, the isostructural EuCo$_3$/PCN and CeCo$_3$/PCN clusters were also studied. As shown in Fig. 4d, under light ($\lambda > 300$ nm) irradiation, EuCo$_3$/PCN and CeCo$_3$/PCN show the photocatalytic H$_2$ production rate of 279.1 and 274.5 μmol h$^{-1}$ g$^{-1}$ respectively, which are close to that of NdCo$_3$/PCN-c. The time courses of H$_2$ and O$_2$ evolutions of EuCo$_3$/PCN and CeCo$_3$/PCN in 12 hours under light ($\lambda > 300$ nm) irradiation were displayed in Supplementary Fig. 14 and 15. To exclude the contribution of other species for the catalytic activity in this system, the control experiments by combining CoO, Co$_3$O$_4$ and Co(Ac)$_2$, Nd(NO$_3$)$_3$ with PCN as the photocatalysts respectively for overall water splitting based on the same method as that of NdCo$_3$ was performed. As shown in Supplementary Fig. 16, CoO/PCN, Co$_3$O$_4$/PCN and Nd(NO$_3$)$_3$/PCN showed very low catalytic activity. Although the Co(Ac)$_2$/PCN can gave rise to significant capability of water splitting (H$_2$ production rate of 126.4 μmol h$^{-1}$ g$^{-1}$), compared with the activity of [Co(Ac)$_2$+Nd(NO$_3$)$_3$]/PCN under the same conditions, the NdCo$_3$/PCN-c shows the much higher performance with 297.7 μmol h$^{-1}$ g$^{-1}$. These control experiments suggested that the NdCo$_3$ itself boost the activity in the system.

Electrochemical impedance spectroscopy (EIS) Nyquist plots and the transient
photocurrent were measured to characterize the electron-hole transfer efficiency. \( \text{NdCo}_3/\text{PCN-c} \) has a much smaller semicircle diameter and lower interfacial charge-transfer resistance than those of PCN, demonstrating the enhanced interfacial charge transfer of \( \text{NdCo}_3/\text{PCN-c} \) (Supplementary Fig. 17). Consistently, \( \text{NdCo}_3/\text{PCN-c} \) has better photocurrent responses under irradiation than that of PCN (Supplementary Fig. 18). Photoluminescence (PL) and the time-resolved fluorescence spectra of PCN and \( \text{NdCo}_3/\text{PCN-c} \) were performed (Supplementary Fig. 19a). They were monitored at 430 nm under irradiation by a 368 nm laser at room temperature. Time-resolved fluorescence spectra revealed the average lifetimes of approximately 2.17 and 1.91 ns for \( \text{NdCo}_3/\text{PCN-c} \) and PCN, respectively (Supplementary Fig. 19b).

The photocatalytic \( \text{H}_2 \) or \( \text{O}_2 \) production reaction in the presence of hole acceptor or electron acceptor could be performed to reveal more details about the two processes. The photocatalytic \( \text{H}_2 \) evolution of \( \text{NdCo}_3/\text{PCN-c} \) was enhanced in the presence of \( \text{CH}_3\text{OH} \) as hole acceptor as compared to that without sacrificial agent (Supplementary Fig. 20), indicating that the intrinsic catalytic activity of the HER side is higher than that exhibited in overall water splitting. The rate-determining step is thus likely on the OER side. However, the photocatalytic \( \text{O}_2 \) evolution of \( \text{NdCo}_3/\text{PCN-c} \) in the presence of \( \text{AgNO}_3 \) as electron acceptor was slower than that without sacrificial agent (Supplementary Fig. 21), which suggests that hole injection into \( \text{NdCo}_3 \) is not the rate-determining step in the OER [41]. We thus conclude that the OER rate is still limited by catalysis.

Femtosecond time-resolved transient absorption (fs-TA) spectroscopy was used to detect the ultrafast excited state dynamics of the system (Supplementary Fig. 22) [42, 43]. The dynamics in the fs-ps time scale can be fitted to a five-component exponential model as shown by the time trace at 520 nm (excited at 360 nm) (Fig. 5a, b). In the initial 100 ps, negative signals due to ground state bleach (GSB) are prominent, which reflect the behavior of holes on the valence band (VB). Evolution of the initial GSB signal can be described by three time constants: \( \tau_1 = 1.02 \text{ ps} \), \( \tau_2 = 4.46 \text{ ps} \), \( \tau_3 = 69.8 \text{ ps} \) for PCN, and \( \tau_1 = 0.14 \text{ ps} \), \( \tau_2 = 1.76 \text{ ps} \), \( \tau_3 = 54.5 \text{ ps} \) for \( \text{NdCo}_3/\text{PCN-c} \). The \( \tau_1 \) and \( \tau_2 \) correspond to initial vibrational cooling of energetic holes, and \( \tau_3 \) may
be attributed to hole transfer process to surface trap site. Compared to PCN sample in the early 100 ps, NdCo₃/PCN-c has shorter relaxation times of all the three components. The accelerated hole transfer rate may be related to fast hole transfer to the NdCo₃ cluster in NdCo₃/PCN-c. After a few hundred picoseconds, electrons and holes complete the transfer to trap states. The TA signals of both PCN and NdCo₃/PCN-c samples showed a significant signal growth on the timescale of hundreds of ps to ns (τ₄). This growth may be due to stimulated emission (SE) from trap states, which are supported by fluorescence lifetimes on ns timescale. The NdCo₃/PCN-c sample shows a longer τ₄ time than PCN (τ₄ =1.84 ns for NdCo₃/PCN-c vs τ₄ =1.24 ns for PCN) because hole transfer to the cluster competes against populating the surface trap sites and thus delays the emissive electron-hole recombination. The fifth time constant (τ₅ =2.39 ns for NdCo₃/PCN-c vs τ₅ =1.81 ns for PCN) represents the fluorescence process, which is consistent with the result from time-resolved fluorescence (Supplementary Fig. 19b). The τ₅'s determined by TA spectra are not very accurate due to the limited number of points on the long waiting time. Based on these analyses, we can understand the reason why NdCo₃/PCN-c improves higher photocatalytic performance (Fig. 5c). The cluster not only acts as a reaction center for water oxidation but also suppresses electron-hole recombination due to fast hole injection into the clusters. This efficient hole transfer leads to an increase in hole utilization and finally improves the overall efficiency.

To further investigate the catalytic OER, spin polarized DFT+ U calculations were carried out using the VASP software [44]. NdCo₃ clusters can easily lose two Ac⁻ ligands from the Nd³⁺ and Co³⁺ ions in aqueous solution, resulting in two coordination unsaturated sites (CUS). A series of geometrical optimizations reveals that the CUS of one Co (III) ions prefers to coordinate with PCN by the anchoring site of P atom (dₚ-Co = 2.436 Å) with an adsorption energy of -1.01 eV, while another Co³⁺ (CUS) can serve as the catalytic center. Water molecule adsorbs on this CUS of Co³⁺ ions with a dₚ-O of 2.191 Å and adsorption energy (E_ads) of -0.74 eV. Both charge density difference and Electron Localization Function (ELF) value (around 0.5) suggest that the 3d orbital of Co³⁺ (CUS) ions effectively overlap with 2p orbital of O₇, resulting in the
formation of one weak coordination bond. Partial density of states curves of spin up and spin down indicate that spin carriers (e.g. Nd and Co ions, P and N of C₃N₄) present apparent spin polarization at the vicinity of Fermi level (Supplementary Fig. 25). Moreover, possible reaction intermediate species of *OH, *O, *OOH exhibits strong adsorption on this reaction center \( E_{\text{ads}} = -3.14 \text{ eV for } *\text{OH}, -3.94 \text{ eV for } *\text{O and } -1.22 \text{ eV for } *\text{OOH} \). While \( \text{H}_2\text{O} \) and *OH only locates on the CUS of Co\(^{3+}\) ion, *O and *OOH attach to both Co\(^{3+}\) ion and Nd\(^{3+}\) ion. The highly charged Nd\(^{3+}\) effectively stabilized these electron-rich intermediate to facilitate water oxidation.

Oxidation states of metal ions are poorly described by Bader charge calculation \([45]\). As a result, magnetic moments were evaluated to assist oxidation state identification, considering their similar coordination field from oxygen atoms \([46]\). The spin states of each intermediate were investigated by using symmetry-broken calculations (Supplementary Table 5). Initially, both Co (P) and Co (CUS) ions feature low spin state Co\(^{III}\) ions, while the middle divalent Co(M) ion features high spin state Co\(^{II}\) ion. After two hole injections to the cluster, the water molecule attached to the Co\(^{III}\)(CUS) ion is deprotonated and converted to *OH. The injected two holes bring the Co\(^{III}\)(P), Co\(^{II}\)(M), and Co\(^{III}\)(CUS) ions to the oxidation states of +4, +3, +3, respectively. Then, another hole injection induced the deprotonation of *OH, yielding bridging *O in Co\(^{IV}\)(CUS)-oxo-Nd\(^{III}\) (spin magnetization of 2.875 \( \mu_B \) on Co). The Co\(^{IV}\)(CUS)-oxo is electron deficient, which is an ideal target for a nucleophilic attack by a second water in a concerted process of forming one O-O bond and one O-Nd\(^{III}\) coordination while losing one proton upon injection of another hole. A bridging *OOH species and high oxidation state Co\(^V\)(CUS)-hydroperoxyl-Nd\(^{III}\) (spin magnetization of -2.648 \( \mu_B \) on Co) is formed. Finally, the liberation of \( \text{O}_2 \) from the cluster with concomitant deprotonation and reduction of the cluster to regenerate its initial oxidation state happens at low activation energy. Generally speaking, the Ln\(^{3+}\) ion stabilizes negatively charged intermediates, and the other two Co ions that are not directly attached to water molecules serve as hole reservoirs to store oxidation equivalents and thus avoid the building-up of too high oxidation potential on one Co ion. All four metal ions in the cluster synergistically
catalyze the water oxidation (Supplementary Fig. 28).

CONCLUSION

In summary, we demonstrated a bio-inspired lanthanide-transition metal cluster as oxygen-evolving center anchored on P-doped graphitic carbon nitrides for efficient photocatalytic overall water splitting. The obtained \( \text{LnCo}_3 \) clusters not only display high stability but also show excellent oxygen-evolving activity. The combination of \( \text{LnCo}_3 \) clusters and PCN achieves efficient separation of electrons and holes and enables rapid production of \( \text{H}_2 \) and \( \text{O}_2 \). Mechanistic investigation shows synergistic effects of lanthanide ion and variable-valence Co ions in the oxygen-evolving reaction. This work not only prepares a synthetic model of bio-inspired oxygen-evolving center but also develops an avenue to design efficient catalysts for overall water splitting by coupling bio-inspired clusters and photoactive supports.

METHODS

Synthesis of \([\text{NdCo}_3(\text{btp-3H})_2(\text{Ac})_2(\text{NO}_3)_2] \cdot (\text{NO}_3) \cdot 2\text{H}_2\text{O}\).

A mixture of \( \text{Nd(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (0.438 g, 1 mmol), \( \text{Co(Ac)}_2 \cdot 4\text{H}_2\text{O} \) (0.125 g, 0.5 mmol), and bis-tris-propane (btp, 0.141 g, 0.5 mmol) were dissolved in methanol (10.0 mL); followed by the addition of trimethylamine (150 \( \mu \)L). The mixture was heated to reflux for 40 minutes and then filtered after cooling. Lamella-shaped brown crystals of \( \text{I} \) were obtained in 35% yield (based on \( \text{Nd(NO}_3)_3 \cdot 6\text{H}_2\text{O} \)) after the filtrate was kept at room temperature for 1 week. For \( \text{C}_{26}\text{H}_{56}\text{N}_7\text{Co}_3\text{NdO}_{27} \) (FW = 1219.8): C, 25.60; H, 4.63; N, 8.04. Found: C, 25.43; H, 4.85; N, 8.08.

Synthesis of P-doped \( \text{C}_3\text{N}_4 \) photocatalyst (PCN).

A mixture of 0.5 g the prepared \( \text{C}_3\text{N}_4 \) and 0.25 g \( \text{NaH}_2\text{PO}_2 \) grind with motar. Then, the mixture was heated to 350 \( ^\circ \text{C} \) in 2 \( ^\circ \text{C} /\text{min} \) in muffle furnace and then heated for 2 h in a \( \text{N}_2 \) atmosphere. The resultant precipitate was ultrasonicated and washed with water and ethanol for twice, collected by filtration and dried at 70 \( ^\circ \text{C} \) overnight.
**Synthesis of NdCo$_3$/PCN photocatalysts.**

45 mg PCN was dispersed in methanol solution (3 mg/mL) with sonication, and then transferred to flask with stirring, then 1 mg, 2 mg, 3 mg, 5 mg and 7 mg NdCo$_3$ cluster in 1 mL methanol were dropped into the suspension and refluxed for 12 h, respectively. The resultant precipitate was collected by filtration and dried at 70 °C overnight.

**Photocatalytic reactions.**

The photocatalytic experiments were performed via a photocatalytic evaluation system (CEL-SPH2N, CEAULight, China) in a 300 mL Pyrex flask. A 300 W Xenon arc lamp with a wavelength range of 300-800 nm was used as the light source. The focused intensity on the flask was about 200 mW·cm$^{-2}$. In a typical photocatalytic experiment, 40 mg of photocatalyst was suspended in aqueous solution. Before irradiation, the system was vacuumed for 10 min via the vacuum pump to completely remove the dissolved oxygen. The evolved gases contents were analyzed by gas chromatography (GC7920, CEAULight, China). The apparent quantum efficiency (QE) was measured under the identical photocatalytic reactions. Single wavelength 365 nm, 420 nm, 450 nm, 500 nm and 600 nm filters were employed as the light sources to trigger the photocatalytic reactions, respectively.

**Photochemical studies.**

Cyclic voltammograms (CV), Electrochemical Impedance Spectroscopy (EIS) data, photocurrent and the Mott–Schottky spots were recorded using Electrochemical workstation (CHI 760E, Shanghai Chenhua). The Indium tin oxide (ITO) glasses with samples were served as the working electrodes. Electrochemical impedance spectra (EIS) measurements were recorded over a frequency range of 100 kHz-200 kHz with ac amplitude of 20 mV at 0 V. Water was used as the supporting electrolyte. The Mott-Schottky plots were also measured over an alternating current (AC) frequency of 1,000 Hz, 1,200 Hz and 1,500 Hz. These three electrodes were immersed in the 0.2 M Na$_2$SO$_4$ aqueous solution (pH = 6.6).
All other experimental details, as well as TA spectroscopy characterizations and the DFT calculations, are provided in the Supplemental Experimental Procedures.

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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AUTHOR CONTRIBUTIONS

R.C. and X.-J.K. designed research; R.C. synthesized and characterized the compound. Z.-Y.W. measured TA spectra. Y.-J.G. and G.-L.Z. performed the DFT calculations. Y.Z. synthesized the cluster. Z.L. analyzed the XAS data. M.-H.D. performed the ESI-MS experiments. S.-Y.Z. performed the TEM. X.-J.K., C.W., L.-S.L. and L.-S.Z. analyzed data. R.C. and X.-J.K. wrote the manuscript with contributions from all authors. All authors discussed the results and commented on the manuscript. We also thanks Chao-Long Chen for repeating the experiments.

Conflict of interest statement. None declared.

References

1. Zhang C, Chen C, Dong H, Shen J R, Dau H and Zhao J. A synthetic Mn₄Ca-cluster
mimicking the oxygen-evolving center of photosynthesis. *Science* 2015; **348**: 690-693.

2. Wigginton N. S. Mimicking the oxygen evolution center. *Science* 2015; **348**: 644-646.

3. Umena Y, Kawakami K, Shen J R and Kamiya N. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature* 2011; **473**: 55-60.

4. Sun L. A closer mimic of the oxygen evolution complex of photosystem II. *Science* 2015; **348**: 635-636.

5. Barber J. Photosynthetic Water Splitting Provides a Blueprint for Artificial Leaf Technology. *Joule* 2017; **1**: 5-9.

6. Barber J. A mechanism for water splitting and oxygen production in photosynthesis. *Nat. Plants* 2017; **3**: 17041.

7. Evangelisti F, Moré R, Hodel F, Luber S and Patzke G R. 3d–4f {CoII₃Ln(OR)₄} Cubanes as Bio-Inspired Water Oxidation Catalysts. *J. Am. Chem. Soc.* 2015; **137**: 11076-11084.

8. Wang Z, Li C and Domen K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* 2019; **48**: 2109-2125.

9. Zhang B and Sun L. Artificial photosynthesis: opportunities and challenges of molecular catalysts. *Chem. Soc. Rev.* 2019; **48**: 2216-2264.

10. Ye S, Ding C, Liu M, Wang A, Huang Q and Li C.. Water Oxidation Catalysts for Artificial Photosynthesis. *Adv. Mater.* 2019; **31**: 1902069.

11. Ullman A M, Liu Y, Huynh M, Bediako D K, Wang H, Anderson B L, Powers D C, Breen J J, Abruna H D and Nocera D G. Water Oxidation Catalysis by Co(II) Impurities in Co(III)₄O₄ Cubanes. *J. Am. Chem. Soc.* 2014; **136**: 17681-17688.

12. Stracke J J and Finke R G. Electrocatalytic Water Oxidation Beginning with the Cobalt Polyoxometalate \([\text{Co}_4\text{(H₂O)}_2\text{(PW}_9\text{O}_{34})_2]\)^{10⁻}: Identification of Heterogeneous CoOx as the Dominant Catalyst. *J. Am. Chem. Soc.* 2011; **133**: 14872-14875.

13. McCool N S, Robinson D M, Sheats J E and Dismukes G C. A Co₄O₄ “Cubane” Water Oxidation Catalyst Inspired by Photosynthesis. *J. Am. Chem. Soc.* 2011;
14. Evangelisti F, Güttinger R, Moré R, Luber S and Patzke G R. Closer to Photosystem II: A Co₄O₄ Cubane Catalyst with Flexible Ligand Architecture. *J. Am. Chem. Soc.* 2013; 135: 18734-18737.

15. Berardi S, La Ganga G, Natali M, Bazzan I, Puntoriero F, Sartorel A, Scandola F, Campagna S and Bonchio M. Photocatalytic Water Oxidation: Tuning Light-Induced Electron Transfer by Molecular Co₄O₄ Cores. *J. Am. Chem. Soc.* 2012; 134: 11104-11107.

16. Song F, Moré R, Schilling M, Smolentsev G, Azzaroli N, Fox T, Luber S and Patzke G R. {Co₄O₄} and {CoₓNi₄₋ₓO₄} Cubane Water Oxidation Catalysts as Surface Cut-Outs of Cobalt Oxides. *J. Am. Chem. Soc.* 2017; 139: 14198-14208.

17. Chen X, Shi R, Chen Q, Zhang Z, Jiang W, Zhu Y and Zhang T. Three-dimensional porous g-C₃N₄ for highly efficient photocatalytic overall water splitting. Nano Energy 2019; 59: 644-650.

18. Kumar P, Vahidzadeh E, Thakur U K, Kar P, Alam K M, Goswami A, Mahdi N, Cui K, Bernard G M, Michaelis V K and Shankar K. C₃N₅: A Low Bandgap Semiconductor Containing an Azo-Linked Carbon Nitride Framework for Photocatalytic, Photovoltaic and Adsorbent Applications. *J. Am. Chem. Soc.* 2019; 141: 5415-5436.

19. Che W, Cheng W, Yao T, Tang F, Liu W, Su H, Huang Y, Liu Q, Liu J, Hu F, Pan Z, Sun Z and Wei S. Fast Photoelectron Transfer in (Cring)–C₃N₄ Plane Heterostructural Nanosheets for Overall Water Splitting. *J. Am. Chem. Soc.* 2017; 139: 3021-3026.

20. Ran J, Ma T Y, Gao G, Du X W and Qiao S Z. Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H₂ production. *Energ. Environ. Sci.* 2015; 8: 3708-3717.

21. Chen L, Xu Y and Chen B. In situ photochemical fabrication of CdS/g-C₃N₄ nanocomposites with high performance for hydrogen evolution under visible light. *Appl. Catal. B: Environ.* 2019; 256: 117848.

22. Liu J, Liu Y, Liu N, Han Y, Zhang X, Huang H, Lifshitz Y, Lee S T, Zhong J and
Kang Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* 2015; **347**: 970-974.

23. Cao Y, Chen S, Luo Q, Yan H, Lin Y, Liu W, Cao L, Lu J, Yang J, Yao T and Wei S. Atomic-Level Insight into Optimizing the Hydrogen Evolution Pathway over a Co$_1$-N$_4$ Single-Site Photocatalyst. *Angew. Chem. Int. Ed.* 2017; **56**: 12191-12196.

24. Yu F, Wang Z, Zhang S, Ye H, Kong K, Gong X, Hua J and Tian, H. Molecular Engineering of Donor–Acceptor Conjugated Polymer/g-C$_3$N$_4$ Heterostructures for Significantly Enhanced Hydrogen Evolution Under Visible-Light Irradiation. *Adv. Funct. Mater.* 2018; **28**: 1804512.

25. Cao S, Li H, Tong T, Chen H C, Yu A, Yu J and Chen H M. Single-Atom Engineering of Directional Charge Transfer Channels and Active Sites for Photocatalytic Hydrogen Evolution. *Adv. Funct. Mater.* 2018; **28**: 1802169.

26. Xu J H, Guo L Y, Su H F, Gao X, Wu X F, Wang W G, Tung C H and Sun D. Heptanuclear CoII5CoII2 Cluster as Efficient Water Oxidation Catalyst. *Inorg. Chem.* 2017; **56**: 1591-1598.

27. Peng J-B, Zhang Q C, Kong X J, Ren Y P, Long L S, Huang R B, Zheng L S and Zheng Z. A 48-Metal Cluster Exhibiting a Large Magnetocaloric Effect. *Angew. Chem. Int. Ed.* 2011; **50**: 10649-10652.

28. Peng J-B, Zhang Q C, Kong X J, Zheng Y Z, Ren Y P, Long L S, Huang R B, Zheng L S and Zheng Z. High-Nuclearity 3d–4f Clusters as Enhanced Magnetic Coolers and Molecular Magnets, *J. Am. Chem. Soc.* 2012; **134**: 3314-3317.

29. Cotton, S. Lanthanide and Actinide Chemistry; John Wiley & Sons: Chichester, U. K. 2006.

30. Lee C I, Lakshmi K V and Brudvig G W. *Biochemistry* 2007; **46**: 3211.

31. Lin P H, Takase M K, Agapie T. Investigations of the Effect of the Non-Manganese Metal in Heterometallic-Oxido Cluster Models of the Oxygen Evolving Complex of Photosystem II: Lanthanides as Substitutes for Calcium. *Inorg. Chem.* 2015; **54**: 59-64.

32. Maayan G, Gluz N and Christou G. A bioinspired soluble manganese cluster as a water oxidation electrocatalyst with low overpotential. *Nat. Catal.* 2018; **1**: 48-54.
33. Guan J, Duan Z, Zhang F, Kelly S D, Si R, Dupuis M, Huang Q, Chen J Q, Tang C and Li C. Water oxidation on a mononuclear manganese heterogeneous catalyst. *Nat. Catal.* 2018; 1: 870-877.

34. Brudvig G W. Catalysing water oxidation using nature’s metal. *Nat. Catal.* 2018; 1: 10-11.

35. Ghosh T and Maayan G. Efficient Homogeneous Electrocatalytic Water Oxidation by a Manganese Cluster with an Overpotential of Only 74 mV. *Angew. Chem. Int. Ed.* 2019; 58: 2785-2790.

36. Liu W, Cao L, Cheng W, Cao Y, Liu X, Zhang W, Mou X, Jin L, Zheng X, Che W, Liu Q, Yao T and Wei S. Single-Site Active Cobalt-Based Photocatalyst with a Long Carrier Lifetime for Spontaneous Overall Water Splitting. *Angew. Chem. Int. Ed.* 2017; 56: 9312-9317.

37. Liu W, Hu E, Jiang H, Xiang Y, Weng Z, Li M, Fan Q, Yu X, Almam E I and Wang, H. A highly active and stable hydrogen evolution catalyst based on pyrite-structured cobalt phosphosulfide. *Nat. Commun.* 2016; 7: 10771.

38. Zhang Y, Mori T, Ye J and Antonietti M. Phosphorus-Doped Carbon Nitride Solid: Enhanced Electrical Conductivity and Photocurrent Generation. *J. Am. Chem. Soc.* 2010; 132: 6294-6295.

39. Chilton N F, Langley S K, Moubaraki B and Murray K S. Synthesis, structural and magnetic studies of an isostructural family of mixed 3d/4f tetranuclear ‘star’ clusters. *Chem. Commun.* 2010; 46: 7787-7789.

40. Savva M, Skordi K, Fournet A D, Thuijs A E, Christou G, Perlepes S P, Papatriantafyllopoulou C and Tasiopoulos A J. Heterometallic Mn$^{III}$$_4$Ln$_2$ (Ln = Dy, Gd, Tb) Cross-Shaped Clusters and Their Homometallic Mn$^{III}$$_4$Mn$^{II}$$_2$ Analogues. *Inorg. Chem.* 2017; 56: 5657-5668.

41. Li R, Weng Y, Zhou X, Wang X, Mi Y, Chong R, Han H and Li C. Achieving overall water splitting using titanium dioxide-based photocatalysts of different phases. *Energy Environ. Sci.* 2015; 8: 2377-2382.

42. Bi W, Li X, Zhang L, Jin T, Zhang L, Zhang Q, Luo Y, Wu C and Xie Y. Molecular co-catalyst accelerating hole transfer for enhanced photocatalytic H$_2$...
43. Li X, Bi W, Zhang L, Tao S, Chu W, Zhang Q, Luo Y, Wu C and Xie, Y. Single-Atom Pt as Co-Catalyst for Enhanced Photocatalytic H2 Evolution. Adv. Mater. 2016; 28: 2427-2431.

44. Kresse G and Hafner J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 1993; 47: 558-561.

45. Walsh A, Sokol A A, Buckeridge J, Scanlon D O and Catlow C R A. Oxidation states and ionicity. Nat. Mater. 2018; 17: 958-964.

46. Daelman N, Capdevila-Cortada M and López N. Dynamic charge and oxidation state of Pt/CeO2 single-atom catalysts. Nat. Mater. 2019; 18: 1215-1221.
Figure 1. Crystal structures of the synthetic NdCo$_3$ cluster and the native CaMn$_4$ of PSII. (a) Crystal structure of NdCo$_3$. (b) Structure of [NdCo$^{II}$Co$^{III}$]$^2_2$ core. (c) Structure of the native CaMn$_4$O$_5$ of photosystem II. (d) CaMn$_{3III}$Mn$_{2IV}$O$_5$ core in photosystem II [1]. Nd, Co, Mn, Ca, O, N, and C are shown in purple, green, teal, pink, red, blue and grey, respectively. For clarity, all H atoms are omitted.
Figure 2. The synthetic schematic diagram process of $\text{NdCo}_3$/PCN and Electron microscopy of $\text{NdCo}_3$/PCN-c. (a) Nd, Co, O, N, C and P are shown in purple, green, red, blue, grey and yellow, respectively. (b) TEM image of $\text{NdCo}_3$/PCN-c. (c) (d) Representative HAADF-STEM images of $\text{NdCo}_3$/PCN-c. (E) Elemental mappings of Nd, Co and P. Nd: green; Co: red; P: purple.
Figure 3. Characterization of NdCo$_3$/PCN-c. (a) The Co K-edge XANES spectra and (b) corresponding Co $k^3$-weighted FT spectra for Co foil, Co$_2$O$_3$, CoO, NdCo$_3$, NdCo$_3$/PCN-c and NdCo$_3$/PCN-c-AR. (c) Co 2p XPS spectra of NdCo$_3$/PCN-c. (d) P 2p XPS spectra of NdCo$_3$/PCN-c and PCN.
Figure 4. Photocatalytic performance of NdCo$_3$/PCN-c. (a) H$_2$ yield rate of CN, PCN, NdCo$_3$/PCN-a, NdCo$_3$/PCN-b, NdCo$_3$/PCN-c, NdCo$_3$/PCN-d and NdCo$_3$/PCN-e. (b) Time course of H$_2$ and O$_2$ evolution of NdCo$_3$/PCN-c for 12 hours. (c) The UV-vis absorption spectrum (black) and wavelength-dependent quantum efficiency (red dots) of water splitting (irradiated by a 300 W Xe lamp using a band-pass filter). (d) Gases evolutions of NdCo$_3$/PCN-c, EuCo$_3$/PCN and CeCo$_3$/PCN.
Figure 5. Spectroscopic evidence for effective charge separation process and DFT calculations of NdCo$_3$/PCN-c. Representative ultrafast TA kinetics probed at 520 nm (pumped at 360 nm) for (a) PCN and (b) NdCo$_3$/PCN-c. The TA signal (i.e., the absorbance changes, or \( \Delta \text{Abs.} \) in short) is given in mOD where OD stands for optical density. (c) Schematic illustration of the mechanism involved.