Spatially separating redox centers on 2D carbon nitride with cobalt single atom for photocatalytic H$_2$O$_2$ production

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Redox cocatalysts play crucial roles in photosynthetic reactions, yet simultaneous loading of oxidative and reductive cocatalysts often leads to enhanced charge recombination that is detrimental to photosynthesis. This study introduces an approach to simultaneously load two redox cocatalysts, atomically dispersed cobalt for improving oxidation activity and anthraquinone for improving reduction selectivity, onto graphitic carbon nitride (C$_3$N$_4$) nanosheets for photocatalytic H$_2$O$_2$ production. Spatial separation of oxidative and reductive cocatalysts was achieved on a two-dimensional (2D) photocatalyst, by coordinating cobalt single atom above the void center of C$_3$N$_4$ and anchoring anthraquinone at the edges of C$_3$N$_4$ nanosheets. Such spatial separation, experimentally confirmed and computationally simulated, was found to be critical for enhancing surface charge separation and achieving efficient H$_2$O$_2$ production. This center/edge strategy for spatial separation of cocatalysts may be applied on other 2D photocatalysts that are increasingly studied in photosynthetic reactions.

2D photocatalyst | spatially separated cocatalysts | single-atom catalyst | hydrogen peroxide

Harvesting solar photon energy to drive redox reactions involving water and oxygen is the most espoused strategy for the green synthesis of alternative fuels such as H$_2$ and H$_2$O$_2$ (1–4). Yet, solar-to-energy conversion efficiencies achieved using current semiconductor photocatalysts remain relatively low (5, 6), due to inherent limitations in material properties such as prevalent charge recombination in low-bandgap materials and the insufficient selectivity toward the fuel synthesis reaction (7). One promising material engineering strategy is to decorate the semiconductor surface with cocatalysts that are crucial for efficient photocatalytic synthesis of compressed H$_2$ due to recent advances in H$_2$O$_2$ fuel-cell technology (21). C$_3$N$_4$ exhibits valence-band (VB) and conduction-band (CB) potentials that span those of H$_2$O/O$_2$ and H$_2$O$_2$/O$_2$ reactions within a single material. Nevertheless, unregulated loading of oxidative and reductive cocatalysts on a substrate in trace amounts to achieve efficient H$_2$O$_2$ production. We report that redox cocatalysts are spatially separated on a two-dimensional (2D) photocatalyst, which opens an approach for achieving both efficient oxidation and reduction reactions on 2D photocatalysts.

Significance

Photocatalysts frequently require simultaneous loading of oxidative and reductive cocatalysts to achieve both efficient half-reactions within a single material. Nevertheless, unregulated loading and distribution of two cocatalysts will result in direct contact between oxidation and reduction centers, leading to detrimental charge recombination. This research presents a center/edge approach to load two redox cocatalysts with controlled physical separation in atomistic scale (Fig. 1D). We use cobalt and anthraquinone (AQ) as cocatalysts that are crucial for efficient photocatalytic synthesis of the substrate structure and cannot be readily extended to 2D materials such as graphitic carbon nitride (C$_3$N$_4$). C$_3$N$_4$ has often been used as the semiconductor material for the photocatalytic synthesis of H$_2$O$_2$(3, 19, 20), an emerging substitute for compressed H$_2$ due to recent advances in H$_2$O$_2$ fuel-cell technology. C$_3$N$_4$ exhibits valence-band (VB) and conduction-band (CB) potentials that span those of H$_2$O/O$_2$ and H$_2$O$_2$/O$_2$ redox pairs and is capable of harnessing broad spectrum of sunlight due to its low-bandgap energy. However, solar-to-fuel conversion efficiencies remain, in general, relatively low due to limitations that are commonly found in other materials: 1) ineffective hole scavenging via water oxidation and the resulting charge recombination (3, 19), which often necessitates the addition of organic electron donors (22–25), and 2) low selectivity toward H$_2$O$_2$ synthesis via two-electron reduction of O$_2$ (2H$^+$ + 2e$^−$ → H$_2$O) as compared to four-electron reduction of O$_2$ (2O$_2$ + 4H$^+$ + 4e$^−$ → 2H$_2$O) or two-electron H$_2$ evolution (2H$^+$ + 2e$^−$ → H$_2$) (3, 19).

Here we introduce an innovative strategy to load two cocatalysts onto 2D C$_3$N$_4$, with controlled physical separation in atomistic scale (Fig. 1D). We use cobalt and anthraquinone (AQ) as cocatalysts that are crucial for efficient photocatalytic synthesis of...
of H₂O₂. Co is anchored to void center of the C₃N₄ as a single atom (Co₁) and serves to facilitate the water oxidation (26–30). At the same time, AQ is attached to amine anchors that are present only on the edge of C₃N₄, ensuring that it is not in direct contact with the Co centers. The AQ enhances the selectivity of O₂ reduction to H₂O₂, following the mechanism widely exploited in current industrial H₂O₂ production process (31). The composite catalyst, Co₁/AQ/C₃N₄, photocatalytically produces H₂O₂ at high efficiency under simulated solar irradiation without the supply of a sacrificial agent.

We first prepared ultrathin C₃N₄ nanosheets by exfoliating bulk C₃N₄ under probe sonication (32). We examined the changes in morphology of C₃N₄ nanosheets by using HAADF-STEM imaging (Figure 2G). After irradiation, Co₁/AQ/C₃N₄@Al₂O₃ was separated from Au nanoparticles (Figure 2G). FT-IR spectra of C₃N₄ and Co₁/AQ/C₃N₄ were measured.

Fig. 1. (A) Randomly loading two cocatalysts leads to detrimental sequences of reactions involving oxidant (Ox) and reductant (Red). (B) Core/shell structured photocatalysts and (C) photocatalysts with different exposed crystalline facets to achieve controlled spatial separation of oxidative and reductive cocatalysts. (D) Spatial separation of Co single atom (as oxidation center) and AQ (as reduction center) cocatalysts by anchoring them in the center (i.e., pyridinic N) and on the edge (i.e., primary/secondary amine N) of 2D ultrathin C₃N₄, respectively.

Fig. 2. (A and B) HRTEM and EDS images of Co₁/AQ/C₃N₄. (C) Photooxidative deposition of Mn on Co₁/C₃N₄. (D and E) HAADF-STEM image of C₃N₄ and Co₁/AQ/C₃N₄. (F) FT-IR spectra of C₃N₄ and Co₁/AQ/C₃N₄. (G) Photoreductive deposition of Au on AQ/C₃N₄.
Co atoms are also distributed across the C3N4 surface and serve readily observed by low-resolution TEM (Fig. 2C), as suggested by this site having the lowest relative energy (34, 35). After pyrolysis under N2 atmosphere, Co ions were further phosphodized under PH3 atmosphere to enhance their activity for water oxidation (26, 33, 36).

Energy-dispersive X-ray spectroscopy (EDS) elemental mapping suggests that Co is uniformly distributed across the C3N4 surface (Fig. 2B). To further provide a visual confirmation, we photooxidatively deposited Mn2+ to grow MnOx nanoparticles (Mn2+ + xH2O [2x-2]h+ → MnOx + 2xH+) on Co as seed sites (16, 37, 38). The formation of MnOx across the C3N4 surface readily observed by low-resolution TEM (Fig. 2C) suggests that Co atoms are also distributed across the C3N4 surface and serve as oxidation centers. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images indicate that the Co is likely atomically dispersed [Fig. 2E as compared to C3N4 before Co loading (Fig. 2D)], since the radii of Co were estimated to be ~0.5 Å. Notably, all Co single atoms identified were located at least ~1 nm away from the edge of C3N4 (Fig. 2E and SI Appendix, Fig. S2), indicating the selective loading of Co on the surface, not the edge, of C3N4 nanosheet.

Consistent with the absence of Co metallic clusters in HAADF-STEM images, another strong piece of evidence for the atomic dispersion of Co is provided by the absence of Co-Co coordination in K-edge spectrum from Fourier-transformed extended X-ray absorption fine-structure spectroscopy (FT-EXAFS, Fig. 3A). The spectrum also indicates that Co atoms are primarily coordinated by P (i.e., peak at 1.8 Å in FT-EXAFS) (33), which confirms the complete phosphidation. The coordination with P is further supported by the occurrence of a prominent Co-P peak at 129.6 eV in the X-ray photoelectron spectroscopy (XPS) spectrum (Fig. 3D). A P-N peak at 133.6 eV also suggests that P atoms coordinate with N atoms in heptazine rings of C3N4. Best-fit parameters extracted from the FT-EXAFS spectra (Fig. 3B) suggest an average Co-P coordination distance at 2.29 Å and coordination number of 4.1 (SI Appendix, Table S1), consistent with previous observations (33). Co atoms are found to be positively charged with partially unoccupied 3d orbitals. Comparison of the Co K-edge normalized near-edge X-ray absorption spectroscopy (XANES) of Co1/AQ/C3N4 with those of reference compounds shows that the spectral line shape and the absorption edge position closely resemble those of CoO (Fig. 3C), indicating that the oxidation state of the Co single atoms is close to +2. Density-functional theory calculations (DFT; see SI Appendix, section S6 for details) confirm that Co atoms are positively charged. The above results collectively suggest that Co cocatalysts are uniformly loaded in the center of C3N4 nanosheet as positively charged single atoms.

XAFS measurements at the P K-edge further provide a clue on the structure of Co single atom and its surrounding. EXAFS spectrum at the P K-edge indicates that P atoms are primarily coordinated by Co atoms (i.e., peak at 1.87 Å in FT-EXAFS;
SI Appendix, Fig. S3A), which is consistent with the corresponding FT-EXAFS data recorded at Co K-edge (Fig. 3B). These P atoms are further coordinated with N atoms in heptazine rings of C₃N₄ as well as O atoms, as evidenced by P-N peak at 133.5 eV and P-O peak at 134.5 eV in XPS spectrum (Fig. 3D). XANES spectrum at the P K-edge shows that the preedge region is dominated by the strong feature at 2,143.6 eV, which is assigned to low-valence phosphidic species (SI Appendix, Fig. S3B) (39). The higher-energy, broader peak centered around 2,152.0 eV is consistent with high-valence P (SI Appendix, Fig. S3B) (40). Comparison of intensities of the two maxima suggests that 20–30% of the phosphorus atoms exist in high-valence state. Alternatively speaking, Co atoms are coordinated with three low-valence P atoms (i.e., coordinated with N atoms in heptazine rings of C₃N₄) and one high-valence P atom (i.e., coordinated with O atoms). Geometry optimization conducted under these constraints using DFT confirms that the proposed Co center structure is stable (Fig. 1D, top and side view of Co center), in which Co is placed out of C₃N₄ plane. Other configurations, particularly in-plane P substitutions and Co insertions, resulted in sheet disintegration or massive structural rearrangement. Loading Co single atoms significantly enhanced C₃N₄ for water oxidation (2H₂O → O₂ + 4H⁺ + 4e⁻), as indicated by an

**Fig. 4.** (A) Time course of O₂ evolution measured under 0.6-kPa Ar pressure and 300-W xenon lamp irradiation with 0.5 g/L of catalyst, 1 g/L La₂O₃, and 20 mM AgNO₃ in 100 mL water. (B) Selectivity of H₂O₂ production. (C and D) Time course of H₂O₂ production measured under simulated sunlight irradiation (xenon lamp solar simulator, 100 mW/cm², AM 1.5G) with 0.5 g/L of catalyst under O₂-saturated condition. Solid lines are the fitting result of the kinetic model. Dotted lines are H₂O₂ productions estimated assuming additive enhancement of each cocatalyst. (E and F) H₂O₂ formation and decomposition rate constants. Error bars represent the SDs of triplicates.

**Fig. 5.** Density of states computed with DFT for (A) C₃N₄, (B) C₃N₄ loaded with Co single atom cocatalyst (SAC), (C) C₃N₄ loaded with Co nanoparticle (showing Co₄ as an example), and (D) Co loaded with AQ.
8.4-fold enhancement on 4-h O₂ production (Fig. 4A and see SI Appendix, section S5 for details). According to our DFT calculations (see SI Appendix, section S6 for details), the enhanced water oxidation is attributed to strong adsorption of water molecule on Co single atom (exothermic by 2.7 eV when replacing the phosphate moiety), while no adsorption is observed on the plane C₃N₄ sheet. In addition, atomically dispersed Co produces two distinct, occupied, midgap states ~0.5 and 0.9 eV above the VB maximum when the H₂O is absorbed, promoting the localization of photoexcited holes and subsequent charge separation (Fig. 5A and B), whereas Co nanoparticles completely fill the bandgap and thus act as charge recombination centers (Fig. 5C). All of these results indicate that Co loading enhances the hole quenching by water and therefore the overall charge-separation, i.e., more electrons are available for the reductive H₂O₂ synthesis. Secondly, we loaded AQ cocatalyst onto Co₁/C₃N₄ by forming amide bonds between carboxylic groups in anthraquinone-2-carboxylic acid and primary/secondary amine groups on the edge of C₃N₄ (Fig. 1D) (8, 35). Successful loading of AQ was confirmed by XPS in which Co₁/AQ/C₃N₄ exhibits strong peak corresponding to C-C fragments (284.7 eV) that mostly originate from AQ molecules (Fig. 3D). The AQ molecules remained bound to C₃N₄ after extensive solvent washing, suggesting that they are chemically attached rather than physically adsorbed (25). The successful loading of AQ was also confirmed by Fourier-transform infrared spectroscopy (FT-IR) spectroscopy. As shown in Fig. 2F, the intensities of the FT-IR peaks corresponding to the amide functionalities, including the C=O stretching vibration peak at 1627 cm⁻¹ and the N-H stretching vibration peak at 3,076 cm⁻¹, increased dramatically with AQ loading. The quantitative analysis of XPS spectra indicates that AQ was loaded at 16% (wt/wt).

To provide a visual confirmation of the site-selective loading of AQ, we photoreductively deposited noble metals by reducing metal precursors (i.e., H₂AuCl₄ or H₂PtCl₆) on AQ as seed sites (M⁰⁺ + ne⁻ → M⁺) (16). TEM images clearly showed that the Au and Pt nanoparticles were selectively deposited on the edge of C₃N₄ nanosheets (Fig. 2G and SI Appendix, Figs. S4 and S5), which were in stark contrast to random deposition of Au nanoparticles on pristine C₃N₄ surface without AQ functionality (SI Appendix, Fig. S6) (41). These results confirm that AQ cocatalysts were selectively loaded on the edge of C₃N₄ nanosheets and served as reduction centers. DFT calculations showed that the electron withdrawal by the AQ cocatalyst, where AQ molecule generates an empty state that is only 0.3 eV below the CB of C₃N₄; while filled AQ states, where a hole would occupy, sits more than 0.8 eV below the VB of C₃N₄ (Fig. 5D). Therefore, transfer of a photoexcited electron to AQ is allowed but transfer of a photoexcited hole is prohibited, leading to enhanced charge separation.

Loading AQ cocatalyst onto C₃N₄ had a significant impact on enhancing the selectivity of H₂O₂ synthesis from ~30% by pristine C₃N₄ to over 60% (Fig. 4B); H₂O₂ production selectivity is defined as the ratio of electrons utilized for H₂O₂ synthesis to the total number of electrons consumed (SI Appendix, section S3 and ref. 22). In contrast, C₃N₄ exfoliation or Co loading had limited impact on H₂O₂ production selectivity (Fig. 4B). The enhanced H₂O₂ production selectivity is attributed to the two-step reaction catalyzed by AQ: 1) reductive hydrogenation of AQ to hydroxylanthraquinone (AOH₂) utilizing 2 e⁻ from photoexcited C₃N₄ followed by 2) H₂O₂ formation from concurrent oxygen reduction and dehydrogenation of AOH₂ back to AQ (SI Appendix, Fig. S7).

The photocatalytic H₂O₂-production performance of the as-prepared catalysts was evaluated under simulated sunlight irradiation in the absence of organic electron donor. Exfoliation of bulk C₃N₄ to nanosheets enhanced the photocatalytic H₂O₂ production performance of C₃N₄ (Fig. 4C) due to a larger number of exposed reaction sites and improved light-harvesting capability (8, 32). The light-harvesting capability of C₃N₄ was further improved with Co loading, as indicated by the lowered bandgaps [refer to the band-structure diagram (SI Appendix, Fig. S8)] constructed from XPS valence spectra (SI Appendix, Fig. S9) and diffuse reflectance spectra (SI Appendix, Fig. S10). Co cocatalyst loading promoted the water oxidation reaction and consequently reduced detrimental exciton recombination (26, 33, 34, 42), leading to enhanced H₂O₂ production (Fig. 4C). For instance, when Co was loaded as nanoparticles (see SI Appendix, section S2 for synthesis details), i.e., not as single atoms, H₂O₂ production was enhanced, albeit slightly; when Co was loaded as single atoms, H₂O₂ production was enhanced by 4.0-fold. On the other hand, loading AQ cocatalyst onto ultrathin C₃N₄ improved H₂O₂ production selectivity, resulting in a 1.9-fold enhancement in H₂O₂ production (Fig. 4C).

Simultaneous loading of Co single atoms and AQ cocatalyst significantly enhanced H₂O₂ production by a factor of 7.3 (Fig. 4D). For the solar photocatalytic H₂O₂ production performed in the absence of electron donor, the initial production rate of 62 μM/h (apparent quantum efficiency = 0.054% over the full spectrum of sunlight; see SI Appendix, sections S8 and S9 for calculation details) and the cumulative production of 230 μM over 8-h period (SI Appendix, Fig. S11) achieved by Co₁/AQ/C₃N₄ in this study are among the highest reported (SI Appendix, Table S2) (43, 44). When the suspension was N₂-purged, the H₂O₂ production was mostly inhibited, confirming that O₂ reduction was the major pathway for H₂O₂ production (SI Appendix, Fig. S12). The stability of Co₁/AQ/C₃N₄ was demonstrated by the stable catalytic performance through repetitive use up to five cycles (SI Appendix, Fig. S13). XPS (SI Appendix, Fig. S14) and TEM (SI Appendix, Fig. S15) analyses show no significant change in chemical composition or ultrathin layered structure of Co₁/AQ/C₃N₄ after 8-h irradiation. We note that a better intersheet packing control may be achieved by immobilizing Co₁/AQ/C₃N₄ to facilitate its application in large-scale photolysis device setup (43, 44).

The enhancement on H₂O₂ production by loading of Co single atoms and AQ is close to the multiplication of individual enhancements (Fig. 4D); i.e., the 4.0-fold enhancement by Co single atom cocatalyst times the 1.9-fold enhancement by AQ cocatalyst is close to the observed 7.3-fold enhancement on 60-min H₂O₂ production. This collaborative effect suggests that two cocatalysts contribute to H₂O₂ production enhancement independently without any negating effect. In contrast, when Co was loaded as nanoparticles onto AQ-C₃N₄, H₂O₂ production was much lower than the expected sum of enhancements by Co nanoparticles and AQ (i.e., the observed 1.2-fold enhancement is much lower than the 1.5-fold enhancement by Co nanoparticle in the 1.9-fold enhancement by AQ on 60-min H₂O₂ production; Fig. 4D). This is due to random distribution of large Co nanoparticles across C₃N₄ and likely contact between Co cocatalyst and AQ cocatalyst. Such a contact would facilitate direct electron transfer without H₂O₂ evolution or water splitting (Fig. 4L). Loading Co as single atom, in contrast, ensures that Co is spatially separated from AQ. Since Co atom occupies the void center of C₃N₄ and AQ is located only at the edge of C₃N₄, molecular structure of C₃N₄ inherently maintains their separations at the minimum of 0.8 nm (SI Appendix, Fig. S16). Consistently, the steady-state photoluminescence from Co₁/AQ/C₃N₄ was markedly reduced compared not only to C₃N₄ but also to Co₃N₄/AQ/C₃N₄, indicating that the radiative recombination is more effectively retarded with Co single atom than Co nanoparticle (Fig. 6A). Time-resolved photoluminescence (TRPL, Fig. 6B) analyses show that the lifetime of excited-state Co₁/AQ/C₃N₄ (1.73 ns) is shorter than that of C₃N₄ (3.23 ns) and Co₃N₄/AQ/C₃N₄ (2.23 ns), highlighting the improved photoelectron dissociation in Co₁/AQ/C₃N₄ that was realized by spatial separation of AQ and Co single atoms.

We further analyze the H₂O₂ production by evaluating the rate of H₂O₂ formation (k₁) separately from the rate of H₂O₂ decomposition (k₂) (see SI Appendix, section S7 for the kinetic analysis). The results show that H₂O₂ formation rate constant increased upon individual loading of Co single atom, Co nanoparticle, or AQ. While
simultaneous loading of Co single atom and AQ lead to additive enhancement on \( k_D \). Simultaneous loading of Co nanoparticle and AQ had an antagonistic effect on \( k_D \) (Fig. 4E), once again highlighting the importance of controlled physical separation between Co and AQ. It is also noteworthy that Co may negatively impact \( \text{H}_2\text{O}_2 \) synthesis performance by enhancing the oxidative decomposition of \( \text{H}_2\text{O}_2 \) (Fig. 4F). This catalyzed \( \text{H}_2\text{O}_2 \) decomposi-tion was minimized by separating \( \text{H}_2\text{O}_2 \) production centers (i.e., AQ) from Co decomposition sites, as indicated by much lower \( k_D \) in Co/AQ/C3N4 system as compared to CoO/C3N4 system (Fig. 4F).

Results of our study suggest a facile strategy to anchor two spatially separated cocatalysts on a 2D photocatalyst. Such spatial separation ensures that the functions of both cocatalysts (i.e., Co for enhanced water oxidation activity and AQ for improved \( \text{H}_2\text{O}_2 \) production selectivity) are fully utilized, resulting in additive enhancement in \( \text{H}_2\text{O}_2 \) photosynthesis. Here, atomic dispersion of metal cocatalyst presents advantage over conventional nanoparticles because the small size and strong ligand–metal coordination of single atom allow for facile manipulation of loading sites. The stark contrast on the performance of Co single atoms versus nanoparticles emphasizes the exclusive benefits of single atom catalysts in this material design. This center-edge strategy for loading two spatially separated cocatalysts may be also applicable on other 2D photocatalysts for achieving efficient charge separation while maintaining the effectiveness of both cocatalysts.

**Methods**

**Preparation of Photocatalysts.** Bulk C3N4 was prepared following a thermal polymerization procedure by heating melamine powder in a ceramic crucible at a heating rate of 1 °C/min to 550 °C and annealing for 5 h in a muffle furnace. As-prepared bulk C3N4 was grounded, exfoliated under probe sonication for 8 h, separated by centrifugation, washed with deionized water, and dried at 80 °C overnight. As-prepared ultrathin C3N4 (160 mg) was dispersed in 50 mL water under ultrasonication for 30 min, followed by addition of 1.5 mL Co(NO3)2 solution (2 g/L). The mixture was stirred and heated at 70 °C for 18 h, separated by centrifugation, dried at 80 °C overnight, and annealed at 400 °C for 2 h in a tube furnace under \( \text{N}_2 \) gas. The obtained powder was ground, mixed with Na2O·2H2O (twice the weight of obtained powder), and heated at 300 °C for 2 h in a tube furnace under \( \text{N}_2 \) gas. Photoluminescence (PL) emission spectra were obtained using a fluorescence spectrophotometer (Shimadzu RF-5301). PL lifetime decays were measured by an inverted-type scanning confocal microscope (MicroTime-200, Picoquant) with a 20x objective. A single-mode pulsed diode laser (excitation wavelength at 375 nm with an instrumental response function of ~240 ps in pulse width) was used to excite the samples coated on glass substrate. A dichroic mirror (490 DCXR, AHF), a long-pass filter (HQ500lp, AHF), and an avalanche photodiode detector (PDM series, MPD) were used to collect the entire emission (400–800 nm) from the samples. Photon counting and exponential fitting of the obtained PL decays were performed using the SynchroTime software (version 5.3).

**Photocatalytic Activity Tests.** Photocatalytic production of \( \text{H}_2\text{O}_2 \) was assessed by irradiation of photocatalyst suspension (12 mL, 0.5 g/L) using a xenon lamp solar simulator (model 10500; Abet Technologies, Inc.). The light intensity was adjusted to 100 mW/cm² (AM 1.5G; irradiation area = 1.77 cm²). The suspension was purged with \( \text{O}_2 \) before (for 5 min) and during irradiation. At designated time points, small aliquots from suspensions were taken for analysis of \( \text{H}_2\text{O}_2 \) productions.

**Data Availability.** All data of this study are included in the text and SI Appendix.

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**Catalyst Characterizations.** HAADF-STEM images were taken using a Titan Themis Z STEM (ThermoFisher Scientific) operated at 200 kV, coupled with a probe aberration corrector to improve imaging spatial resolution to less than 1 Å. XPS measurements were performed with a Versa Probe II Scanning XPS Microprobe [Physical Electronics (PHI)]. We performed a survey scan across the entire energy range and higher-resolution analyses in the N 1s, C 1s, P 2p, and O 1s regions. The XAS spectra at Co K edge were measured at Beamline 8-ID (5S) of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, using a Si (111) double-crystal monochromator and a passivated implanted planar silicon fluorescence detector. XANES data were collected at room temperature, with energy calibrated using Co foil. The P K-edge XAS data were collected at 8-BM of NSLS-II under fluorescence mode, employing a Si (111) crystals monochromator (45S). Each sample was scanned for seven times to get better signal to noise ratio. Photoluminescence (PL) emission spectra were obtained using a fluorescence spectrophotometer (Shimadzu RF-5301). PL lifetime decays were measured by an inverted-type scanning confocal microscope (MicroTime-200, Picoquant) with a 20x objective. A single-mode pulsed diode laser (excitation wavelength at 375 nm with an instrumental response function of ~240 ps in pulse width) was used to excite the samples coated on glass substrate. A dichroic mirror (490 DCXR, AHF), a long-pass filter (HQ500lp, AHF), and an avalanche photodiode detector (PDM series, MPD) were used to collect the entire emission (400–800 nm) from the samples. Photon counting and exponential fitting of the obtained PL decays were performed using the SynchroTime software (version 5.3).
1. T. Hisatomi, J. Kubota, K. Domen, Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem. Soc. Rev. 43, 7520–7535 (2014).
2. C. Chu et al., Electronic tuning of metal nanoparticles for highly efficient photocatalytic hydrogen peroxide production. ACS Catal. 9, 626–631 (2019).
3. Y. Kofuji et al., Carbon nitride-aromatic diazole-graphene nano-hybrids: Metal-free photocatalysts for solar-to-hydrogen energy conversion with 0.2% efficiency. J. Am. Chem. Soc. 138, 10019–10025 (2016).
4. Y. Shiraishi et al., Resorcinol-formaldehyde resin as metal-free semiconductor photocatalysts for solar-to-hydrogen peroxide energy conversion. Nat. Mater. 18, 985–993 (2019).
5. S. Liu et al., Water splitting. Metal-free efficient photocatalyst for stable visible light splitting via a two-electron pathway. Science 347, 970–974 (2015).
6. Y. Goto et al., A particulate water-splitting catalyst-panel for large-scale solar hydrogen generation. Joule 2, 509–520 (2018).
7. X. Chen, S. Shen, L. Guo, S. S. Mao, Semiconductor-based photocatalytic hydrogen generation. Chem. Rev. 110, 6503–6570 (2010).
8. W. J. Ong, L. T. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability? Chem. Rev. 116, 7159–7329 (2016).
9. D. Wang et al., Core/Shell photocatalyst with spatially separated co-catalysts for efficient reduction and oxidation of water. Angew. Chem. Int. Ed. Engl. 52, 11252–11256 (2013).
10. K. Maeda et al., Photocatalytic overall water splitting promoted by two different cocatalysts for hydrogen and oxygen evolution under visible light. Angew. Chem. Int. Ed. Engl. 49, 4096–4099 (2010).
11. S. S. K. Ma, K. Maeda, R. Abe, K. Domen, Visible-light-driven nonsacrificial water oxidation over tungsten trioxide powder modified with two different cocatalysts. Energy Environ. Sci. 5, 8390–8397 (2012).
12. A. Li et al., Thin heterojunctions and spatially separated cocatalysts to simultaneously reduce bulk and surface recombination in photocatalysts. Angew. Chem. Int. Ed. Engl. 55, 13734–13738 (2016).
13. D. Zheng, X. N. Cao, X. Wang, Precise formation of a hollow carbon nitride structure with a Janus surface to promote water splitting by photoredox catalysis. Angew. Chem. Int. Ed. Engl. 55, 11512–11516 (2016).
14. M. Xing et al., Spatially separated CoS6 shells exposed with reduction surfaces for enhancing photocatalytic hydrogen evolution. Adv. Funct. Mater. 27, 170264–1702634 (2017).
15. J. Zhang et al., Porous TiO2 nanotubes with spatially separated platinum and CoO2 cocatalysts produced by atomic layer deposition for photocatalytic hydrogen production. Angew. Chem. Int. Ed. Engl. 56, 816–820 (2017).
16. R. Li et al., Spatial separation of photogenerated electrons and holes among 010 and 110 crystal facets of BiVO4. Nat. Commun. 4, 1432–1439 (2013).
17. R. G. Li, H. X. Han, F. X. Zhang, D. G. Wang, C. Li, Highly efficient photocatalysts constructed by rational assembly of dual-cocatalysts separately on different facets of BiVO4. Energy Environ. Sci. 7, 1369–1376 (2014).
18. A. Meng, J. Zhang, D. Xu, B. Cheng, J. Yu, Enhanced photocatalytic H2-production activity of anatase TiO2 nanosheet by selectively depositing dual-cocatalysts on (101) and (001) facets. Appl. Catal. B 198, 286–294 (2016).
19. Y. Shiraishi et al., Sunlight-driven hydrogen peroxide production from water and molecular oxygen by metal-free photocatalysts. Angew. Chem. Int. Ed. Engl. 53, 13454–13459 (2014).
20. Y. Kofuji et al., Graphitic carbon nitride doped with biphenyl diimide: Efficient photocatalyst for hydrogen peroxide production from water and molecular oxygen by sunlight. ACS Catal. 6, 7021–7029 (2016).
21. K. Mase, M. Yoneda, Y. Yamada, S. Fukuzumi, Seawater usable for production and consumption of hydrogen peroxide as a solar fuel. Nat. Commun. 7, 11470–11476 (2016).
22. Y. Shiraishi et al., Highly selective production of hydrogen peroxide on graphitic carbon nitride (g-C3N4) photocatalyst activated by visible light. ACS Catal. 4, 774–780 (2014).
23. X. Hou, Y. Choi, S. Hu, W. Choi, J.-H. Kim, Photocatalytic hydrogen peroxide production by anthraquinone-augmented polymeric carbon nitride. Appl. Catal. B 229, 121–129 (2018).
24. Y. Shiraishi et al., Effects of surface defects on photocatalytic H2O2 production by mesoporous graphitic carbon nitride under visible light irradiation. ACS Catal. 5, 3058–3066 (2015).
25. G.-H. Moon et al., Eco-friendly photochemical production of H2O2 through O2 reduction over carbon nanoframes incorporated with multiple heteroelements. ACS Catal. 7, 2886–2895 (2017).
26. D. C. Zhang, D. R. Gamelin, Photocatalytic water oxidation by cobalt catalyst (“Co-Pt)(Fe3+)2O4) composite photoanodes: Oxygen evolution and resolution of a kinetic bottleneck. J. Am. Chem. Soc. 132, 4202–4207 (2010).
27. M. Barroso et al., The role of cobalt phosphate in enhancing the photocatalytic activity of γ-Fe2O3 toward water oxidation. J. Am. Chem. Soc. 133, 14868–14871 (2011).
28. R. S. Khnyan et al., Structure and activity of photochemically deposited "CoP" oxygen evolving catalyst on titania. ACS Catal. 2, 2150–2160 (2012).
29. G. H. Moon, W. Kim, A. D. Bokare, N. E. Sung, W. Choi, Solar production of H2O2 on reduced graphene oxide-TiO2 hybrid photocatalysts consisting of earth-abundant elements only. Energy Environ. Sci. 7, 4023–4028 (2014).
30. M. W. Kan, Y. Suresh, P. G. Nore, K. Cobalt-phosphate oxygen-evolving compound. Chem. Soc. Rev. 38, 109–114 (2009).
31. J. M. Campos-Martín, G. Blanco-Brieva, J. L. G. Fierro, Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. Angew. Chem. Int. Ed. Engl. 45, 6962–6984 (2006).
32. Q. Zhang et al., Enhanced photosresponsive ultrathin graphitic-phase Cr7N9 nanosheets for bioimaging. J. Am. Chem. Soc. 135, 18–21 (2013).
33. W. Liu et al., Single-site active cobalt-based photocatalyst with a long carrier lifetime for spontaneous overall water splitting. Angew. Chem. Int. Ed. Engl. 56, 9312–9317 (2017).
34. Y. Zheng et al., Molecule-level g-C3N4 coordinated transition metals as a new class of electrocatalysts for oxygen electrode reactions. J. Am. Chem. Soc. 139, 3336–3339 (2017).
35. F. K. Kessler et al., Functional carbon nitride materials-design strategies for electrochemical devices. Nat. Mater. 2, 17030–17047 (2017).
36. M. W. Kanan, D. G. Nosera, In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co2+. Science 321, 1072–1075 (2008).
37. R. Chen et al., Charge separation via asymmetric illumination in photocatalytic Cu2O particles. Nat. Energy 3, 655–663 (2018).
38. Q. Zhang et al., Effect of redox catalysts location on photocatalytic overall water splitting over cubic NaTaO3 semiconductor crystals exposed with equivalent facets. ACS Catal. 6, 2182–2191 (2016).
39. S. T. Oyama, P. Clark, V. L. S. Teixeira da Silva, E. J. Lede, F. G. Requejo, XAFS characterization of highly active alumina-supported molybdenum phosphate catalysts for water oxidation. J. Phys. Chem. B 105, 4961–4966 (2001).
40. Z. Shi et al., Phosphorus-Mo6C2Carbon nanowires toward efficient electrochemical hydrogen evolution: Composition, structural and electronic regulation. Energy Environ. Sci. 10, 1262–1271 (2017).
41. J. Xue, S. Ma, Y. Zhou, Z. Zhang, M. He, Facile photochemical synthesis of AuPt/γ-C3N4 with plasmon-enhanced photocatalytic activity for antibiotic degradation. ACS Appl. Mater. Interfaces 7, 9630–9637 (2015).
42. J. Mao et al., Accelerating water dissociation kinetics by isolating cobalt atoms into ruthenium lattice. Nat. Commun. 9, 4958–4966 (2018).
43. H. Hirakawa et al., Au nanoparticles supported on BiVO4: Effective inorganic photocatalysts for H2O2 production from water and O2 under visible light. ACS Catal. 6, 4976–4982 (2016).
44. F. Shiraishi, T. Nakasako, Z. Z. Hua, Formation of hydrogen peroxide in photocatalytic reactions. J. Phys. Chem. A 107, 11072–11081 (2003).
45. P. Northrup, The TES beamline (8-BM) at NSLS-II: Tender-energy spatially resolved X-ray absorption spectroscopy and X-ray fluorescence imaging. J. Synchrotron Radiat. 26, 2064–2074 (2019).