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 photocatalysis. 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 (1, 8), ideally both reductive and oxidative cocatalysts within a single photocatalytic material. Nevertheless, randomly loading two cocatalysts often results in direct contact between oxidation and reduction centers, worsening the charge recombination that is detrimental to photocatalytic reactions (Fig. 1A) (9).

Placing two cocatalysts without direct contact requires sophisticated material architecture and synthesis strategy. One cocatalyst, typically oxidative, can be loaded on a substrate in trace amounts to minimize such contact but only at the expense of the available catalytic sites and thus the overall efficiency (10, 11). A more promising strategy is to design the substrate photocatalysts to provide physically separated sites for cocatalyst hosting. For instance, Wang et al. (9) recently fabricated a core/shell photocatalyst that can host reductive and oxidative cocatalysts separated inside and outside of the shell surfaces (Fig. 1B). Following this seminal work, various core/shell structures have been prepared, which typically require complicated synthesis procedures involving the use of sacrificial templates (e.g., SiO$_2$) (12–15). Alternatively, different facets of photocatalytic materials were found to selectively load different cocatalysts, allowing spatial segregation (Fig. 1C) (16–18).

The existing strategies to prepare spatially separated cocatalysts, however, exclusively rely on the three-dimensional nature 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 of choice 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 (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$_2$ 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$_2$ (O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$) as compared to four-electron reduction of O$_2$ (O$_2$ + 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 H$_2$O$_2$.

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 using single-atom architecture. This spatial separation is critical for enhancing surface charge separation and achieving 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.


The authors declare no competing interest.

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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). The C₃N₄ nanosheets

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. 2). Co ions are attached to the void center of C3N4 synthesis: attachment of Co precursors to anchor sites followed by pyrolysis (33). Co ions are further phosphodized under PH3 atmosphere, Co ions were further phosphodized under PH3 atmosphere to enhance their activity for water oxidation (26, 33, 36). Co3O4.\( (\text{Mn}^{2+} + \text{H}_2\text{O}) \rightarrow \text{MnO}_x + 2\text{H}^+ \) on Co as seed sites.

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 MnOx nanoparticles (\( \text{Mn}^{2+} + \text{H}_2\text{O} + [2\times2]^h \rightarrow \text{MnO}_x + 2\text{H}^+ \)) on C3N4 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 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 atom 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; Fig. 3A). FT EXAFS spectra of Co1/AQ/C3N4 at the Co K edge. The intensity of CoOx and Co1/AQ/C3N4 was normalized to the same maximum of Co foil to facilitate the comparison of radial distances by multiplying with a factor of 2.1 and 3.6, respectively. (B) Fit of Co1/AQ/C3N4 EXAFS spectra using Co foil and CoOx. (Inset) Corresponding K-space curves. (C) Normalized XANES of Co1/AQ/C3N4 at the Co K edge. (D) Binding energy of N 1s, C 1s, P 2p, and O 1s for ultrathin C3N4 and Co1/AQ/C3N4 by high-resolution XPS.
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. 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 H2O2 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 CN4 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/CN4 by forming amide bonds between carboxylic groups in anthraquinone-2-carboxylic acid and primary/secondary amine groups on the edge of C-N4 (Fig. 1D) (8, 35). Successful loading of AQ was confirmed by XPS in which Co1/AQ/CN4 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 CN4 after intensive 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 3076 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 photoeductively deposited noble metals by reducing metal precursors (i.e., H2AuCl4 or H2PtCl6) on AQ as seed sites (M⁺⁺ + ne⁻ → M) (16). TEM images clearly showed that the Au and Pt nanoparticles were selectively deposited on the edge of CN4 nanosheets (Fig. 2G and SI Appendix, Figs. S4 and S5), which were in stark contrast to random deposition of Au nanoparticles on pristine CN4 surface without AQ functionality (SI Appendix, Fig. S6) (41). These results confirm that AQ cocatalysts were selectively loaded on the edge of CN4 nanosheets and served as recombination centers. DFT calculations then predicted the electron withdrawal by the AQ cocatalyst, where AQ molecule generates an empty state that is only 0.3 eV below the CB of CN4; while filled AQ states, where a hole would occupy, sits more than 0.8 eV below the VB of CN4 (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 CN4 had a significant impact on enhancing the selectivity of H2O2 synthesis from ~30% by pristine CN4 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, CN4 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 hydroxyanthraquinone (AOH2) utilizing 2 e⁻ from photoexcited CN4 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 CN4 to nanosheets enhanced the photocatalytic H2O2 production performance of CN4 (Fig. 4C) due to a larger number of exposed reaction sites and improved light-harvesting capability (8, 32). The light-harvesting capability of CN4 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 CN4 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/CN4 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/CN4 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 ultrafine layered structure of Co1/AQ/CN4 after 8-h irradiation. We note that a better inter-sheet packing control may be achieved by immobilizing Co1/AQ/CN4 to facilitate its application in large-scale photolysis device setup (43, 44).

The enhancement on H2O2 production by coloading 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 negative effect. In contrast, when Co was loaded as nanoparticles onto AQ-CN4, H2O2 production was much lower 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 CN4 improved H2O2 production selectivity, resulting in a 1.9-fold enhancement in H2O2 production (Fig. 4C).

We further analyze the H2O2 production by evaluating the rate of H2O2 formation (k4) separately from the rate of H2O2 decomposition (k6) (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.
simultaneous loading of Co single atom and AQ lead to additive enhancement on $k_3$, simultaneous loading of Co nanoparticle and AQ had an antagonistic effect on $k_3$ (Fig. 4E), once again highlighting the importance of controlled physical separation between Co and AQ. It is also noteworthy that Co may negatively impact H$_2$O$_2$ synthesis performance by enhancing the oxidative decomposition of H$_2$O$_2$ (Fig. 4F). This catalyzed H$_2$O$_2$ decomposition was minimized by separating H$_2$O$_2$ production centers (i.e., AQ) from Co decomposition sites, as indicated by much lower $k_3$ in Co/AQ/C$_3$N$_4$ system as compared to Co$_{C}$C$_3$N$_4$ 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$_1$ for enhanced water oxidation activity and AQ for improved H$_2$O$_2$ production selectivity) are fully utilized, resulting in additive enhancement in H$_2$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 C$_3$N$_4$ 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 C$_3$N$_4$ 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 C$_3$N$_4$ (160 mg) was dispersed in 50 mL water under ultrasonication for 30 min, followed by addition of 1.5 mL Co(NO$_3$)$_2$ 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 N$_2$ gas. The obtained powder was grounded, mixed with NaPO$_2$H$_2$O (twice the weight of obtained powder), and heated at 300 °C for 2 h in a tube furnace under N$_2$ gas. The suspension was purged with O$_2$ before (for 5 min) and during irradiation. At designated time points, small aliquots from suspensions were taken for analysis of H$_2$O$_2$ productions.

Photocatalytic Activity Tests. Photocatalytic production of H$_2$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/cm$^2$ (AM 1.5G; irradiation area 1.0 cm$^2$). The suspension was purged with O$_2$ before (for 5 min) and during irradiation. At designated time points, small aliquots from suspensions were taken for analysis of H$_2$O$_2$ productions.

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

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