CHEMISTRY

Atomically isolated Sb(CN)₃ on sp²-c-COFs with balanced hydrophilic and oleophilic sites for photocatalytic C-H activation

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Activation of carbon-hydrogen (C-H) bonds is of utmost importance for the synthesis of vital molecules. Toward achieving efficient photocatalytic C-H activation, our investigation revealed that incorporating hydrophilic C=N-Sb(CN)₃ sites into hydrophobic sp² carbon-conjugated covalent organic frameworks (sp²-c-COFs) had a dual effect: It simultaneously enhanced charge separation and improved generation of polar reactive oxygen species. Detailed spectroscopy measurements and simulations showed that C=N-Sb(CN)₃ primarily functioned as water capture sites, which were not directly involved in photocatalysis. However, the potent interaction between water molecules and the Sb(CN)₃-modified framework notably enhanced charge dynamics in hydrophobic sp²-c-COFs. The reactive species $\cdot O_2^-$ and $\cdot OH$ (ad) subsequently combined with benzyl radical, leading to the formation of benzaldehyde, benzyl alcohol, and lastly benzyl benzoate. Notably, the Sb(CN)₃-modified sp²-c-COFs exhibited a 54-fold improvement in reaction rate as compared to pristine sp²-c-COFs, which achieved a remarkable 68% conversion rate for toluene and an 80% selectivity for benzyl benzoate.

INTRODUCTION

Activation of carbon-hydrogen (C-H) bonds plays a crucial role in accessing a wide range of important molecules widely used in chemical and pharmaceutical industries (1-7). Unfortunately, traditional methods for synthesizing these useful molecules involve chlorination or metalcatalyzed reaction using halogens in acidic/basic solvents or reactions at conditions of high temperature/pressure (2, 3, 5). To mitigate these issues, photocatalysis was introduced as an eco-friendly method that utilizes light as the energy source under ambient conditions (7-9). Heterogeneous selective photocatalytic oxidation is capable of generating reactive oxygen species (ROS), which play a vital role as oxidant in organic synthesis. The photogenerated ROS from dissolved oxygen or water are highly reactive and can react with organic substrates (10). Unlike the traditional heterogeneous catalytic system, where surface kinetics usually dominates the overall catalytic activity, an ideal photocatalytic system highly relies on efficient charge dynamics, which defines the amount of available surface electrons and holes. In photocatalytic C-H activation, both hydrophilic and oleophilic sites are essential to simultaneously realize the generation of polar oxidants and adsorption of organic reactants on the catalytic surface (11). Therefore, toward achieving efficient charge dynamics and surface kinetics for C-H activation, a photocatalyst not only needs to have excellent charge transport properties but also must have balanced hydrophilic and oleophilic reactive sites.

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Over the past few years, two-dimensional (2D) sp² carbon-conjugated covalent organic frameworks (sp²-c-COFs) have received great attention as promising polymeric photocatalysts for various applications (12–15). The porous nature of sp²-c-COFs allows for exceptionally large surface area ($S_{BET} \sim 600 \text{ m}^2 \text{ g}^{-1}$), and the organic units within the layered 2D π lattices serve as effective sites to adsorb oleophilic organic molecules (16, 17). However, the majority of these 2D sp²c-COFs lack hydrophilic sites, which are crucial for generating ROS in photocatalysis. This limitation causes unbalanced reactive sites for organic reactant adsorption and oxidant formation. In addition, the much larger effective masses ($m_{e,h+}^*$), smaller dielectric constant (ε_r 5 to 10), and higher exciton binding energy (E_{xBE}) of COFs result in lower intrinsic exciton diffusion length and poorer charge separation efficiency of COFs as compared with inorganic semiconductors (18). Most of the recent works focused on tuning the COF structure to form donor and acceptor pairs to improve charge separation. However, even with introducing strong electron-withdrawing groups (19-21) or electron-donating groups (22) into the building blocks of COFs, these modification strategies could only slightly change the dielectric constant (ε_r 10 to 20, 293 K) (23). As a result, the dominant transitions in these functionalized COFs still maintained localized, i.e., large Coulomb interaction between photogenerated electrons and holes suppressed the efficient charge separation (19). On the other hand, if the pores of the COFs can be filled by water, then the high dielectric constant of water ($\varepsilon_r \sim 80, 293$ K) may increase the effective dielectric property of the material, leading to the notably enhanced built-in electric field for driving charge separation. The highly oleophilic surface of COFs becomes the largest obstacle that prevents water diffusion from bulk into the inner pore, resulting in poor charge separation efficiency and sluggish surface kinetics of COFs in selective photocatalytic oxidation reactions.

Cyanide-bridged amorphous metal-organic frameworks exhibit excellent water adsorption behavior with reversible amorphous/ crystalline transitions (24–27). The metal cyanides in the framework can effectively capture H_2O molecules by changing the local

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coordination geometry of the metal center. For instance, 1 mol of Ni(CN)₄ can chemically adsorb 6 mol of H₂O by forming (H₂O)₂·4H₂O at $P/P_0 = 0.8$ (24). Unfortunately, the reported transition metal centers, including Fe, Ni, Pd, and Pt, are difficult to couple into a photocatalytic system due to their high charge recombination characteristics, originating from the intermediate band formed by the half-filled *d* electrons. Constructing photocatalysts with d¹⁰ metal sites has been proven effective in eliminating the formation of intermediate bands in the band structure of polymeric photocatalysts (28, 29). In this study, we design and develop an efficient photocatalytic system to realize selective photocatalytic oxidation of toluene in an aqueous solution under visible light illumination. Sb(CN)₃ (see the Supplementary Materials) was adopted to modify the inner pores of sp²-c-COFs to enhance hydrophilicity through the formation of C≡N-Sb(CN)₃ (referred to as Sb-sp²-c-COFs). After surface modification, the Sb-sp²-c-COFs exhibited two orders of magnitude improvement in selective photocatalytic toluene oxidation to benzyl benzoate: In 5 hours, the conversion of toluene reached 68% with a benzyl benzoate selectivity of 80% in a saturated toluene aqueous solution (0.57 g liter⁻¹, 303 K) (Fig. 1). The $C \equiv N-Sb(CN)_3$ sites can substantially enhance charge concentration and charge separation, but only in the presence of water. Time-dependent density functional theory (TD-DFT) calculations indicate that the introduction of Sb(CN)3 can result in typical charge transfer transitions with delocalized photogenerated electrons and holes within the π -conjugated framework of sp²-c-COFs. This finding is further supported by the long-lived carrier lifetime of Sb-sp²-c-COFs

measured by transient absorption spectroscopy (TAS) in an aqueous solution. The concept of utilizing hydrophilic sites to simultaneously enhance surface kinetics and charge dynamics offers a practical design guideline for the development of more advanced systems for artificial photosynthesis.

RESULTS

Crystallinity and porosity

To prepare amorphous Sb(CN)₃, 0.01 mol of SbF₃ was stabilized in a polar solvent such as ethanol (EtOH) or methanol (MeOH). Upon adding 0.03 mol of NaCN, the fluorine atoms in SbF3 were replaced by CN species from NaCN (fig. S1). After removing the solvent from the system, the molar ratio of Sb to CN species was determined to be 1:3 through a combination of inductively coupled plasma spectroscopy and a titration method using silver nitrate (AgNO₃). Next, the amorphous Sb(CN)₃ was dispersed in deuterated dimethyl sulfoxide (DMSO-d6). The ¹³C NMR (nuclear magnetic resonance) spectra reveal chemical shifts at 124, 57, and 19 parts per million (ppm), corresponding to -CN, -OCH₂, and -CH₃ groups in Sb(CN)₃, respectively (Fig. 2, A and B). These results are in good agreement with the simulated data and the previously reported $Sb(CN)_3(THF)_2$ in the literature (30). The sp²-c-COFs were prepared via a Doebner-Knoevenagel reaction between tetrakis(4-formylphenyl)pyrene (TFPPy) and phenylenediacetonitrile (PDAN) under solvothermal conditions (15, 16) in a mixture of mesitylene and dioxane (1:5 v/v), 4 M NaOH for 5 days



Fig. 1. Amphiphilic sites for photocatalytic C-H activation of toluene. (**A**) Schematic diagram of the oleophilic surface of pristine sp²-c-COFs. (**B**) Comparison of contact angle of sp²-c-COFs by using a droplet of water (left) and toluene (right). (**C**) Schematic diagram of toluene adsorption over pristine sp²-c-COFs. (**D**) Schematic diagram of Sb-sp²-c-COFs surface with balanced hydrophilic and oleophilic sites. (**E**) Contact angle of Sb-sp²-c-COFs by using a droplet of water (left) and toluene (right). (**F**) Schematic diagram of toluene adsorption and water adsorption over Sb-sp²-c-COFs.



Fig. 2. Crystallinity and porosity of Sb(CN)₃-modified sp²-c-COFs. (A) ¹³C NMR spectrum of amorphous Sb(CN)₃ dispersed in DMSO-d6. (**B**) Simulated ¹³C NMR spectrum of Sb(CN)₃(EtO)_{3-x}(OH)_x by ChemBioDraw Ultra 12.0. (**C**) Powder x-ray diffraction (PXRD) patterns of the as-prepared sp²-c-COFs and Sb5-sp²-c-COFs. (**D**) The simulated sp²-c-COFs using COFs.cif downloaded from materials project, in which the pyrene units have 2-nm periodic spacing. The figure is plotted by the package of VESTA. (**E** and **F**) Isotherm linear plot (E) and pore volume (F) of sp²-c-COFs (pore size distribution was obtained by the derivation of plot in pore volume). (**G** and **H**) Isotherm linear plot (G) and pore volume (H) of Sb5-sp²-c-COFs (pore size distribution was obtained by the derivation of plot in pore volume). a.u., arbitrary units.

(fig. S2). The resulting sp^2 -c-COFs display powder x-ray diffraction (PXRD) peaks at 3.6°, 5.2°, 5.9°, 7.3°, 11.2°, 11.8°, 14.2°, and 24.7° corresponding to the (110), (200), (210), (220), (240), (420), (520), and (001) facets, respectively (Fig. 2C, black curve) (14). The simulated sp²-c-COFs structure consists of sp² carbon chains extending along the x and y directions, with pyrene units acting as interweaving registry points pitched periodically at 2-nm intervals (Fig. 2D) (4, 28). Nitrogen sorption isotherm analysis shows that the as-prepared sp²c-COFs exhibit a reversible adsorption-desorption behavior, with a Brunauer-Emmett-Teller (BET) surface area of $652 \text{ m}^2 \text{ g}^{-1}$ (Fig. 2E). The pore-size distribution profile reveals a microporous feature of sp²-c-COFs with a mean pore size of 1.86 nm (Fig. 2F) and a pore volume of 0.29 cm³ g⁻¹ (Fig. 2F). Upon introducing Sb(CN)₃ species into sp²-c-COFs [abbreviated as SbX-sp²-c-COFs, where X represents the amount of Sb(CN)3 added; table S1], both the PXRD patterns and BET surface areas remain almost unchanged (Fig. 2, G and H). Taking Sb5-sp²-c-COFs as an example, the BET surface area was measured to be $604 \text{ m}^2 \text{ g}^{-1}$, with an average pore size of 1.83 nm and a pore volume of 0.27 cm³ g⁻¹.

Elemental characterization of Sb(CN)₃-modified sp²-c-COFs

To investigate the composition and chemical state of $Sb(CN)_3$ species in sp²-c-COFs, amorphous $Sb(CN)_3$ was prepared and characterized (fig. S3). Similar to $Sb(CN)_3$ (THF)₂ (30), Sb(CN)₃ could form a stable

solution in EtOH (Fig. 3A), suggesting that the Sb centers are isolated in the as-prepared amorphous Sb(CN)₃(EtOH)_{3-x}(H₂O)_x [referred as amorphous Sb(CN)₃]. The second (outer) coordination sphere involves van der Waals interactions with both EtOH molecules and one adjacent N atom of a neighboring Sb(CN)3 species (30). Fouriertransform infrared (FTIR) spectroscopy reveals a peak at 2220 cm⁻¹ that can be assigned to the cyano group (fig. S4A), and the peak at 2720 cm⁻¹, resulting from the C-H bond of the aldehyde group, was greatly attenuated, indicating successful polymerization between TFPPy and PDAN in the presence of Sb(CN)₃ (30). Both TFPPy and PADN are highly hydrophobic, as well as the prepared sp²-c-COFs (Fig. 1, B and C, and fig. S5A). On the contrary, the appearance of a broad peak at 3500 cm⁻¹ over amorphous Sb(CN)₃ (fig. S4B) indicates a strong affinity of Sb(CN)₃ to water molecules (24, 26). The peak intensity gradually increased in the FTIR spectra of Sb(CN)₃-modified sp²c-COFs with increasing Sb(CN)3 content, indicating that H2O could be captured by Sb(CN)₃. The same conclusion was verified by the surface contact angle measurement. The water contact angle on Sb5sp²-c-COFs surface decreased to 31° from 132° on pristine sp²-c-COFs (fig. S4) (31), i.e., Sb5-sp²-c-COFs showed almost amphipathic properties with both water and toluene (fig. S5, B to D). Water and toluene uptake curves of Sb5-sp²-c-COFs and sp²-c-COFs also supported that the pristine sp²-c-COFs showed strong affinity for toluene but weak affinity for water (fig. S6). After the introduction of Sb(CN)₃,

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Fig. 3. Composition and chemical state of Sb(CN)₃ in sp²-c-COFs. (**A**) Photograph of Sb(CN)₃ dissolved in EtOH and the possible chemical structure obtained based on the Sb(CN)₃(THF)₂ (*30*). (**B**) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Sb5-sp²-c-COFs and the possible chemical structure of Sb species. The estimated size distribution of bright spots shows that about 99.5% of the Sb species are less than 0.2 nm. The scale bar in the HAADF-STEM image is 2 nm. (**C**) C 1s x-ray photoelectron spectroscopy (XPS) spectra of amorphous Sb(CN)₃, sp²-c-COFs, and Sb5-sp²-c-COFs. (**D**) Solid-state ¹³C NMR spectra of sp²-c-COFs and Sb5-sp²-c-COFs. (**E**) O 1s and Sb 3d XPS spectra of amorphous Sb(CN)₃, sp²-c-COFs, and Sb5-sp²-c-COFs. (**F**) K-edge x-ray absorption near edge structure spectra of Sb(CN)₃(EtO)_{3-x}(OH)_x, Sb5-sp²-c-COFs, Sb₂O₃, Sb-foil, and Sb₂O₅. (**G**) Extended x-ray absorption fine structure fitting results for amorphous Sb(CN)₃ and Sb5-sp²-c-COFs.

the toluene and water adsorption was well-balanced, which showed good consistency with the changing tendency revealed by the contact angle measurement. As displayed in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 3B), the isolated bright spots can be assigned to the atomically dispersed Sb, which are uniformly distributed in the matrix of sp²-c-COFs (Fig. 3B and figs. S7 and S8).

To investigate the interactions between the Sb(CN)₃ species and the sp²-c-COFs backbone, x-ray photoelectron spectroscopy (XPS) measurements were conducted (Fig. 3 and fig. S9). As shown in the high-resolution C 1s XPS spectrum of amorphous Sb(CN)₃, a peak at 285.4 eV could be assigned to Sb-C \equiv N (Fig. 3C). In Sb5-sp²-c-COFs, the 285.4 eV XPS peak is well reserved, indicating successful introduction of Sb(CN)₃ into sp²-c-COFs [note that the C 1s binding energy of N-C=N in pristine sp²-c-COFs (286.5 eV) is slightly larger than that of Sb-C=N in Sb(CN)₃] (32). The same conclusion was further supported by the solid-state ¹³C NMR results. The height ratio of the peak at 104 ppm (assignable to cyano groups) to the peak at 127 ppm (assignable to C=C groups) slightly increased from 0.106 to 0.159 (Fig. 3D), which is due to the introduction of cyanamide complexes in Sb(CN)₃ (31, 33). In the high-resolution Sb 3d XPS spectrum, the peak at 540.2 eV over Sb5-sp²-c-COFs could be assigned to Sb 3d_{3/2}, which is very close to the binding energy of Sb 3d_{3/2} in Sb(CN)₃ (Fig. 3E). The unchanged chemical state of Sb species in Sb5-sp²-c-COFs as compared to that in Sb(CN)₃ can be attributed to the weak interaction (van der Waals interaction) between N-C=N and $Sb(CN)_3$ species (30). In addition, the peak at 532.5 eV could be assigned to adsorbed water (Fig. 3E). The greatly increased intensity at 532.5 eV indicated improved water adsorption after the introduction of $Sb(CN)_3$, matching well with the FTIR result.

To further dig out the chemical state and the Sb coordination structure in Sb5-sp²-c-COFs, we performed x-ray absorption near edge structure (Fig. 3, F and G) measurements at the Sb K-edge. As compared in Fig. 3F, the Sb absorption edge for Sb5-sp²-c-COFs, Sb⁺³₂O₃, and amorphous Sb(CN)₃ are about 2.5 eV higher than that for Sb⁰ foil and 1.9 eV lower than that for Sb⁺⁵₂O₅, suggesting around +3 valence state of Sb in Sb5-sp²-c-COFs. Fourier-transformed extended x-ray absorption fine structure (FT-EXAFS) spectrum obtained from the k³-weighted K-space (Fig. 3G and figs. S10 and S11) of Sb5-sp²-c-COFs shows only one peak at about 1.53 Å, and no Sb-Sb bond at around 2.7 Å can be detected, implying that the Sb sites in Sb5-sp²-c-COFs are atomically dispersed. Note that the FT-EXAFS spectrum of amorphous Sb(CN)₃ shows a Sb-Sb coordination at 2.7 to 3.0 Å, which can be assigned to the x-ray scattering of Sb atoms. The disappearance of Sb-Sb coordination further supported isolated Sb sites in Sb5-sp²-c-COFs. To identify the Sb coordination structure, models of sp²-c-COFs with single Sb sites (fig. S12) (18, 34, 35) were simulated by DFT. The calculation results reveal that Sb is coordinated with three C atoms and one N atom in sp²-c-COFs (the N atom in sp²-c-COFs exhibits an extremely weak interaction with Sb). In addition, the fitting results of Sb5-sp²-c-COFs indicate that each Sb atom is coordinated with eight to nine C, N, and/or O atoms on average (table S2). Note that the saturated coordination number of Sb is 6. Such a large coordination number (~10) of Sb in Sb5-sp²-c-COFs could be attributed to water adsorption over the Sb(CN)₃ species, similar to water adsorption via lattice change in Ni(CN)₄) (24, 26).

Optical and charge dynamic properties of Sb5-sp²-c-COFs

The optical properties of Sb5-sp²-c-COFs and pristine sp²-c-COFs were investigated by ultraviolet-visible (UV-vis) spectroscopy. The introduction of Sb(CN)₃ species did not change the bandgap of sp²c-COFs (Fig. 4A) if adsorbed water was removed by drying at 120°C for 12 hours in a vacuum oven. However, once Sb5-sp²-c-COFs adsorbed water, the bandgap of Sb5-sp²-c-COFs shrank from 2.10 to 1.95 eV (Fig. 4A). Verified by valence band XPS and Mott-Schottky plots, the introduction of water showed negligible influence on the highest occupied molecular orbital (HOMO) of sp²-c-COFs and Sb5-sp²-c-COFs, matching well with the simulation results by the polarizable continuum model (PCM; solvent = water) (figs. S13 to S15). On the contrary, the lowest unoccupied molecular orbital (LUMO) of Sb5-sp²-c-COFs shifted down by 0.2 eV after the introduction of water (fig. S15, E and F), which is also consistent with the simulation result. As depicted in the energy diagram, a previously undetected state primarily composed of C 2p electrons emerges in the partial density of states between the HOMO and LUMO levels (fig. S15D). This newly emerged C 2p state is attributed to the strong polarization of water, which affects the charge distribution in Sb5-sp²-c-COFs. As shown in (Fig. 1 B and E), it is observed that the water contact angle on the surface of pristine sp²-c-COFs exceeds 130°. In contrast, the water contact angle on the surface of Sb5-sp²-c-COFs is close to 30°, suggesting that the strong interaction between water and Sb5-sp²-c-COFs results in the pronounced polarization of C 2p electrons (36), which positively shifts the LUMO level of Sb5-sp²-c-COFs upon water adsorption and creates a new trapping state for free carriers. As shown in

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Fig. 4B, the number of unpaired electrons in sp²-c-COFs remains largely unaffected after light irradiation when water is introduced, indicating the minimal influence of water on the excitation process of pristine sp²-c-COFs. Conversely, the unpaired electrons in Sb5-sp²-c-COFs substantially increase after light irradiation with water adsorption, suggesting that this newly formed state can efficiently enhance the population of free carriers by trapping photogenerated electrons.

The notably increased number of unpaired electrons in Sbsp²-c-COFs after exposing Sb-sp²-c-COFs to moisture suggests the crucial role water adsorption played toward improving charge separation. Of note, the dielectric constants of polymeric semiconductors are usually very small (37–39), leading to strong Coulomb interaction between photogenerated electrons and holes. Therefore, the large binding energy of excitons and almost absence of a spacecharge layer usually occur in an organic semiconductor photocatalytic system. Generally, increasing porosity will decrease the effective dielectric constant of a material. If the pores of a porous organic semiconductor photocatalyst can be filled with water, then the high dielectric constant of water (~80) as compared with that of the solid material may help to extract charge carriers from the framework, thus assisting charge separation. To better understand whether water introduced into sp²-c-COFs can improve charge dynamics (18), TAS measurements were conducted over Sb5-sp²-c-COFs and pristine sp²-c-COFs that were dissolved in 50% (v/v) N,N'-dimethylformamide (DMF) aqueous solution. We did not use pure water as a solvent because of the extremely poor dispersibility of pristine sp²-c-COFs in pure water. To investigate the relationships between shallow and deep traps, the kinetics at 680 nm was recorded after excitation at 345 nm (Fig. 5, A and B) (40). The kinetics fitting results of sp^2 c-COFs are summarized in Table 1, which shows two of the threetime constants with $\tau_1 = 3.262$ ps and $\tau_2 = 241.7$ ps, resulting from the recombination of free photogenerated electrons and holes, and the shallow charge trapping. The kinetics of Sb5-sp²-c-COFs can be fitted by three times constants with $\tau_1 = 5.499$ ps, $\tau_2 = 366.9$ ps, and $\tau_3 > 2$ ns. The lifetime of the deeply trapped electrons in Sb-sp²-c-COFs and sp²-c-COFs are almost the same (Table 1, τ_3), indicating that the introduction of Sb(CN)3 species could barely influence long-lived intermediates (with a time scale larger than 2 ns). Therefore, the shallow trapped electrons (τ_1 and τ_2) of sp²-c-COFs are highly concentrated at the surface after the introduction of Sb(CN)₃ in the presence of water, leading to an elongated lifetime of mobile charge carriers (29, 41, 42).

TD-DFT calculations were further performed to get insights into the charge dynamics of sp²-c-COFs and Sb-sp²-c-COFs. To give a comprehensive understanding of the influence of water on the excitation properties of sp²-c-COFs and Sb-sp²-c-COFs, models of sp²c-COFs and Sb-sp²-c-COFs were calculated in vacuum or in PCM (solvent = water) conditions. All transition densities of the 50 excited states (ES) were calculated by function of ω97xd (Fig. 5D). The simulated absorption spectrum of sp²-c-COFs and Sb-sp²-c-COFs look almost the same, matching well with the experimental results that introducing Sb(CN)₃ species into sp²-c-COFs did not influence the band diagram (Fig. 4A). When water was adopted as solvent in PCM condition, the simulated spectrum of sp²-c-COFs still showed almost no change. However, two new states could be detected at the low energy levels. By comparing the UV-vis spectrum with the simulated absorption spectrum, the water adsorption induced newly formed ES (ES2 and ES3; Fig. 5D) expand the light absorption region of

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Fig. 4. Optical properties of Sb5-sp²-c-COFs and sp²-c-COFs before and after the introduction of water. (**A**) UV-vis spectra of sp^2 -c-COFs and Sb5-sp²-c-COFs under the condition with/without water adsorption. (**B**) Electron paramagnetic resonance (EPR) spectra of sp^2 -c-COFs and Sb5-sp²-c-COFs in dark conditions (line a) or under light irradiation for 30 min (line b). The sample was measured in the condition with/without water adsorption. The sample without water adsorption was prepared by drying in a vacuum oven at 120°C for 12 hours. Then, the sample was cooled down in a desiccator in a vacuum to avoid water re-adsorption. To prepare the sample with water adsorption, the sample was stored in moisture ($P/P_0 = 0.8$) for 12 hours. Line c represents the ESR spectra obtained by subtracting signals from line a and line b. The integration of line c allows us to observe the overall change in the signal corresponding to the presence of unpaired electrons after light irradiation, which is depicted in line d.

Sb-sp²-c-COFs (Fig. 4A). Note that the redshift of the simulated spectrum is larger than the experimentally measured one, which is due to the large delocalization correlation exchange contents of the ω 97xd function that usually overestimates the excitation energy and enlarges the energetic difference between orbitals (43). Compared to models calculated in vacuum and sp²-c-COFs calculated in PCM, only ES2 and ES3 of Sb-sp²-c-COFs calculated in PCM (solvent = water) show higher electron/hole density. On the contrary, for sp²-c-COFs in PCM (solvent = water), no ES can be observed in the low-energy region. The distance between the centroid of simulated electrons or holes (D index) of all systems was further studied to estimate the possible charge separation efficiency of the photogenerated electrons and holes. Notably, the newly appeared ES (ES2 and ES3) show notably decreased exciton binding energy (1.450 eV of ES2 and 1.531 eV of ES3) (fig. S16). In addition, the D index values for ES2 and ES3 of Sb-sp²-c-COFs in PCM (solvent = water) are much larger as compared with other representative states (Fig. 5E), suggesting that the interaction between water and sp²-c-COFs induced by Sb(CN)₃ can promote charge separation. Furthermore, the delocalized state densities of photogenerated electrons and holes only appear in these two transitions (Figs. 5, F and G, and 4, H and I). All other transitions (see Supplementary Text and figs. S17 to S25) show highly localized electron-hole distributions.

Such highly overlapped electron-hole distributions reveal strong Coulomb interactions between photogenerated electrons and holes, which shall lead to fast charge recombination during photoexcitation. Note that no electrons or holes accumulate at the Sb(CN)₃ sites in Sb-sp²-c-COFs, suggesting that the Sb sites may not participate in the photocatalytic reaction. In situ XPS measurements further indicate that there is no obvious charge transfer to Sb during light irradiation (fig. S26), as well as the control experiment by using pure Sb(CN)₃ (fig. S27). The suppressed charge recombination of Sb5sp²-c-COFs in an aqueous solution and the two new charge transfer transitions appearing in Sb-sp²-c-COFs indicate that Sb(CN)₃ only works as an efficient water-capturing site. The interaction between H_2O and sp^2 -c-COFs can be substantially strengthened by Sb(CN)₃, which will greatly enlarge the dielectric constant of Sb-sp²-c-COFs, promoting the extraction of photogenerated charge carriers in Sbsp²-c-COFs.

Photocatalytic toluene oxidation

To investigate the relationship between photocatalytic performance and water capture by $Sb(CN)_3$ in sp²-c-COFs, selective oxidation of toluene was used as a model reaction (44, 45). Toluene (185 µmol) was added to 30 ml of water to form a saturated toluene aqueous



Fig. 5. Charge dynamic properties of Sb5-sp²-c-COFs and sp²-c-COFs before and after water introduction. (A and B) Femtosecond TAS measurements of sp²-c-COFs and Sb5-sp²-c-COFs in 50% (v/v) DMF aqueous solution (excitation: 345 nm). (C) Temporal change of transient absorption at 680 nm. (D) Simulated UV-vis absorption spectra based on TD-DFT calculations. Representative excitation states (ESs) in the simulated spectra of the sp²-c-COFs and Sb-sp²-c-COFs models are highlighted by comparing the oscillator strength of each transition. Models in vacuum and in PCM (solvent = water) were calculated to reveal the effects of water on the excitation properties of sp²-c-COFs. (E) The distance between the centroid of simulated electrons or holes (D index). (F and G) Electron delocalization index (F) and hole delocalization index (G) of the sp²-c-COFs and Sb-sp²-c-COFs models in a vacuum or in PCM. (H and I) Calculated electron/hole distribution of newly appeared two transitions (ES2 and ES3) in the spectra of the Sb-sp²-c-COFs model simulated by PCM (solvent = water).

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Photocatalyst	A ₁ (%)	τ ₁ (ps)	A ₂ (%)	τ ₂ (ps)	A ₃ (%)	τ ₃ (ps)	τ∗(ps)
sp ² -c-COFs	41.41	3.262	33.16	241.7	25.43	2230	237.7
Sb5-sp ² -c-COFs	35.54	5.499	38.38	366.9	26.08	2594	362.0

solution for investigating the co-effect of both water and hydrophilic Sb-sp²-c-COFs. Figure S28 shows the possible route of heterogeneous toluene oxidation (2). Different products can be formed following different oxidation processes: (i) Active methyl group in toluene can be firstly oxidized to benzyl alcohol. (ii) Benzyl alcohol can be further oxidized to benzaldehyde via stepwise oxidation in thermal catalysis. (iii) Coupling of benzaldehyde and benzyl alcohol 2 can produce hemiacetal 5, followed by oxidation to ester. (iv) Benzaldehyde can be further oxidized to benzoic acid. (v) Benzyl benzoate can be formed by direct dehydrative esterification between acid 4 and alcohol 2 (2). Oxidation of toluene could not occur in the absence of light or photocatalyst (table S3). The valence band maximum of Sb-sp²-c-COFs and sp²-c-COFs are close to 1.4 V (versus NHE), which is suitable for the 4e⁻ water oxidation reaction. The ROS on the surface of Sbsp²-c-COFs and sp²-c-COFs could both participate in toluene oxidation. For the reduction side, the CBM of Sb-sp²-c-COFs and sp^2 -c-COFs are at -0.5 V (versus NHE), suitable for the generation of ROS via oxygen reduction. If pristine sp²-c-COFs were used as a photocatalyst, then only 1.3% toluene could be converted to benzaldehyde, while other toluene was almost maintained after the reaction (fig. S29). With the introduction of $Sb(CN)_3$ species into sp²-c-COFs, the main photoreaction product over Sb-sp²-c-COFs changed from benzaldehyde to benzyl benzoate. If 5 µmol of Sb(CN)3 species was introduced, then the total conversion of toluene over Sb5-sp²-c-COFs reached close to 70% in 5 hours (fig. S30) with benzyl benzoate selectivity over 80%. Figure 6A shows the products of toluene oxidation over Sb5-sp²-c-COFs in 5 hours. At the beginning stage, only benzaldehyde was detected (Fig. 6A and fig. S31). Subsequently, benzyl benzoate gradually accumulated with prolonging the photoreaction (Fig. 6A and figs. S32 to S35). Note that almost no CO_2 could be detected in the reaction system of Sb5-sp²-c-COFs (fig. S36). Meanwhile, the total toluene conversion rate over Sb5-sp²-c-COFs reached 2.248 mmol $g_{catalyst}^{-1}$ hour⁻¹, which is 54 times superior to that over pristine sp²-c-COFs. Moreover, the Sb5-sp²-c-COFs photocatalyst could be recycled and tested for five cycles of photoreaction without observing noticeable photoactivity decay (fig. S37). The photocatalytic durability of Sb5-sp²-c-COFs can also be reflected by the retained crystallinity (fig. S38), porosity (fig. S39), and surface species (fig. S40). The action spectrum of Sb5-sp²-c-COFs fits well with the absorption spectrum, indicating that the band excitation contributes to the toluene oxidation (fig. S41). As shown in table S4, the mass content of Sb showed almost no change. In addition, no Sb species were found in the solution phase, indicating excellent stability of the photocatalyst. We further expanded the substrate scope and compared the photocatalytic performance (fig. S42), indicating good application potential for the as-proposed photocatalyst.

To reveal the reaction mechanism of photocatalytic toluene oxidation over Sb5-sp²-c-COFs, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted (Fig. 6C). Once toluene and O₂ are co-adsorbed on Sb5-sp²-c-COFs under light irradiation, a new vibrational peak at 1695 cm⁻¹, which can be attributed to the stretching vibration of the benzaldehyde carbonyl group, appears and increases in intensity with prolonging reaction time in the first 30 min. Then, the intensity of this peak gradually increased coupled with a slight peak shift from 1695 to 1718 cm⁻¹, indicating that benzaldehyde was gradually converted to benzyl benzoate. The peaks centered at 1362 and 1175 cm⁻¹ are ascribed to the hydroperoxide species, which decompose toluene into products through dehydration (7). The peaks near 1500 cm⁻¹ and in the wavenumber range from 2500 to 3100 cm⁻¹ gradually grew, indicating gradual accumulation of toluene oxidation products (boiling point for toluene: 110.6°C; benzyl alcohol 205°C; benzaldehyde: 178.1°C; and benzyl benzoate: 323°C). In addition, no notable peaks for CO_2 at around 2300 cm⁻¹ could be observed, indicating partial oxidation of toluene over Sb5-sp²-c-COFs.

Electron paramagnetic resonance (EPR) spectroscopy experiments were carried out to reveal the generated ROS during photocatalytic toluene oxidation. First, to investigate the interaction between water and oxygen species, the spin signal of $\cdot O_2^-$ was taken in both pure MeOH and 50% (v/v) MeOH aqueous solution. Typical signal of $DMPO-O_2^{-}$ was identified in all systems under light irradiation, verifying generation of $\cdot O_2^-$ (Fig. 6D) (46). No obvious enhancement of DMPO- \cdot O₂⁻ could be detected in the system of sp²-c-COFs even when water was introduced. On the other hand, Sb5-sp²-c-COFs showed notably enhanced DMPO- \cdot O₂⁻ peak with the introduction of water. The strong interaction between water and Sb5-sp²-c-COFs notably improved charge separation (Fig. 5) and the photoactivity for O_2 reduction to generate $\cdot O_2^-$. Then, quenching experiments were performed to identify the key reactive species induced by light for oxidation of toluene (fig. S43). The introduction of 2,2,6,6-tetramethylpiperidine-N-oxyl as the quenching agent for all radicals almost completely suppressed toluene oxidation. Benzoquinone (BQ) and AgNO₃ are usually used to quench $\cdot O_2^-$ and electrons. The toluene oxidation activity was substantially reduced if BQ and AgNO3 were added into the reaction system, indicating that $\cdot O_2^-$ and electrons participated in the toluene oxidation reaction. Furthermore, the addition of triethanolamine as the quenching agent for photogenerated holes (h⁺) caused an apparent decrease in toluene conversion to benzyl benzoate and benzaldehyde, suggesting that holes initiated the C-H activation of toluene. In addition, the introduction of butylated hydroxytoluene as the quenching agent for carbon-centered radicals obviously declined toluene conversion, suggesting that carboncentered radicals are important intermediates in the toluene oxidation reaction. These carbon-centered radicals are mostly benzyl radicals that react with $\cdot O_2^-$ and H⁺ to form ph-CH₂OOH and lastly form benzaldehyde after dehydration (44, 45). Note that the essential condition to form benzyl benzoate is that benzyl alcohol must be generated in the system first to react with acid or aldehyde (fig. S28). EPR results obtained in the Ar atmosphere showed that .OH and carboncentered radicals could be simultaneously detected in the system of Sb5-sp²-c-COFs, while only carbon-centered radicals could be detected in the system of sp²-c-COFs (fig. S44). Benzyl alcohol could be directly formed by a radical reaction between benzyl radical (generated from oxidation of toluene) and ·OH (generated from oxidation of water) (47, 48). Note that the redox potential for \cdot OH (ad) generation is around 1.33 to 1.5 V versus normal hydrogen electrode (48), which is thermodynamically achievable in the Sb5-sp²-c-COFs system (fig. S15). Previous literature also suggested that a very small amount of benzyl alcohol could be generated from ph-CH2OOH during photocatalytic reduction. To further investigate the reaction pathway of photocatalytic toluene oxidation, isotopic experiments were conducted to trace the oxygen in the final reaction products (figs. S45 and S46). $^{18}O_2$ or H₂¹⁸O was respectively used as the precursor to replace $^{16}O_2$ or H₂¹⁶O in the photocatalytic system. Since benzyl benzoate is insoluble

or H_2 ¹⁶O in the photocatalytic system. Since benzyl benzoate is insoluble in water, we separated the aqueous phase and oil phase by extraction. Both the aqueous phase and oil phase were separately measured by a gas chromatography–mass spectrometry equipped with a flame ionization detector (FID). The mass spectra of benzaldehyde (in the

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Fig. 6. Photocatalytic performance and reaction mechanism of toluene oxidation. (**A**) Photocatalytic toluene oxidation products over Sb5-sp²-c-COFs. (**B**) Selectivity and conversion of toluene oxidation over SbX-sp²-c-COFs. Sb-0, Sb-1, Sb-2, and Sb-5 indicate the amount of Sb(CN)₃ (in micromoles) introduced into sp²-c-COFs. (**C**) Diffuse reflectance infrared Fourier transform spectroscopy spectra recorded over Sb5-sp²-c-COFs during photocatalytic toluene oxidation. (**D**) EPR trapping experiments for $\cdot O_2^-$ radicals [from top to bottom: sp²-c-COFs in pure MeOH, sp²-c-COFs in 50% (v/v) MeOH aqueous solution, Sb5-sp²-c-COFs in pure MeOH, and Sb5-sp²-c-COFs in 50% (v/v) MeOH aqueous solution]. (**E**) The kinetic isotope effect experiments using deuterated toluene (toluene-d8). (**F**) The proposed photocatalytic mechanism of Sb5-sp²-c-COFs for photocatalytic oxidation of toluene in aqueous solution.

aqueous phase) and benzyl benzoate (in the oil phase) are given in fig. S45. When the reaction was conducted in ${}^{18}O_2$ and $H_2{}^{16}O$, the mass/charge ratio (*m/z*) of the molecular ion peak for benzaldehyde was 108, indicating that ${}^{18}O_2$ participated in the benzaldehyde generation reaction. On the contrary, the *m/z* of molecular ion peak for benzaldehyde maintained 106 if the reaction was performed in ${}^{16}O_2$ and $H_2{}^{18}O$, suggesting that H_2O was not involved in the formation

of benzaldehyde. The m/z of molecular ion peak for benzyl benzoate formed in ${}^{16}O_2$ and $H_2{}^{18}O$ is 214, compared to 212 of that measured in the ${}^{16}O_2$ and $H_2{}^{16}O$ reaction system. The m/z change from 214 to 194 indicates the loss of an $H_2{}^{18}O$ fragment after the formation of the benzophenone cation, highlighting that the ${}^{18}O$ in benzyl alcohol participated in the formation of the ester group. Therefore, the oxygen source of benzyl alcohol is from water oxidation, rather than oxygen reduction. Our reaction system is weakly acidic (pH 4.5 at the reaction time of 5 hours), suggesting an extremely slow direct ester reaction. The most possible route to generate benzyl benzoate is that benzyl alcohol reacts with benzaldehyde to form hemiacetal, and then the formed hemiacetal is further oxidized to generate ester by the oxygen reduction reaction (ORR) related ROS in the solution. The kinetic isotope effect experiments show a $k_{\rm H}/k_{\rm D}$ value of 4.18, which reveals that the C(*sp*³)—H bond activation process may be the rate-determining step (Fig. 6E) (7, 49).

DISCUSSION

On the basis of the above studies, the reaction mechanism of photocatalytic toluene oxidation over Sb5-sp²-c-COFs photocatalyst is proposed as follows (Fig. 6F; the detailed reaction equations are presented in the Supplementary Materials): O_2 was first reduced to $\cdot O_2^-$ by photogenerated electrons on Sb5-sp²-c-COFs, while photogenerated holes simultaneously oxidized water and toluene to form $\cdot OH$ (ad) and benzyl radicals. Subsequently, benzyl radicals reacted with $\cdot O_2^-$ to generate ph-CH₂OOH, which was further converted to benzaldehyde after a dehydration reaction. Benzyl radicals could also directly combine with $\cdot OH$ (ad) to generate benzyl alcohol. The generated benzyl alcohol and benzaldehyde could react with each other to form hemiacetal catalyzed by Brönsted acid (could be released H⁺ during direct oxidation of toluene and water by photogenerate holes), and the hemiacetal could be further oxidized to generate ester by the ORR related ROS in solution.

In conclusion, Sb(CN)₃ species are applied to modify the inner pores of sp²-c-COFs to enhance hydrophilicity through the formation of C=N-Sb(CN)₃. Although atomically dispersed C=N-Sb(CN)₃ sites do not work as reactive sites for photoredox reaction, the modification substantially enhances charge concentration and charge separation of Sb-sp²-c-COFs in the presence of water, supported by the long-lived carrier lifetime of Sb-sp²-c-COFs measured by TAS in an aqueous solution. After surface modification, the Sb5-sp²-c-COFs exhibit 54 times improvement in conversion rate for selective photocatalytic toluene oxidation. The concept of utilizing hydrophilic sites to simultaneously enhance surface kinetics and charge dynamics offers a practical design guideline for the development of more advanced photocatalytic systems for artificial photosynthesis.

MATERIALS AND METHODS

Characterization of CN species

To release CN species in Sb(CN)₃, phosphoric acid and disodium EDTA were first added into Sb(CN)₃ aqueous solution, followed by heating and distillation at pH < 2. At the same time, 0.02 g of paradimethylaminobenzalrhodanine (silver spirit) was dissolved in 100 ml of acetone. This regent was stored in a brown bottle that could remain stable for one month in the dark. The total CN in Sb(CN)₃ was measured by a titration method using 0.01 M AgNO₃ solution (silver spirit was used as an indicator).

Regents

Tetrahydrofuran (THF), acetone, acetonitrile, mesitylene, dichloromethane, MeOH, chloroform, DMF, and 1,4-dioxane were purchased from Sigma-Aldrich. Sodium hydroxide, potassium carbonate, and sodium methoxide were obtained from Wako Chemicals. Acetonitrile was super dehydrated grade and further treated with activated molecular sieve (4 Å). TFPPy monomer was purchased from Zhengzhou Anmschem Co. Ltd. PDAN, SbF₃, and NaCN were purchased from Wako Chemicals.

Catalysts preparation

All syntheses were performed in argon using the Schlenk line. sp²c-COFs were synthesized on the basis of a reported method with slight modification. Briefly, a 100-ml Pyrex tube was charged with TFPPy (150.00 mg, 0.24 mmol), PDAN (75.8 mg, 0.48 mmol), mesitylene/1,4-dioxane (1 ml, ¹/₅ by vol.), and aqueous NaOH solution (1 ml, 4 M), and the mixture was sonicated for 20 min, degassed through three freeze-pump-thaw cycles, sealed under vacuum, and heated at 90°C for 5 days. Afterward, the mixture was cooled to room temperature, and the precipitate was collected by centrifugation, washed with deionized water and THF several times, Soxhlet-extracted in THF for 3 days, and dried under vacuum at 120°C for 24 hours to obtain red crystallites in 84% isolated yield. Elemental analysis: calculated C (89.49%), H (3.99%), and N (6.52%) and observed C (87.13%), H (4.31%), and N (5.46%). To prepare Sb(CN)₃, 10 mmol of SbF3 was dispersed in 60 ml of EtOH. followed by adding 30 mmol of NaCN. The mixture was refluxed at 60°C for 7 days. After filtration, the solution was stored in a fridge. The amount of Sb was measured by inductively coupled plasma-atomic emission spectrometry and the total CN in Sb(CN)₃ was measured by a titration method using 0.01 M AgNO₃ solution (silver spirit was used as an indicator). Take 100 ml \pm 0.08 ml of sample (if the cyanide content in the sample is high, a smaller amount of sample can be taken and diluted to 100 ml with deionized water) into a conical flask. Then, 0.2 ml \pm 0.006 ml silver nitrate indicator was added into the container and shaken the container well. Titrate the solution with standard silver nitrate solution until the color changes from yellow to orange-red and make sure to record the reading. Before titrating the sample with standard silver nitrate solution, measure the pH value using the pH meter. If necessary, adjust the sample to a pH greater than 11 by adding sodium hydroxide solution. For the blank experiment, take another 100 ml \pm 0.08 ml of a blank test sample into a conical flask and perform the titration according to the above step. If the cyanide concentration in the sample is below 1 mg liter⁻¹, then we use a 0.001 M silver nitrate standard solution for the titration (GB/T 7487-1987).

The observed Sb to CN ratio in the as-prepared Sb(CN)₃ was ~1: 3 (fig. S3). To prepare Sb(CN)₃-modified sp²-c-COFs (SbX-sp²-c-COFs), a 100-ml Pyrex tube was charged with TFPPy (150.00 mg, 0.24 mmol), PDAN (75.8 mg, 0.48 mmol), mesitylene/1,4-dioxane (1 ml, 1/5 by vol.), and aqueous NaOH solution (1 ml, 4 M), followed by adding 1 ml of Sb(CN)₃ EtOH solution (0.00, 0.002, and 0.005 mmol). The mixture was then sonicated for 20 min. Elemental analysis of Sb5-sp²-c-COFs gave C (85.12%), H (4.17%), and N (5.98%) (note that the elemental ratio was measured over the Sb5-sp²-c-COFs sample dried at 120°C for 24 hours; the mass percentage of H could be markedly increased if the sample was exposed to moisture).

Photocatalytic toluene oxidation

Photocatalyst (30 mg) was added into 30 ml of toluene aqueous solution saturated with O₂ (185 µmol of toluene) in a borosilicate glass bottle (φ : 60 mm; capacity: 100 ml), and the bottle was sealed with a rubber septum cap. The photocatalyst was dispersed by ultrasonication for 15 min, and O₂ was bubbled through the solution for 30 min. The bottle was kept in a temperature-controlled air bath at 30° ± 0.5°C with wind flow and was irradiated at $\lambda > 420$ nm using a 300-W Xe lamp (PXE-500, USHIO Inc.) under magnetic stirring. After the reaction, the gaseous products (H₂, CO, and CH₄) were quantified by a gas chromatograph (Agilent 7890) equipped with a FID for CO and a thermal conductivity detector for H₂ and CO₂ quantification. Ultrapure helium (He; 99.9999%) was used as the carrier gas. The liquid products were quantified by high-performance liquid chromatography (HPLC; Agilent 1290 Infinity) with a UV detector (257 nm) using a capillary column (Agilent, Poroshell 120HPH-C18 4.6 250 mm, 4 µm). One mole of benzyl benzoate needs 2 mol toluene conversion, and 1 mol of benzyl alcohol, benzaldehyde, or benzoic acid needs 1 mol toluene conversion. The total conversion amount of toluene in 3 hours is calculated for the conversion rate and the definition of improvement. Benzyl alcohol, benzaldehyde, and benzoic acid were quantified by HPLC equipped with a reverse-phase EC-18 column (Poroshell120, 4 μ m, 4.6 \times 250 mm). A flow phase of 30% acetonitrile and 70% water was used for separation of these products. For separating benzyl benzoate, a flow phase of 60% acetonitrile and 40% was used. The working curve of each sample was given in the Supplementary Materials (figs. S47 to S49).

Action spectra acquirements

The photocatalytic reaction was carried out in pure deionized water (30 ml) with photocatalyst (60 mg) in a borosilicate glass bottle. After ultrasonication and O₂ bubbling, 185 μ mol of toluene was added to the suspension. Then, the bottle was irradiated by an Xe lamp for 5 hours under magnetic stirring. The incident light was monochromated by band-pass glass filters (Perfect light), where the full width at half maximum of the light is 11 to 16 nm. All the light intensity in each region was controlled to be 1 mW cm⁻².

Instruments

High-resolution transmission electron microscopy (HRTEM), HAADF-STEM, selected area electron diffraction, and energy-dispersive xray spectroscopy were performed on a Titan Cubed Themis G2 300 electron microscope at an accelerating voltage of 300 kV. Electron energy loss spectroscopy was conducted using a Quantum ER/965 P detector. The crystalline phases were characterized by a PXRD instrument (MiniFlex II, Rigaku Co.) with CuK α ($\lambda = 1.5418$ Å) radiation (cathode voltage: 30 kV, current: 15 mA). Light absorption properties of the samples were determined using the diffuse reflection method on a UV/VIS/NIR spectrometer (UV-2600, Shimadzu Co.) attached to an integral sphere at room temperature. XPS measurements were performed on a Kratos AXIS Nova spectrometer (Shimazu Co., Japan) with a monochromatic Al Ka x-ray source. The binding energy was calibrated by taking the carbon (C) 1s peak of adventitious carbon at 284.6 eV. Valence band x-ray photoelectron spectroscopy was performed on an ESCALAB 250Xi (Thermo Fisher Scientific, USA). The equilibration of the Fermi level of the instrument was performed by measuring the VB-XPS of the Au metal basis as the reference. The Fermi level of the instrument was equilibrated at 4.5 eV. In this case, the numerical value of the binding energy in the calibrated VB-XPS spectrum is the same as the potential versus standard hydrogen electrode (SHE). Electron spin resonance signals of spin-trapped paramagnetic species with 5,5-dimethyl-1-pyrroline N-oxide (DMPO; MeOH solution) were recorded on an A300-10/12 spectrometer. The pH of the solution was measured by a pH meter (HORIBA pH meter D-51, HORIBA, Ltd.). The water contact angle was measured by a Theta Flex (Finland, BIOLIN) contact angle analyzer. The x-ray absorption spectroscopy for Au K-edge was measured at beamline BL01C at the

SP-8 (Japan). The data analysis for the x-ray absorption spectroscopy using IFEFFIT was performed by the Demeter system (version 0.9.25). All of the BET measurements were conducted on the Micro-Active for ASAP 2460 (Micromeritics Instrument Corp., USA). TAS measurements were performed on a Helios (ultrafast systems) spectrometer using a regeneratively amplified femtosecond Ti:sapphire laser system (Spitfire Pro-F1KXP, Spectra-Physics; frequency, 1 kHz; max pulse energy, ~8 mJ; pulse width, 120 fs) at room temperature. The Mott-Schottky measurements were performed in the potential range from 0.4 to 1.0 V versus SHE with an ac voltage amplitude of 5 mV in a frequency range from 250 to 1000 Hz. Each increase of potential is 0.05 V. The quiet time for each test is 2 s.

DRIFTS experiments

The in situ DRIFTS spectra were collected on an FTIR spectrometer (Thermo Fisher Scientific iS50) equipped with a liquid nitrogen cooled HgCdTe (MCT) detector, along with Praying Mantis diffuse reflectance accessory, and a high-temperature reaction chamber (HARRICK, HVC-DRM-5) with zinc selenide (ZnSe) windows and a temperature control module (HARRICK ATC-024-2). The catalyst was pretreated in an Ar atmosphere with a flow rate of 10 ml min⁻¹ at 300°C for 30 min. Toluene and H₂O vapor were introduced into the reactor by O₂-Ar bubbling with a flow rate of 30 ml min⁻¹ for 30 min, then the physisorbed toluene was removed by O₂-Ar flow for 30 min. The background spectra were recorded before irradiation. When the light was turned on, the spectra were recorded at the time interval of 5 min. A 300-W Xe lamp equipped with a cutoff filter (UVC420) was used to supply visible light.

In situ XPS measurements

A 300-W Xe lamp equipped with a cutoff filter (UVREF420) was used to supply UV light ($\lambda \leq 420$ nm) during XPS measurements. The XPS spectra were recorded by controlling light on or off at specific time intervals.

Details for TD-DFT calculations

The optimization and frequency combined with the vertical excitation properties were performed via TD-DFT in the Gaussian 09 program S2, which was carried out by utilizing ω97xd/6-311 g(d) level of theory for C, N, and H elements and SDD for Sb element. To give a comprehensive understanding of the relationships between the electronic configuration during excitation and the realistic experimental results, 50 excited states (ES) were used to simulate the absorption spectra (50). Note that the absorption edge of the simulated spectra is usually larger than that of the experimental value because of the following two reasons: (i) To simulate the charge-transfer properties with high qualities, the function of ω 97xd, a function including a large amount of Hartree-Fock exchange, was used. These exchange functions usually overestimate the excitation energies, as well as the simulated HOMO-LUMO gaps (43, 50, 51); (2) in the solid state, p-conjugated molecules adjacent to the one carrying a charge do strongly polarize, an effect that stabilizes the cationic and anionic states (each generally by about 1 eV in p-conjugated materials). In this case, the bandgap is typically considerably smaller in energy than the molecular fundamental gap, as well as the optical gap (43). Since the evitable system error cannot be eliminated, the changes in the simulated HOMO-LUMO gap provide the changing tendencies for experimental results, rather than the exact energetic shift in the experimental results. For analysis of the excitation and charge transfer properties, Multiwfn ver. 3.6 (released on 21 May 2019) was performed (50). Visualization of hole, electron, and transition density was also performed by Multiwfn; functions of IOp(9/40 = 3) were set during the vertical excitation based on TD-DFT calculation. To further investigate the influence of water on the excitation properties, the wave function analysis of the representative transitions were carefully conducted in each system (19, 52): sp²-c-COFs in vacuum (ES1, ES2 and ES5), sp²-c-COFs in PCM models (ES1 and ES5), and Sb-sp²-c-COFs in vacuum (ES1 and ES5) or PCM models (ES2–3, ES22–23, and ES33), where all these transitions all have large oscillator strength at the vertical excitation states. The electron distributions were presented as heatmaps by a combination of GaussView and Multiwfn. The iso-surface of electrons and holes was presented by setting the iso-value to 0.005.

Supplementary Materials

This PDF file includes: Supplementary Text Figs. S1 to S51 Tables S1 to S4

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