Infrared response in photocatalytic polymeric carbon nitride for water splitting via an upconversion mechanism

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Broad-spectrum light activation in photocatalytic materials is considered vital for effective solar-to-hydrogen energy conversion. Here, we propose an upconversion process in oxygen-doped polymeric carbon nitride (C₃N₄) nanosheets, resulting in high photocatalytic activity for hydrogen generation from water splitting under infrared light irradiation. Due to the upconversion, the photoexcited electrons are transferred to the conduction band, and a σ* carbon-oxygen orbital localized on the triazine matrix ring resulting from oxygen doping extends the lifetime of photogenerated electrons, which increases the photocatalytic activity under both infrared and visible light. Our material exhibits high apparent quantum efficiency of 0.014% and 23% at 850 nm and 420 nm, respectively. Under infrared light (λ ≥ 800 nm, 24 mW cm⁻²), the hydrogen production rate of our material is 22.84 μmol h⁻¹ g⁻¹, which can reach a yield similar to that of pristine C₃N₄ under visible light.
Photocatalysis is considered one of the most promising technologies for converting abundantly available solar energy into useful chemical energy. In particular, solar-driven water splitting for H\textsubscript{2} generation has attracted much attention because it is a sustainable strategy for producing renewable energy\textsuperscript{1,2}. However, the low utilization efficiency for solar energy is still a bottleneck in photocatalysis because photocatalysts typically have a narrow absorption range. For example, TiO\textsubscript{2}, the most well-studied photocatalyst, can respond only to ultraviolet light (5% of total solar energy)\textsuperscript{3}. The theoretical maximum efficiency for the water splitting reaction by a single photocatalyst increases with the wavelength; i.e., values of 2, 16, and 32% are obtained upon increasing the wavelength from UV to 400, 600, and 800 nm, respectively\textsuperscript{4,5}. Therefore, to improve the solar energy utilization efficiency, developing a photocatalyst with broad-spectrum responsiveness is one of the most effective strategies for solar-to-hydrogen energy conversion. Theoretically, the water splitting reaction can proceed only in a photocatalyst whose band gap straddles the reduction and oxidation potentials of water. It is, therefore, a great challenge to find a good material that simultaneously has a broad-spectrum response and suitable redox potentials. Neither new materials such as black phosphorus (phosphene) nor TiO\textsubscript{2-x} obtained from band gap engineering has achieved the desired photocatalytic activity due to the low redox capacity of these materials\textsuperscript{6,7}.

We propose a different strategy to design infrared light-responsive photocatalysts. The strategy is based on a single photocatalyst in which the infrared light response is achieved by an upconversion process and high activity is guaranteed by the prolonged lifetime of the photoexcited carriers achieved by the introduction of a new energy level in conduction band. Polymeric carbon nitride (C\textsubscript{3}N\textsubscript{4}) has been one of the most popular materials in photocatalysis in the past decade since its discovery as a visible light-responsive photocatalyst in 2009\textsuperscript{8}. However, C\textsubscript{3}N\textsubscript{4} has never been applied as an infrared light-responsive material or an upconversion material, despite very limited reports on its upconversion properties, which have been ascribed to the quantum size effect\textsuperscript{9,10}. Herein, we demonstrate that upconversion, which we believe is an important but overlooked process, is an “intrinsic” process even in bulk C\textsubscript{3}N\textsubscript{4} (PCN).

In this work, when the weight ratio of melamine to cyanuric acid reaches M/C ≤ 1/3, we obtain a carbon nitride in the form of porous nanosheets, in which O is doped at the position of the triazine matrix ring to form a new energy level in conduction band. We find the energy level provided by the C–O bond, which is beneficial for prolonging the life time of photogenerated electrons. Moreover, the O–C bond is next to the C–N–C moiety, which makes the electrons easy to be photogenerated to the level even by infrared light (two-photon absorption). Therefore, our carbon nitride not only generates H\textsubscript{2} from water splitting under infrared light irradiation, but also the H\textsubscript{2} generation rate of MCN1-4 under visible light irradiation is 85.7 times higher than that of PCN.

Results
Characterization of PCN and MCN1-4. The texture, structure, and morphology of the samples were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). PCN shows large particles with a stacked sheet structure (Fig. 1a, b). On the other hand, MCN1-4 shows a translucent thin layer morphology with a porous surface and folded edges (Fig. 1c, d). As shown in the AFM image (Fig. 1e), the nanosheets of MCN1-4 have an average thickness of approximately 3.5 nm and an average planar area of ~18 μm\textsuperscript{2}. MCN1-4 has a Brunauer-Emmett-Teller (BET) specific surface area of 150.0 m\textsuperscript{2} g\textsuperscript{-1}, which is 14 times higher than that of PCN (11.3 m\textsuperscript{2} g\textsuperscript{-1}), indicating that most MCN1-4 samples exhibit an ultra-thin nanosheet morphology (see Supplementary Table 1). The total Barrett-Joyner-Halenda (BJH) pore volume of MCN1-4 is up to 0.79 cm\textsuperscript{3} g\textsuperscript{-1}, which is almost 8 times higher than that of PCN (0.10 cm\textsuperscript{3} g\textsuperscript{-1}). Notably, MCN1-4 has a microporous structure (0.02 cm\textsuperscript{3} g\textsuperscript{-1}), which not only provides a number of reaction sites, but also decreases the charge transfer distance and thus effectively increases the photocatalytic activity (see Supplementary Fig. 6c).

Figure 2a shows X-ray diffraction (XRD) patterns of PCN and MCN1-4 samples. PCN has two peaks at 13.1 degrees and 27.6 degrees, which are assigned to in-plane repeating units (100) of the tri-s-triazine matrix and the interlayer distances of parallel conjugated aromatics (002), respectively\textsuperscript{11}. The characteristic peaks of MCN1-4 are located at 13.1 degrees and 27.8 degrees, indicating that MCN1-4 has the same structure as PCN. The most intense peak of MCN1-4 shifts slightly to 27.8 degrees, suggesting that MCN1-4 has a shorter stacking interlayer distance (0.326 nm) than does PCN (0.3232 nm). Simultaneously, the peak at 27.8 degrees becomes less pronounced, indicating that the number of layers in the structure is reduced to form a thinner structure\textsuperscript{12}, which agrees with the morphology results presented in Fig. 1. Both the reduction in the interlayer distance and the nanosheet morphology are beneficial to increasing the lifetime of photoexcited carriers to enhance photocatalytic activity.

To further identify the functional groups of molecules, Fourier transform infrared (FT-IR) spectroscopy was employed (Fig. 2b). Both samples give rise to a peak characteristic of the tri-s-triazine ring mode at approximately 806.1 cm\textsuperscript{-1}. The MCN1-4 spectrum presents several new peaks from 1238 and 1070 cm\textsuperscript{-1}, which are assigned to stretching vibrations of the C–O–C group\textsuperscript{13,14}. The bands between 1700 and 1200 cm\textsuperscript{-1} are attributed to the skeletal stretching vibration of aromatic C–N heterocycles. These peaks in the spectrum of MCN1-4 shift to lower wavenumbers than those of PCN, which may be due to the presence of a C–O–C moiety. No significant changes are detected in the peaks at 3100–3300 cm\textsuperscript{-1} (see Supplementary Fig. 7b), which correspond to ν–NHx moieties. The FT-IR results confirm the O doping in the C\textsubscript{3}N\textsubscript{4}.

To further elucidate the O doping position, the chemical states of elements were studied by X-ray photoelectron spectroscopy (XPS). As shown in the XPS survey spectra (see Supplementary Fig. 8), MCN1-4 is composed of C, N, and O, similar to PCN. The C1s XPS spectrum of PCN shows two fitting peaks at 284.6 and 288.0 eV, corresponding to the C–C and N–C–N bonds (Fig. 2c). The spectrum of MCN1-4 shows three fitting peaks, including a new peak at 286.2 eV attributed to the C–O bond\textsuperscript{13}. Figure 2d shows the O1s XPS spectra of the samples. The spectra of both samples show a peak at 532.0 eV, which is ascribed to chemisorbed oxygen (H\textsubscript{2}O). Note that the spectrum of MCN1-4 has a new peak at approximately 533.2 eV, which is attributed to the C–O–C moiety\textsuperscript{14}. In the C\textsubscript{3}N\textsubscript{4} structure, C–O–C may exist in two positions: at the linker position N\textsubscript{1}–N\textsubscript{2}–N\textsubscript{3} and at the triazine matrix ring N\textsubscript{4} (C–N–C). As shown in Fig. 2e, the N1s spectra of the two samples exhibit three fitted peaks at 398.5, 399.6, and 401.0 eV, which are attributed to C–N–C, N–(C\textsubscript{3}) and C–NHx, respectively. For PCN, the ratios of the N1 (C–N–C) peaks are 66%, 28%, and 6%, respectively, but the ratios of these three peaks in MCN1-4 are 59%, 32%, and 9% (see Supplementary Tables 4–6)\textsuperscript{13}. Only the ratio of N1 (C–N–C) decreased, indicating that the O atom of C–O–C is located at the N position of the triazine matrix ring in MCN1-4.

The results of elemental analysis (EA) and XPS elemental analysis (XPS-EA) are shown in Supplementary Tables 2 and 3 and illustrate the distribution of the elements. The surface O ratio of MCN1-4 is 28% and 9% higher than that of PCN, as seen from
the XPS-EA and EA results, respectively; these results indicate that C–O–C is mainly distributed on the surface of MCN1-4, since XPS is more surface sensitive. Compared with the surface C/N ratio of PCN, that of MCN1-4 increases, but the overall C/N ratio decreases. The results show that the C content gradually increases from the inside to the surface of MCN1-416, which is beneficial for charge transfer from the inside to the surface.

Electron paramagnetic resonance (EPR) spectra of the samples are shown in Fig. 2f. The spectra of both samples exhibit an isotropic singlet with a Lorentzian line shape at $g = 2.0042$, which is assigned to the lone pair electrons of the sp2-hybridized carbons in the $\pi$-bonded aromatic rings17. The peak intensity of MCN1-4 is lower than that of PCN, indicating a decrease in the unpaired electron density. This finding is probably due to the replacement of N with O on the triazine matrix ring, which partially destroys the $\pi$ bonding structure of the entire ring.

Solid-state NMR (nuclear magnetic resonance) was used to verify the structure of the surface species (Fig. 3a, b). For PCN, the $^{13}$C magic-angle spinning (MAS) NMR spectrum shows two peaks at 156.7 and 164.7 ppm, which can be assigned to (C)$_3$N and (C)$_2$N-NH$_x$18; the $^1$H MAS NMR spectrum shows two peaks at 4.5 and 9.6 ppm19,20, which can be ascribed to R–NH$_2$ and R–NH–R, respectively. MCN1-4 presents new peaks at 163.3 and 3.4 ppm in the $^{13}$C and $^1$H MAS NMR spectra, respectively.
in addition to the peaks at the same positions as those for PCN. The peaks at 163.3 ppm and 3.4 ppm are attributed to –O–CN and –CH–O– (according to the database “Chem 605” provided by Hans J. Reich, University of Wisconsin.), respectively, indicating the presence of C–O–C in the triazine matrix ring of MCN1-4 (inset of Fig. 3b). Since the oxygen in C–O–C has two lone pairs of electrons, the other peaks shift downfield, which is consistent with the EPR results.

A schematic illustration of the formation of O-doped porous nanosheet carbon nitride is shown in Fig. 3c. Hydrothermal treatment of the appropriate weight ratio of melamine and cyanuric acid results in O doping in the triazine matrix ring to replace N(C=N)=C). Moreover, we find that the M/C weight ratio of 1/3 is the key point, as shown in Supplementary Fig. 13. Because a melamine molecule can form hydrogen bonds with three cyanuric acids\(^{21,22}\), when melamine is surrounded by cyanuric acid, spatial distance will exist between melamine molecules, which results in the formation of the O-doped porous nanosheet morphology.

**Photocatalytic activities.** Figure 4a shows the time course of \(\text{H}_2\) generation from water splitting under infrared light (\(\lambda \geq 800\) nm) irradiation. PCN catalyses no \(\text{H}_2\) production, whereas MCN1-4 generates 4.27 \(\mu\)mol of \(\text{H}_2\) after 4 h of irradiation (generation rate of 22.84 \(\mu\)mol h\(^{-1}\) g\(^{-1}\)). Considering that the intensity of infrared light is only 24.4 mW cm\(^{-2}\), the photocatalytic activity of MCN1-4 exhibits even higher under 100 mW cm\(^{-2}\) of infrared light than...
that of PCN under visible light (37.09 μmol h⁻¹ g⁻¹) as shown in Supplementary Fig. 14.

Figure 4b shows the photoluminescence (PL) spectra of PCN and MCN1-4 upon excitation at 800 nm. The PL spectra of both samples show a peak in the blue region (450–500 nm), indicating that the samples have upconversion properties. The PL spectra together with time-resolved fluorescence decay spectra are used to evaluate the charge separation dynamics of the samples. PCN gives rise to a peak centred at 468 nm, and MCN1-4 gives rise to a peak centred at 496 nm. The peak intensity in the spectrum of MCN1-4 is lower than that in the spectrum of PCN, demonstrating that MCN1-4 has a lower recombination rate of photoexcited carriers. Furthermore, MCN1-4 has a much longer average lifetime of 7.63 ns than does PCN, with an average lifetime of 4.41 ns (see Supplementary Fig. 15 and Supplementary Table 7). In the case of PCN, the short average lifetime of 4.41 ns and the stacked sheet structure prevent the photoexcited carrier from being transferred from the interior of the material to the reaction site on the surface. Therefore, although electrons are photoexcited to the conduction band of PCN, the lifetime of the excited state is too short for water splitting to proceed. In contrast, MCN1-4 exhibits a long lifetime of 7.63 ns (almost the same as the average lifetime at 365 nm) and a porous nanosheet (3.5 nm) structure; thus, photoexcited electrons have a sufficient lifetime for water splitting. As shown in Fig. 4c, when PCN is excited with an 800 nm laser, white light can be clearly observed from the material even at a laser pump power of ~100 mW cm⁻².

On the other hand, little light can be observed from MCN1-4 under the same condition, which is consistent with the results of PL. Nonlinear optical characteristics can be found from the intensity-dependent fluorescence spectra of MCN1-4 excited at 800 nm. Moreover, it is found that the hydrogen generation rate is proportional to the irradiation intensity (slope = 1.77), thus confirming the existence of two-photon absorption (2PA) mechanism at inferred light (λ ≥ 800 nm, see Supplementary Fig. 16). The nonlinear absorption coefficients (two-photon absorption coefficient) of PCN and MCN1-4 are 0.9696 × 10⁻² cm GW⁻¹ and 6.26 × 10⁻² cm GW⁻¹, respectively, which are calculated from the results of open-aperture Z-scan under 800 nm excitation (see Supplementary Fig. 17).

The photocatalytic activities under visible light were measured by in situ H₂ generation from water splitting. After 6 h of irradiation under visible light (λ ≥ 420 nm), MCN1-4 generates 179.44 µmol of H₂, while PCN generates 1.61 µmol (Fig. 4d). Part of the photoexcited electrons are used to reduce the Pt⁴⁺ available at the beginning of the experiment, resulting in a decrease in the hydrogen production. Thus, the average H₂ generation rate is calculated between 3 and 6 h, during which time the hydrogen production rate tends to be stable. The average H₂ generation rates of MCN1-4 and PCN are 31.79 µmol h⁻¹ and 0.37 µmol h⁻¹, respectively; i.e., the value for MCN1-4 is 85.7 times higher than that for PCN (Fig. 4h).

Figure 4e shows the PL spectra of PCN and MCN1-4 upon excitation at 365 nm, which are similar to those obtained upon 800 nm excitation. The PL peak intensity of MCN1-4 is lower than that of PCN, and the average lifetime of MCN1-4 (7.84 ns) is longer than that of PCN (6.83 ns), confirming the lower recombination rate of photoexcited carriers in MCN1-4 than in PCN (see Supplementary Fig. 15 and Supplementary Table 8). On the other hand, the PL peaks in the PCN spectrum are at the same position after excitation at both 365 and 800 nm. However, the MCN1-4 spectrum shows three distinct peaks with different
excitation wavelengths, indicating that MCN1-4 has a more complex band structure (see Supplementary Fig. 18), which will be discussed in the next section.

AQE is one of the most important parameters used to compare the photocatalytic activities of different materials\(^26\). MCN1-4 presents an AQE of 23.02% under monochromatic 420 nm light irradiation, which is one of the highest recorded values for C3N4. In addition, MCN1-4 still has AQEs of 3.66% and 1.09% under monochromatic 470 nm and 550 nm light irradiation, respectively, indicating that this material has a broad photoresponse. (see Supplementary Fig. 19).

The stability of MCN1-4 was measured by photocatalytic reaction over 36 h of visible light irradiation (see Supplementary Fig. 20). During visible light irradiation, the photocatalytic activity hardly changes in the first 18 h. The activity decreases by ~8% in the third cycle (24–30 h). After adding 5 ml of triethanolamine (TEOA), the activity is slightly higher than that in the first cycle (0–6 h). This change in activity is mainly due to a change in the pH of the solution because TEOA is an alkaline substance. The recovery of activity indicates that MCN1-4 has good stability.

To understand the band structures of the materials, we performed UV-visible diffuse-reflectance spectroscopy (UV-vis DRS), valence band XPS (VB-XPS) and transient absorption spectroscopy (TAS). Figure 5a and Supplementary Fig. 21 show the UV-vis DRS results of the samples. The wavelength of maximum absorbance ($\lambda_{\text{max}}$) of MCN1-4 is located at approximately 385 nm, which is blue-shifted slightly with respect to that of PCN at ~387 nm due to the quantum confinement effect caused by the morphology of the nanosheets. MCN1-4 absorbs from approximately 478 nm to 800 nm, which may originate from
charge transfer of the n–π* lone electron pairs of the O atom in the C–O–C moiety of the heptazine ring. Therefore, the energy gaps of PCN and MCN1-4 are 2.70 and 2.84 eV, respectively, according to the Kubelka–Munk equation and Tauc plot method. As seen from the VB-XPS results, the valence bands of PCN and MCN1-4 are located at 2.03 and 1.93 eV, respectively.

As determined by the TAS analysis, the actual band structure of MCN1-4 is rather complex, especially the intermediate bands. A large signal can be detected from 486 to 1081 nm (2.55 eV to 1.15 eV) in the MCN1-4 spectrum (Fig. 5c, d and see Supplementary Fig. 23), probably originating from the interlayer π bond in MCN1-4 is stronger than that in PCN and that MCN1-4 has a thinner morphology than PCN. MCN1-4 has a new peak at 289.1 eV, which is attributed to σ*C–O of the C–O–C moiety in the triazine matrix ring. The σ*C–O (289.1 eV) orbital energy is 0.4 eV higher than that of π*C=N–C (288.7 eV) in MCN1-4, which means that the energy level of σ*C–O is higher than the conduction band minimum. The electrons photoexcited to the σ*C–O energy level have a longer lifetime, which can be confirmed from the time-resolved PL spectrum, see Supplementary Table 7 and 8. MCN1-4 with a σ*C–O level has a lifetime of τ2 = 10.36 ns, which is almost two times that of PCN without a σ*C–O level (τ2 = 5.52 ns). Furthermore, under 365 nm excitation, the lifetime τ2 = 9.71 ns for MCN1-4 is longer than that for PCN (τ2 = 8.86 ns).

As shown in Supplementary Fig. 25, the crystal structure of MCN1-4 wrinkles by the O doping in the matrix ring, and no extra internal bands can be found from the results of calculation. Figure 7a shows total density of states (TDOS) and partially
density of states (PDOS) spectra of MCN1-4. It can be seen that the O atom starts to contribute to the conduction band from 1.31 eV near the conduction band edge (1.29 eV), and then reaches the maximum contribution at 1.95 eV. To further clarify the contribution of the $\sigma^*_{\text{C-O}}$ in MCN1-4, we present charge density of MCN1-4 the orbital information associated with the selected states in the TDOS of MCN1-4 (see Supplementary Fig. 26). As shown in Fig. 7b, a small amount of charge density can be observed on O atoms at 1.33 eV, which is only 0.05 eV higher than LUMO. The results demonstrate that the photo-generated electrons can be easily transferred to $\sigma^*_{\text{C-O}}$, which is consistent with the experimental results.

![Fig. 6 NEXAFS characterization and schematic from structure to atomic orbital description of PCN and MCN1-4.](image)

**Fig. 6 NEXAFS characterization and schematic from structure to atomic orbital description of PCN and MCN1-4.** NEXAFS spectra of PCN and MCN1-4 at the a nitrogen K-edge and b carbon K-edge. c Schematic description of covalent bonding in terms of atomic orbitals.

![Fig. 7 Computational calculation of MCN1-4.](image)

**Fig. 7 Computational calculation of MCN1-4.** a TDOS and PDOS of MCN1-4 and b the charge density of MCN1-4 derived from DOS at 1.33 eV. The Fermi level is set to zero.
To achieve a full spectrum response and a high activity, in addition to the upconversion properties of the carbon nitride due to defects, it is required that the lifetime of the photoexcited carriers should be sufficiently long. MCN1-4 has three features that result in a long photoexcited carrier lifetime: 1. O doped into the N position of the C=N−N−C moiety in the triazine matrix ring to form a π*C−O+ orbital in conduction band and thus greatly inhibit the recombination of photoexcited electron-hole pairs; 2. a nanosheet morphology (3.5 nm) that provides not only a short distance for charge transfer from the interior of the material to the reaction site; 3. a gradual increase in the C content from the inside to the surface (Fig. 6c). The latest reports on the development of infrared response photocatalysts have several shortcomings. For example, the photocatalysts achieve infrared light response at the expense of the activity under high-energy light irradiation; the photocatalysts must be compounded with other photocatalysts due to their low redox capacity. We believe that our strategy will open a brand-new approach for designing carbon nitride and other photocatalysts that can convert full-spectrum solar energy into chemical energy more efficiently. In addition, non-toxic C2N4 with high efficiency under infrared light provides a promising candidate for phototherapy.

Methods

Materials. Melamine (Aladdin, 99%), Cyanuric acid (Aladdin, 98%), Triethanolamine (Aladdin, AR-98%), TiO2 (degussa, P25), TiO2 (anatase, Macklin, 99.8%, 60 nm) and Hydrochloroplatinic acid (Alfa Aesar, ACS-99.95%, Pt 37.5%) were used as starting materials without further treatment. Deionized water (18.5 MΩ, EREE water systems) was used in the whole experiments.

Preparation of PCN and MCNx-y. Bulk C3N4 (polymeric carbon nitride, PCN) was synthesized by heating 3 g of melamine at 350 °C for 4 h, the heating rate is 5 °C min−1.

Firstly, MCx-y was prepared by a facile hydrothermal treatment. Five grams of melamine and cyanuric acid composite (melamine/cyanuric acid are 2.5/2.5, 2/3, 1.5/3.5 and 1/4 weight ratio) was dispersed in 50 ml water by 15 min sonication and 15 min stirring. The suspension liquid was transferred into a 100 ml Teflon-lined autoclave and then heated at an oven in 150 °C for 6 h. After filtration and evaporation, a white powder was obtained, which was referred to as MCx-y (x and y respectively denote as the added weight of melamine and cyanuric acid).

Then 3 grams of white powder was placed in an alumina crucible with a cover and heated to 550 °C in muffle furnace at a heating rate of ca. 5 °C min−1. After heating at 550 °C for 4 h, MCNx-y was obtained. It is worth noting that the muffle furnace used in here should has a good thermal insulation.

Photocatalytic activity under infrared light irradiation. Fifty mg of sample was dispersed in 100 ml water (10 vol% of TEOA, and H2PtCl6 of 3 wt% Pt to the sample) for 10 min by sonication. The solution was transferred to the photocatalysis reactor, and vacuumed with stirred. Xe lamp (CEAULIGHT: CEL-HEXF300, 300 W) with 420 cut-off filter (CEAULIGHT, CEL-UVCIRUT420) was used to irradiate the solution for 3 h (for Pt deposition). Subsequently, 800 cut-off filter (CEAULIGHT, CEL-UVCIRUT800) was used, the average light intensity was 24.4 mW cm−2. The amounts of generated hydrogen were monitored by gas chromatography (TCD, CEAULIGHT, GC-7920) every 30 min. Ultrapure N2 was used as that under visible light, except that Xe lamp (300 W) with AM 1.5G filter (CEAULIGHT, CEL-AM1.5) was used as the light source (the light intensity of the high position in the middle level of the liquid was 100 mW cm−2).

Photocatalytic activity under visible light irradiation. Ten mg of sample was dispersed in 100 ml water (10 vol% of TEOA, and H2PtCl6 of 3 wt% Pt to the sample) for 10 min by sonication. The solution was transferred to the photocatalysis reactor, and vacuumed with stirred. 300 W Xe lamp with 420 cut-off filter was used as the light source (the light intensity of the high position in the middle level of the liquid was 100 mW cm−2).

Photocatalytic activity under AM 1.5G irradiation. The same procedure was used as that under visible light, except that Xe lamp (300 W) with AM 1.5G filter (CEAULIGHT, CEL-AM1.5) was used as the light source (the light intensity of the high position in the middle level of the liquid was 100 mW cm−2).

Computational details. We investigated the DOS and PDOS of samples by using the Vienna Ab Initio Simulation Package (VASP)97 based on density functional theory (DFT). A large 3 × 3 supercell with perpendicular vacuum of 15 Å was used to eliminate the spurious interaction from the periodic. The generalized gradient approximation (GGA) as proposed by Perdew, Burke, and Ernzerhof (PBE)38 considered the exchange-correlation functional, as well as the projector augmented wave (PAW) potentials. The lattice constants were set to a = b = 6.8 Å, all atoms were relaxed until the total energy converged to 10−3 eV and the residual force on each atom was less than 0.01 eV Å−1. The plane-wave kinetic-energy cutoff was 400 eV and the grid mesh was 2 × 2 × 1.

Data availability

The authors declare that obtained and analyzed data are contained in the paper and the Supplementary Information, and are available from the corresponding author on reasonable request.

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Author contributions
Z.J. conceived the idea and conducted the experiments. X.I. conducted the TAS measurement. Q.Z. measured and analyzed NEXAFS. Z.J., S.H., and L.Z. discussed the experiment detail. T.H. conducted open-aperture the Z-scan measurement. L.H. conducted computational calculation. Y.Z., H.Z., and S.R. supervised the experimental work. Z.J., T.O., and Y. Z. discussed the results and wrote the paper with contributions from the other authors.

Competing interests
The authors declare no competing interests.

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