Stable semiconductor black phosphorus (BP)@titanium dioxide (TiO_2) hybrid photocatalysts

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Over the past few decades, two-dimensional (2D) and layered materials have emerged as new fields. Due to the zero-band-gap nature of graphene and the low photocatalytic performance of MoS_2, more advanced semiconducting 2D materials have been prompted. As a result, semiconductor black phosphorus (BP) is a derived cutting-edge post-graphene contender for nanoelectrical application, because of its direct-band-gap nature. For the first time, we report on robust BP@TiO_2 hybrid photocatalysts offering enhanced photocatalytic performance under light irradiation in environmental and biomedical fields, with negligible affected on temperature and pH conditions, as compared with MoS_2@TiO_2 prepared by the identical synthesis method. Remarkably, in contrast to pure few layered BP, which, due to its intrinsic sensitivity to oxygen and humidity was readily dissolved after just several uses, the BP@TiO_2 hybrid photocatalysts showed a 92% photocatalytic activity after 15 runs. Thus, metal-oxide-stabilized BP photocatalysts can be practically applied as a promising alternative to graphene and MoS_2.

Applications of nanoelectronics and optoelectronics as well as energy-related batteries and cells of two-dimensional (2D) and layered materials such as graphene with zero band gap, not to mention the transition-metal dichalcogenide (TMDC) family (e.g., MoS_2 with 1.23 eV–1.69 eV of indirect band-gap energy), are highly attractive research topics. Although graphene has been widely and intensively developed for electronic and optical device applications, limitations in its semi-metallic characteristics are emerging. These days, black phosphorus (BP) is a cutting-edge material due to its direct band-gap nature (i.e., ~2.0 eV for several layers and ~0.3 eV for the single layer, mainly depending on exfoliation of BP layers). Comparing the three main allotropes (white, red, and black) of phosphorus, the BP has merits including thermodynamic stability and insolvency in most solvents and lesser chemical reactivity and non-flammability. As for crystalline structures, BP is present in three types, orthorhombic, rhombohedral, and cubic, along with the amorphous state.

Several-layer BP crystals have been reported to demonstrate single-sheet-BP (i.e., phosphorene) practical feasibility, showing, compared with the graphene- and MoS_2-based alternatives, higher carrier mobility and both p- and n-type configurations in field-effect transistor (FET) sensors. Moreover, BP is used in lithium-ion batteries and thin-film solar cells that demonstrate large specific capacity and excellent cyclic performance, respectively which characteristics result in ~18% higher power-conversion efficiency than has been reported for trilayer graphene@ TMDCs solar cells.

Notwithstanding BP’s superior optoelectronics, its photocatalytic performances in environmental and biomedical applications remain largely unexplored. Herein, taking into consideration semiconducting few layered BP and intercalation of TiO_2 into a BP-layer system (BP@TiO_2 hybrid) by one-pot reaction at room temperature, and comparing that system with an MoS_2@TiO_2 hybrid system fabricated by the identical preparation method, intriguingly novel photocatalytic performances over those of the traditional graphene-TiO_2 hybrid photocatalytic composites were demonstrated.
**Results**

Morphological structures and elemental analysis. BP is generally known to have a puckered honeycomb structure with out-of-plane ridges in which each phosphorus atom is covalently linked to three neighboring single-layer phosphorus atoms while individual layer sheets are stacked vertically by van der Waals interaction\(^{11,20,21}\), as like the usual graphite pattern. The orthorhombic BP can be consisted of monolayer, bilayer and trilayer model structures (Fig. 1A). The well-defined crystalline morphology of few layered BP, which is prepared by an ultrasound-assisted delaminating process, displays crystal lattice fringes of \(\sim2.5\ \text{Å}\) (Supplementary Fig. 1) towards the (111) plane. A high-resolution transmission electron microscopy (HR-TEM) image of TiO\(_2\) substituted onto the BP surface reveals clearly distinct defects (Supplementary Fig. 1, yellow arrows)\(^{22}\), exactly corresponding to the modelling of the BP@TiO\(_2\) hybrid system (Fig. 1B), as looking like irregularly contained eggs (TiO\(_2\)) in the tray. Reaction equations 1 and 2 show a possible BP@TiO\(_2\) formation mechanism. Ti(O\(_4\))\(_4\), when dropped into water, begins to rapidly hydrolyze, forming Ti(OH)\(_4\) on the few layered BP surface.

\[
\text{Ti-OH} + \text{HO-Ti} \rightarrow \text{Ti-O-Ti} + \text{H}_2\text{O} \tag{1}
\]

\[
\text{BP surfaces-P-OH} + \text{HO-Ti} \rightarrow \text{BP surfaces-P-O-Ti} + \text{H}_2\text{O} \tag{2}
\]

Then, Ti-OH was aggregated, forming Ti-O-Ti or Ti-O(H) bonds. Finally, an ultrasound irradiation process, the resultant ultrasonic cavitations creating a unique environment, induces a BP@TiO\(_2\) hybrid system with a better crystal structure\(^{15-20}\).

Elemental analyses of the BP@TiO\(_2\) hybrid photocatalysts entailed energy-dispersive X-ray (EDX) mapping of P, Ti, and O, where P is emitted from few layered BP, Ti indicates the presence of TiO\(_{2-x}\) (related titania compounds), and O originates from both few layered BP and TiO\(_2\) (Fig. 1C). Notably, Ti is uniformly distributed through the entire phosphorene surface. In the literature, TiO\(_2\) on graphene and MoS\(_2\), is deposited predominantly on the edges, due to the abundant functional groups of several-layer matrixes there\(^{27,28}\), leading to poor photocatalytic activity. As a result, it is needed additional carbon-coating steps to improve the uniformity of TiO\(_2\) nanoparticle distribution on the basal plane of MoS\(_2\)\(^{29,30}\) or reduction in TiO\(_2\) band-gap energy\(^{18}\).

X-ray diffraction (XRD) patterns and X-ray photoelectron spectra (XPS) analysis. In order to confirm the crystalline structures and impurities of the novel photocatalysts, the X-ray diffraction (XRD) patterns (Fig. 2A) and X-ray photoelectron spectra (XPS) (Fig. 2B, Supplementary Fig. 2 and Table 1) were examined. The phases of as-synthesized TiO\(_2\) are composed of anatase/brookite at room temperature by sol-gel processing and ultrasound irradiation\(^{11}\). In particular, the synthesis of TiO\(_2\) nanoparticles with conjugation or substitution of other nanomaterials, the brookite phase in as-synthesized TiO\(_2\) was disappeared (data not shown)\(^{32}\). The XRD pattern of few layered BP was matched to the orthorhombic phase, with representative peaks of \(d_{020} = 5.243\ \text{Å}\), \(d_{040} = 2.6216\ \text{Å}\), and

![Figure 1](figure1.png)

**Figure 1** | Modelled structures and elemental mapping analysis. Modelled mono-, bi-layer, and tri-layered BP structures (A), TiO\(_2\) substitution on BP structure (B), and line profile (top panel) and its elemental mapping (bottom panel) of P, Ti, and O elements in BP@TiO\(_2\) hybrid photocatalyst (C).
33; the BP@TiO$_2$ hybrid, meanwhile, formed results (B) for few layered BP and BP@TiO$_2$ hybrid photocatalysts. The XPS profiles revealed, moreover, that the phosphorus ions at the surface of the BP@TiO$_2$ exist in the P$^{5+}$ species. The XPS fitting of P$_{2p}$ and O$_{1s}$ was plotted to confirm, via general scanning, the presence of Ti$_{2p}$, O$_{1s}$, P$_{2p}$, Au$_{4f}$ as a substrate, Sn$_{3d}$ (catalyst for BP preparation) and I$_{3d}$ (catalyst for BP preparation); in the pure few layered BP XPS spectra by contrast, Ti was not detected (Fig. 2B and Supplementary Table 1). XPS fitting of P$_{2p}$ and O$_{1s}$ was plotted to obtain specific information on the Ti-P and phosphated titania peaks at 128.6 and 134.4 eV, respectively (Supplementary Fig. 2). The phosphate titania exhibited a binding energy for P$_{2p}$ at 134.4 eV, indicating that the phosphorus in the sample exists in the pentavalent-oxidation state and apparently as P-O bonded species. The XPS profiles revealed, moreover, that the phosphorus ions at the surface of the BP@TiO$_2$ exist in the P$^{5+}$ and P$^{3+}$ states.

### Optical properties of photocatalysts

In a further optical investigation of the few layered BP and BP@TiO$_2$ hybrid photocatalysts, Ultraviolet-visible-near infrared (UV-Vis-NIR) reflection (%) and the absorbance spectra in few layered BP and BP@TiO$_2$ hybrid photocatalysts showed most of the solar spectral regimes to be between the 250 nm and 1200 nm wavelengths, whereas the reference naked TiO$_2$ was found mainly in the ultraviolet (UV)-absorbable region (Supplementary Fig. 3). These results indicated that few layered BP and BP@TiO$_2$ hybrid photocatalysts are strongly responsive in visible-light regions, unlike naked TiO$_2$, which is activated under UV-light irradiation. Photoluminescence (PL) spectra (Supplementary Fig. 4) at ~600 nm, for the few layered BP and BP@TiO$_2$ hybrid photocatalysts at 350 nm excitation, showed mostly quenching phenomena, which was reflected in the fact that the BP@TiO$_2$ hybrid photocatalyst was blue-shifted 40 nm, by which inhibition of electron-hole recombination and persistent production of powerful ·OH free radicals would be expected.

### Photocatalytic mechanism

Also, the electron spin resonance (ESR) spectra derived in the present study suggest spin-trapping method of photocatalysis for the few layered BP and BP@TiO$_2$ hybrid photocatalysts (Fig. 3). After 5 mins’ 365 nm irradiation of BP, a weak 1:2:2:1 pattern of ·OH free radicals was shown, but under light emitting diode (LED) irradiation, weaker and more negligible peaks were shown. Contrastingly, the BP@TiO$_2$ hybrid photocatalyst exhibited strong ·OH free radical peaks under 365 nm UV-light irradiation, and even under LED irradiation, produced half-intensity ·OH free radical peaks. According to the order in the ·OH free radical peak intensity for the few layered BP and BP@TiO$_2$ hybrid photocatalysts, the order of the photocatalytic activity under visible-light irradiation was BP@TiO$_2$ hybrid > few layered BP > TiO$_2$. On this basis, the mechanism of the photocatalytic performance of the BP@TiO$_2$ hybrid was derived (Supplementary Fig. 4). One fundamental assumption on the use the BP@TiO$_2$ hybrid structure under visible-light irradiation is that the heterojunction between few layered BP and TiO$_2$ will enhance the photo-generated electron-hole pair separation with electrons from the conduction band (CB) of the TiO$_2$ injected into the few layered BP, while the hole trapped from valence band (VB) in the few layered BP and/or TiO$_2$ will have longer lifetimes (Supplementary Fig. 5).

### Photocatalytic performances under UV- and visible light

Based on the measured intensities of the ·OH free radicals in the few layered BP and BP@TiO$_2$ hybrid photocatalysts, the degradation of RB 5 (an anionic dye model) and Roh B (a cationic dye model) were tested. As plotted in Fig. 4A, during 70 min UV irradiation, the only-UV-light, few layered BP photocatalyst, naked TiO$_2$ photocatalyst, P$_{25}$, and BP@TiO$_2$ hybrid photocatalysts showed apparent rate constants of 0.04, 0.37, 3.04, 4.28 h$^{-1}$ and 0.04, 0.42, 2.39, 3.72, 4.62 h$^{-1}$ for RB 5 and Roh B, respectively. The UV-light condition of the BP@TiO$_2$ hybrid photocatalyst afforded an apparent rate constant double that of naked TiO$_2$ photocatalyst. By contrast, visible-light irradiation for the only-visible-light, few layered BP photocatalyst, naked TiO$_2$ photocatalyst, P$_{25}$, and BP@TiO$_2$ hybrid photocatalysts showed apparent rate constants of 0.03, 0.18, 0.07, 0.20, 2.38 h$^{-1}$ and 0.02, 0.03, 0.19, 0.20, 2.05 for RB 5 and Roh B, respectively (Fig. 4B), highlighting an almost ten-times-higher apparent rate constant for the BP@TiO$_2$ hybrid system than for few layered BP photocatalyst. Few layered BP photocatalyst, meanwhile, showed an approximately three-fold-higher rate constant relative to that of naked TiO$_2$ photocatalyst. As the reference experiments, in dark conditions, the photocatalytic activities in BP@TiO$_2$, TiO$_2$, P$_{25}$, and few layered BP photocatalysts showed negligible performances (Supplementary Fig. 6). Next, the intermediate by-products concentration including dyes was measured by a total organic carbon (TOC) analyzer (Supplementary Fig. 7). After 70 min treatment, most of TOC values had reached ~92% with detoxified CO$_2$ and H$_2$O formation. As regards the recovery of the BP@TiO$_2$ hybrid photocatalysts (Supplementary Fig. 8), significantly, even after the 15th run, ~92.04% activity was maintained. Pure few layered BP photocatalyst, gradually decreasing after repeated runs, showed only ~30% photocatalytic activity-by the 8th run, all of it had dissolved into the liquid state, thereby illustrating the difficult BP recovery. The robust stability of the BP@TiO$_2$ hybrid system possibly is related to the substitution of Ti atoms into BP atomic lattices, which system effects resistance to humid and oxygen conditions. Furthermore, similarly to the visible-light photocatalytic dye-degradation performance, the apparent rate constants of the antibacterial activities under the only-visible-light, few layered BP, TiO$_2$, P$_{25}$, and BP@TiO$_2$ hybrid photocatalysts were 0.01, 0.33, 0.24, 0.26, and 2.48 h$^{-1}$ for *Escherichia coli* (*E. coli*), as a
Figure 3 | Detection of generated radicals. Electron spin resonance (ESR) spectra of few layered BP (A, B) and BP@TiO₂ hybrid photocatalysts (C, D) at 365 nm and light-emitting diode (LED) irradiation, respectively.

Figure 4 | Photocatalytic performances. Relative concentrations and apparent reaction rate constants of RB 5 and Rho B of BP@TiO₂ hybrid, P25, and few layered BP photocatalysts under UV- (A) and visible-light (B) irradiation, and antibacterial activities (C) and apparent reaction rate constants of E. coli and S. aureus.
gram negative species) and 0.02, 0.32, 0.22, 0.29, and 2.06 h⁻¹ for *Staphylococcus aureus* (*S. aureus*, as a gram-positive species) (Fig. 4C). The colloidal behavior of the few layered BP and BP@TiO₂ hybrid photocatalysts showed ~+12.73 mV and ~+3.18 mV zeta potentials in ethanol and ~−40.47 mV and ~−24.87 mV in distilled water, respectively. Clearly, in aqueous solution, few layered BP was hydrolyzed to form PO₄³⁻ with a negatively charged surface, which resulted in a significantly diminished mechanistic stability. The BP@TiO₂ hybrid system, though, was less hydrolyzed, and evidenced BP stabilization by displacement of TiO₂ nanoparticles. In detail, at the empty sites of P atoms in few layered BP, Ti atoms were displaced at those positions in few layered BP < 5 nm-sized TiO₂ particles were substituted and formed onto the BP surface, uniformly and with negligible aggregations, finally producing BP@TiO₂ hybrid photocatalysts and improving mechanical and photocatalytic stabilities in practical environmental and biomedical applications. According to zeta potential of BP@TiO₂ hybrid photocatalysts, it exhibited negatively charged surface, but the adsorption amount of two different dyes displayed no marked difference. Thus, organic dye Rho B as a cationic dye resulted in slightly enhanced apparent rate of 4.60 h⁻¹, compared to that of organic dye RB 5 (an anionic dye model).

**Discussion**

In the diverse literature on graphene-based TiO₂ hybrid photocatalytic activity enhancement, graphene has played a multi-functional role. First of all, graphene enhances the visible-light absorbance region and the inhibition of electron-hole recombination by electron transfer from TiO₂ to the graphene matrix as well as by reduction of TiO₂ nanoparticle aggregation. Secondly, adsorption of target pollutants onto graphene/TiO₂ hybrid photocatalysts accelerates degradation by TiO₂ nanoparticles in graphene (oxide). Correspondingly, Lee *et al.* found that the wrapping of graphene sheets onto TiO₂ nanoparticles decreased the band-gap energy in TiO₂ for activation even under visible light. For comparative purposes, in the present study, we investigated the photocatalytic activities of MoS₂@TiO₂ hybrid photocatalysts prepared according to the identical protocol. In the results, relatively very low apparent rate constants were obtained (Supplementary Fig. 9), resulting in approximately 20% dye degradation activity and antibacterial activity under visible-light irradiation. These poor photocatalytic activities can be attributed to the difficulty of uniformly decorating TiO₂ nanoparticles on the MoS₂ surface, despite the semiconducting action of the several-layer MoS₂ sheets.

In summary, in order to effectively utilize unstable few layered BP in various applications, it is suggested that TiO₂ nanoparticles can be substituted in the P atomic positions of BP with Ti by a simple method. The photocatalytic performances of BP@TiO₂ hybrid photocatalysts in comparison with those of the semiconducting MoS₂@TiO₂ hybrid photocatalysts system were remarkable. Unlike MoS₂, few layered BP can be mass-produced by phase transformation of red phosphorus or via a fast low-pressure transport route. In the near future, studies on promising practical alternatives to graphene and MoS₂, namely other unique metal oxides such as magnetic iron oxide (Fe₃O₄) and cerium oxide (CeO₂), as deposited on few layered BP as a drug-delivery platform or therapeutic agent, currently are being planned, with particular emphasis on cellular targeting and smart retention time in the body.

**Methods**

**Synthesis of BP@TiO₂ hybrid photocatalysts.** All of the reagents including commercial TiO₂ (P25 were of analytical grade (Sigma Aldrich, MO, USA) and were used without further purification. In the typical synthesis, black phosphorous (BP, 0.2 g, 6.4 mmol) was dispersed in a solution of anhydrous ethyl alcohol (400 mL) by high-intensity ultrasound irradiation for 2 h, to form few layered BP. 0.025 mol titanium isopropoxide dissolved ethyl alcohol solution (40 mL) was mixed with the BP-dispersed solution, 2 mL of which was then added drop-wise to deionized (DI) water with vigorous stirring for 10 min and finally treated by high-intensity ultrasound for 30 min. The dark-brown-colored BP@TiO₂ hybrid solution was poured into the petri-dishes and dried on a plate at 60 °C. The obtained product was dried under vacuum at room temperature (RT). Dispersion of BP and crystallization of TiO₂ nanoparticles were performed under high-intensity ultrasound of 20 kHz frequency applied from the top of a polypropylene bottle reactor (~40 mL) using a Sonics and Materials VC750 ultrasonic generator. The electrical energy input was maintained at 100 W.

**Characterization.** The crystalline structures of the BP@TiO₂ hybrid samples were investigated with reference to X-ray diffraction (XRD; Rigaku RDA-CA X-ray diffractometer, Japan) patterns obtained by passing Cu Kα X-ray through a nickel filter. The morphology of the BP@TiO₂ particles was recorded by high-resolution transmission electron microscopy (HR-TEM; JEOL, JEM 2200, Japan). The samples after analysis were placed on carbon coated copper grids and dried under ambient conditions. High-resolution X-ray photoelectron spectroscopy (HR-XPS) carried out using monochromatic Al Kα X-ray radiation (hv = 1846.6 eV) with a power of 120 W (Kratos Analytical, AXIS Nova, UK) was used to investigate the surface properties of the samples. The shift in the binding energy due to the relative surface charging was corrected according to the C1s level at 284.6 eV as an internal standard. Zeta potential measurements were performed with a Zetasizer laser light scattering (DLS, Malvern Zetasizer NanoZS, USA) unit. A He-CD laser (Kimmon, IK, Japan) of 235 nm wavelength and 50 mW power was employed as an excitation source for photoluminescence (PL) measurements carried out using a spectrophotometer (f = 0.5 m, Acton Research Co., Spectrograph 500i, USA) with an intensified Princeton Instrument (PI-MAX3, Princeton charged coupled device (CCD)). Prior to their analysis were placed on carbon coated copper grids and dried under vacuum at room temperature (RT). Dispersion of BP and crystallization of TiO₂ for activation even under visible light. For comparative purposes, in the present study, we investigated the photocatalytic activities of MoS₂@TiO₂ hybrid photocatalysts were performed according to the identical protocol. In the results, relatively very low apparent rate constants were obtained (Supplementary Fig. 9), resulting in approximately 20% dye degradation activity and antibacterial activity under visible-light irradiation. These poor photocatalytic activities can be attributed to the difficulty of uniformly decorating TiO₂ nanoparticles on the MoS₂ surface, despite the semiconducting action of the several-layer MoS₂ sheets.

In summary, in order to effectively utilize unstable few layered BP in various applications, it is suggested that TiO₂ nanoparticles can be substituted in the P atomic positions of BP with Ti by a simple method. The photocatalytic performances of BP@TiO₂ hybrid photocatalysts in comparison with those of the semiconducting MoS₂@TiO₂ hybrid photocatalysts system were remarkable. Unlike MoS₂, few layered BP can be mass-produced by phase transformation of red phosphorus or via a fast low-pressure transport route. In the near future, studies on promising practical alternatives to graphene and MoS₂, namely other unique metal oxides such as magnetic iron oxide (Fe₃O₄) and cerium oxide (CeO₂), as deposited on few layered BP as a drug-delivery platform or therapeutic agent, currently are being planned, with particular emphasis on cellular targeting and smart retention time in the body.

**Measurement of photocatalytic and antibacterial activities.** The photocatalytic activity of BP@TiO₂ hybrid photocatalysts was realized by reacting black 3 (5 mg/L, Sigma-Aldrich, USA) and rhodamine B (RhB; 3 mg/L, pH 5.5, Sigma-Aldrich, USA) solutions by photocatalyst samples (1 g/L) were carried out under UV (source: 4 W, <365 nm, VLAB VL-4CL, Korea) and visible-light (source: 150 W Xe lamp, λ > 420 nm, SCHOTT, USA) irradiation, and the absorbance of the solutions was measured using a UV-Vis-NIR spectrophotometer (Varian, Cary 5000, Australia) in the 200–800 nm wavelength region. Before photocatalytic performances in all samples, adsorption-desorption equilibriums for 30 min were conducted. The concentrations of RB 5 and RhB in the solutions after photoradiation were measured from the absorbance peak intensities of the solutions at 598 and 555 nm, respectively. The changes in the concentration [In(Cu/C)] = kτ, where k is the apparent reaction rate constant, and C0 is the initial and reaction time C. The concentration of RhB of the dye solution with reaction time for the samples were also investigated. To demonstrate the stability of the photocatalysts, the BP@TiO₂ hybrid was reused for the testing of other photocatalytic activities. The recycling tests for evaluation of the photocatalytic activity of BP@TiO₂ hybrid photocatalysts were performed after washing the samples three times with DI water at 8500 rpm centrifugation and drying them in an oven for 6 h after each cycle. Additionally, the total organic carbon (TOC) of the solution was determined by a Shimadzu TOC-V analyzer (ELEMENTAR, vario TOC cub, Japan). The antibacterial activities of the samples were evaluated according to the inhibition of gram-negative Escherichia coli (E. coli) and gram-positive Staphylococcus aureus (*S. aureus*) under visible-light irradiation. Before these tests, all glassware and samples were sterilized by autoclaving at 120 °C for 15 min. Bacterial cultures were grown in Luria-Bertani (LB) media overnight at 37 °C with continuous shaking at ~200 rpm. The treated bacterial cells were diluted with DI water to a cell suspension of ~2 × 10⁶ colony-forming units (CFU/mL). Also, before photocatalytic performances in all samples, adsorption-desorption equilibriums for 30 min were conducted. The mass of the photocatalyst was adjusted to 25 mg/mL. The suspensions were stirred with a magnetic stirrer to prevent the samples from settling, and were then exposed to visible light for various irradiation times (0–70 min). Then, 1 mL of the suspension was sampled, added to the LB plate, and incubated overnight at 37 °C. After incubation, the bacterial colonies were observed and quantified. As the reference experiments, dark experiments for all samples were conducted. In measuring the photocatalytic and antimicrobial test performances, the data were averaged and expressed as mean ± standard deviation (SD). Each test was repeated up to five times. An analysis of variance (ANOVA) statistical analysis was performed, wherein p-values < 0.05 were considered significant.

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Author contributions
H.U.L., Y.-C.L. and J.L. designed the project, organized the entire research. H.U.L., S.C.L., Y.-C.L., S.C., H.-S.K. and J.L. wrote the manuscript. H.U.L., S.C.L., Y.-C.L., J.W., Y.K. and S.Y.P. carried out the sample preparation and characterization. B.-S. performed the XPS analysis. H.U.L. and S.C. performed the photocatalytic performances. All authors discussed the results and commented on the manuscript.

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