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A green approach to the fabrication of TiO₂/NiAl-LDH core–shell hybrid photocatal Strate Online for efficient and selective solar-powered reduction of CO₂ into value-added fuels

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Abstract

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Exploring promising photocatalysts with high efficiency and selectivity for CO₂ reduction holds paramount significance for resolving the energy crisis and various environmental problems associated with traditional fossil fuels. Here, we rationally design a core-shell hybrid photocatalyst in which anatase TiO₂ hollow spheres serve as the core component and NiAl layered double hydroxide (LDH) nanoflakes serve as the shell component. The synthesis of the TiO₂/LDH core–shell hybrid involves hydrothermal and calcination treatments without the use of environmentally toxic solvents or surfactants. Assorted experimental results demonstrate that the TiO₂/LDH core-shell hybrid exhibits strong light-harvesting ability, a large surface area, porous structure, and extraordinary CO₂ adsorption capability. In addition, the unique core-shell geometric structure of the TiO₂/LDH hybrid results in a large interfacial contact area and thus provides a broader platform for efficient charge transfer. Benefiting from these structural and compositional features, the TiO₂/LDH core-shell hybrid exhibits remarkable CO₂ reduction activity, high selectivity (against water reduction), and, more importantly, good stability during consecutive test cycles. Therefore, this work offers a promising approach to the rational design and fabrication of core-shell hybrid photocatalysts with potential applications in solar energy conversion and environmental protection.

Keywords: TiO₂ hollow sphere; layered double hydroxide; core–shell architecture; hybrid heterojunction; CO₂ photoreduction

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The ever-increasing consumption of nonrenewable fossil fuel sources has led to growing concerns about global energy shortages and the unusual increase in atmospheric carbon dioxide (CO_2) levels causing global warming via the greenhouse effect.^{1,2} In this context, the development of advanced technologies for CO_2 capture and conversion is receiving considerable interest within the scientific community. The sunlight-driven photocatalytic transformation of CO_2 into value-added fuels (e.g., CO, CH_4 , CH_3OH , and HCHO), mimicking natural photosynthesis, is regarded as a sustainable approach that would not only manage the global carbon balance but also partly fulfill future energy demand.³⁻⁵ Despite great progress in recent years, this photocatalytic CO_2 conversion approach is still challenging because of the extremely stable chemical bonds in CO_2 molecules, the competing water reduction reaction, and the complex conversion pathway involving the transfer of multiple protons and electrons.^{6,7} Therefore, robust catalysts with highly efficient solar-light utilization, strong reduction capabilities, and enhanced charge separation and transport processes are needed.

Following the seminal discovery of photoelectrochemical CO₂ conversion in aqueous suspensions of semiconductors by Inoue et al. in 1979,⁸ assorted semiconductor materials have been exploited as photocatalysts for the CO₂ reduction reaction.^{9,10} Among them, titanium dioxide (TiO₂) remains the most widely exploited photocatalyst because of its high thermal and chemical stability, cost-effectiveness, and ecofriendly character.¹¹ Optimizing the microstructure and morphology of TiO₂ is critical to enhancing its photocatalytic performance. Thus far, TiO₂ materials with various morphologies (e.g., sheets, wires, tubes, and hollow spheres) have been developed in efforts to improve the photocatalytic activity of TiO₂.¹²⁻¹⁵ In particular, TiO₂ hollow spheres represent a substantial cutting-edge innovation for solar energy conversion because of their peculiar characteristics, which include a large specific surface area, low density, and superior light scattering and reflection properties for better light

harvesting.^{16,17} However, analogous to other unitary photocatalysts, the intrinsic drawbacker april of Adollo4J TiO₂, such as its ultraviolet (UV)-matching or wide bandgap and its rapid recombination of photogenerated charge carriers, result in poor photocatalytic efficiency, thereby greatly limiting the practical applications of pristine TiO₂ materials irrespective of their size and geometric shape.

Different strategies have been adopted to overcome the limitations of TiO₂, including noblemetal deposition,¹⁸ the use of carbon-based conducting materials,¹⁹ and the formation of heterostructures with other semiconductors.²⁰ Among these strategies, integrating TiO₂ with other narrow-bandgap semiconductors to form a hybrid heterostructure has thus far been the most promising approach to boosting the photocatalytic efficiency of TiO2.^{21,22} In particular, layered double hydroxides (LDHs) have received considerable attention as photocatalysts because of their strong visible-light response, controllable particle size, and tunable metal cation composition.²³⁻²⁵ In addition, abundant hydroxyl groups on the surface of LDHs promote the adsorption of CO₂ molecules, which is indispensable for photocatalytic CO₂ conversion.²⁶ Because of these impressive properties, LDHs are an excellent choice for coupling with TiO₂ to construct a hybrid heterostructure that impedes the recombination of photoexcited electronhole pairs and effectively utilizes the full solar spectrum because of the combination of UVlight-responsive TiO₂ and visible-light-responsive LDHs. In addition, the intimate interfacial contact area in hybrid photocatalysts is a key factor for facilitating charge transfer at the interface. In this regard, the fabrication of core-shell hybrid photocatalysts has attracted particular interest because the core-shell geometry can enlarge the interfacial contact area, thereby providing a broader platform for efficient charge transfer.^{27,28} Nevertheless, the fabrication of such efficient core-shell hybrid materials in an ecologically friendly, and economical manner remains a formidable challenge.

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In the present work, we rationally integrated anatase TiO₂ hollow spheres and NiAl Vir Autor nanoflakes to construct a highly efficient TiO₂/LDH hybrid system with a core-shell geometric structure. The TiO₂/LDH core-shell hybrid was obtained via a synthesis route involving hydrothermal and calcination treatments but not involving environmentally toxic solvents or surfactants. We assessed the photocatalytic activity of the fabricated TiO₂/LDH core-shell hybrid by monitoring their ability to produce value-added chemicals via CO₂ reduction under Published on 30 March 2020. Downloaded by Université de Paris on 4/11/2020 2:47:55 PM simulated-solar-light illumination. Importantly, as revealed in this work, the TiO₂/LDH coreshell hybrid displayed substantially improved CO₂ reduction activity compared with TiO₂ hollow spheres, LDH, and commercial P25 catalysts. The effect of the core-shell architecture on the CO₂ photoreduction performance of the TiO₂/LDH hybrid was carefully investigated. A possible mechanism for the notable CO₂ reduction activity of the present TiO₂/LDH core-shell hybrid was proposed on the basis of the results of electron spin resonance (ESR) experiments. The durability and photostability of the core-shell hybrid were also probed using successive test cycles. To the best of our knowledge, this work represents the first report of the fabrication of a TiO₂/LDH core-shell hybrid by integrating TiO₂ hollow spheres and NiAl-LDH nanoflakes for the high-performance photoconversion of CO₂ into value-added fuels.

2 Experimental section

2.1 Synthesis of catalysts

TiO₂ hollow spheres were fabricated via a hydrothermal method followed by calcination treatment using carbon spheres as templates. Carbon spheres were prepared by a hydrothermal route based on the reported procedure with minor changes.²⁹ In a typical procedure, 300 mg of agarose powder was carefully added to 60 mL of preheated water (90 °C) under vigorous stirring. After complete dissolution of the agarose powder, the obtained transparent precursor solution was transferred into a 100 mL Teflon-lined autoclave reactor and heated at 180 °C for

12 h. The resultant dark-brown precipitate was washed and rinsed several times with water and the online finally dried in an oven at 80 °C to obtain the carbon spheres.

To prepare the TiO₂ hollow spheres, 100 mg of the as-prepared carbon spheres were dispersed in 60 mL of water with the assistance of ultrasonication. Thereafter, 1.76 mL of titanium(IV) oxysulfate was added dropwise to the carbon-sphere suspension under constant stirring, and the resulting mixture was agitated for 30 min to ensure adequate diffusion of the titanium ions into the carbon surface layer. The suspension was then transferred to a 100 mL Teflon-lined autoclave reactor that was subsequently heated at 180 °C for 2 h. The product obtained after the hydrothermal reaction was collected by centrifugation, rinsed repeatedly with water, and dried at 80 °C to obtain TiO₂/C powder. The resultant TiO₂/C powder was placed into an alumina crucible with a cover and calcined at 450 °C (heating rate: 2 °C min⁻¹) for 3 h under an air atmosphere to obtain TiO₂ hollow spheres (TiO₂HSs). A TiO₂ nanoparticles (TiO₂NPs) reference sample was obtained via the same method but without the addition of carbon sphere templates.

The TiO₂/LDH core–shell hybrid was prepared via a hydrothermal approach. A specific quantity of as-obtained TiO₂ HSs powder was dispersed in 100 mL of water with the aid of ultrasonication. Ni(NO₃)₂·6H₂O (0.006 M) and Al(NO₃)₃·9H₂O (0.002 M) were added to the dispersion and magnetically stirred for 30 min. Urea (0.05 M) and NH₄F (0.016 M) were subsequently mixed with the aforementioned reaction mixture and agitated for another 30 min. Afterwards, the mixture was transferred to a 150 mL Teflon-lined autoclave reactor that was heated at 120 °C for 6 h. The resultant precipitate was collected by centrifugation, rinsed repeatedly with water until the pH of the wash solution was neutral, and dried at 80 °C overnight to obtain the TiO₂/LDH core–shell hybrid. Pristine LDH was synthesized via a similar procedure but without the addition of TiO₂ hollow spheres.³⁰ A TiO₂ NPs/LDH reference sample was synthesized via the same method as the TiO₂/LDH core–shell hybrid

except that the TiO₂ HSs powder was replaced with the same amount of TiO_{2D}NPs $iJ_{10.1039}$ by A00104J synthesis procedure.

The experimental details for the materials, characterization techniques, and photocatalytic activity tests are provided in the electronic supplementary information.

3 Results and discussion

3.1 Characterization of the photocatalysts

The morphology and microstructure of the prepared samples were determined by FESEM and TEM analyses. The FESEM images in Fig. 1a and b show that the synthesized carbonaceous products are nearly monodispersed, with a spherical morphology. The diameters of the carbon spheres mainly fall within the range 250–350 nm, centered at ~320 nm. The TEM micrographs (Fig. 1c and d) further demonstrate that the surface of these carbon spheres is smooth. The FESEM (Fig. 2a) and TEM (Fig. 2b and Fig. S2) micrographs of the TiO₂/C sample show plentiful tiny particles of TiO₂ uniformly deposited onto the surface of the carbon spheres. Figure 2c illustrates the hollow-sphere morphology of TiO₂ prepared at 450 °C, where the highlighted areas in the image clearly show the hollow nature of the spheres. A high contrast between the pale center and the dark edge of each sphere is observed in the TEM image of the TiO_2 (Fig. 2d), further confirming that each sphere is indeed hollow, with a wall thickness of approximately 30 nm. A close observation of the surface by TEM analysis (Fig. 2d inset) reveals that each hollow sphere is composed of numerous nanosized TiO₂ particles, amongst which numerous voids (or pores) are created. We inferred from these results that, after thermal treatment of the TiO₂/C sample at 450 °C, the carbon sphere templates were completely removed, resulting in the formation of TiO₂ HSs.

Interestingly, the TEM image of the TiO_2/LDH sample (Fig. 3a) shows that the hybrid exhibits a hierarchical flower-like core-shell architecture composed of a TiO_2 hollow-sphere

core and an LDH shell. This TEM image also shows numerous ultrathin LDH_Dnanof Var Adicle Online perpendicularly grafted throughout the TiO₂ hollow-sphere cores, enabling the light to easily pass through the LDH to reach the TiO₂ core. The magnified TEM image of the TiO₂/LDH hybrid (Fig. 3b) further confirms the close integration between the TiO₂ core and the LDH shell. These results suggest that the ultrathin LDH nanoflakes in the reaction mixture are firmly grafted onto the surface of TiO₂ HSs during the hydrothermal treatment, which results in the formation of a TiO₂/LDH core-shell hybrid photocatalyst. The HRTEM image (Fig. 3c) illustrates lattice fringes with d-spacings of 0.35 nm and 0.26 nm, which are assigned to the (101) plane of anatase TiO₂ and the (012) plane of LDH, respectively.^{30,31} In addition, scanning transmission electron microscopy-high-angle annular dark-field (STEM-HAADF) elemental distribution maps of the TiO₂/LDH hybrid (Fig. 3d-h) indicate the presence of Ti, O, Ni, and Al elements; among these elements, Ti and O are observed in the inner core, whereas Ni, Al, and O are distributed homogeneously in the shell component, confirming the core-shell architecture of the TiO₂/LDH hybrid. Furthermore, the EDS spectrum of the TiO₂/LDH coreshell hybrid (Fig. S3) also indicates the presence of Ti, O, Ni, and Al (with a Ni/Al molar ratio of ~ 3.0), consistent with the mapping results.

XRD analysis was conducted to analyze the phase structure of the synthesized samples. The typical diffraction pattern of TiO₂ HSs in Fig. 4a well matches the reference data for anatase TiO₂ (JCPDS: 21-1272), where the reflections at 25.30°, 37.82°, 48.04°, 53.94°, 55.03°, and 62.69° are attributed to the (101), (004), (200), (105), (211), and (204) crystal planes, respectively. All of the diffraction peaks are sharp and intense, suggesting that the anatase TiO₂ HSs are highly crystalline. The XRD pattern of the pristine LDH shows diffraction peaks at 2 θ values of 11.58°, 23.28°, 34.98°, 39.46°, 46.83°, 61.02°, and 62.29°, corresponding to the (003), (006), (012), (015), (018), (110), and (113), respectively, which are well indexed to hexagonal NiAl-LDH (JCPDS No. 22-0452). All of the diffraction peaks that appeared in the XRD pattern

of the TiO₂/LDH core–shell heterostructure are in accordance with the peaks of TiO₂ and NFA^{tricle Online} LDH, indicating successful formation of the TiO₂/LDH hybrid. Moreover, the magnified XRD spectra in Fig. S4 clearly illustrate that the characteristic peak of TiO₂ at 25.3° in the TiO₂/LDH core–shell is slightly shifted from its original position, perhaps because of the minor shrinkage of TiO₂ lattice structure after LDH deposition. A similar kind of shift in the diffraction peak is also observed in previously reported core–shell hybrids.^{32,33}

UV-vis DRS analyses were performed to characterize the light-harvesting properties of the TiO₂ HSs, LDH, and TiO₂/LDH core-shell hybrid samples (Fig. 4b). Analogous to TiO₂ NPs, the TiO₂ HSs exhibit a steep absorption edge at ~400 nm, reflecting its wide bandgap and intrinsic UV-light-responsive characteristics. Meanwhile, LDH displays intrinsic optical absorption bands in both the UV- and visible-light regions; the absorption band in the UV region corresponds to ligand-to-metal charge transfer (LMCT), whereas the bands in the visible-light region are related to d-d transitions.^{30,34} More specifically, the bands at 420 and 655 nm are associated with spin-forbidden transitions ${}^{3}A_{2g}(F) \rightarrow {}^{1}T_{2g}(D)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{1}E_{g}$ (D), respectively; the other bands at 380 and 740 nm are related to spin-allowed transitions ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$, respectively, which result from the d^{8} configuration of Ni²⁺ ions in an octahedral geometry.³⁴⁻³⁶ Interestingly, typical visible-light absorption bands of LDH and the characteristic UV-light absorption of TiO₂ are also observed in the DRS profile of the TiO₂/LDH core-shell hybrid, reflecting the strong synergy between the TiO₂ and LDH in the resulting TiO₂/LDH core-shell hybrid. Because of the presence of the UV-lightresponsive TiO₂ HSs and the visible-light-responsive LDH, the target TiO₂/LDH core-shell hybrid can effectively utilize the full solar spectrum, which can subsequently lead to the generation of the vast number of photoinduced charge carriers required for the photocatalytic reactions.

The FT-IR spectra of the TiO₂ HSs, LDH, and the TiO₂/LDH core–shell_bybrids $M_{A001043}^{10}$ presented in Fig. S5. The TiO₂ HSs exhibit a broad band at 3000–3500 cm⁻¹, which corresponds to physically adsorbed water on the surface of TiO₂.³⁷ The typical bands at wavenumbers less than 900 cm⁻¹ are attributed to Ti–O–Ti and Ti–O stretching vibration modes.¹⁶ The FT-IR spectrum of LDH shows a broad band at 3430 cm⁻¹, which corresponds to the stretching vibrations of surface hydroxyl groups in the LDH host layers and interlayer water molecules; and the weak band at ~1640 cm⁻¹ is assigned to the bending vibrations of water molecules.³⁸ The sharp and intense band at approximately 1360 cm⁻¹ is ascribed to bending vibrations of NO₃⁻ species intercalated into the lamellar network.³⁹ The characteristic bands at wavenumbers less than 800 cm⁻¹ are assigned to lattice vibrations of M–OH and M–O–M (M = Ni, Al).³⁰ Importantly, the FT-IR spectrum of the TiO₂/LDH core–shell hybrid displays characteristic bands related to both TiO₂ and LDH; the LDH bands are dominant, possibly because the ultrathin LDH nanoflakes were grafted throughout the TiO₂ hollow-sphere cores with intimate interactions.

The detailed surface chemical states of the elements in the TiO₂ HSs, LDH, and TiO₂/LDH core–shell hybrid samples were examined by XPS analysis. Among the survey XPS spectra (Fig. S6), the spectrum of the bare TiO₂ HSs shows peaks corresponding to Ti and O, whereas that of LDH shows peaks related to Ni, Al, and O elements. Moreover, the survey XPS profile of the TiO₂/LDH core–shell hybrid demonstrates that the hybrid comprises Ti, Ni, Al, and O elements, in accordance with the results obtained by EDS analysis. The high-resolution Ti 2p spectrum of TiO₂ (Fig. 5a) displays two symmetrical peaks at binding energy (BE) values of 458.4 and 464.2 eV, corresponding to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, indicating that Ti exists in the +4 valence state in the TiO₂ HSs.⁴⁰ Moreover, a notable negative shift in the Ti 2p_{3/2} and Ti 2p_{1/2} BE values was observed for the TiO₂/LDH core–shell hybrid compared with those for TiO₂ HSs. Meanwhile, the Ni 2p spectrum of LDH (Fig. 5b) exhibits two typical

Figure S7 displays the N₂ adsorption–desorption isotherms and the corresponding BJH pore-size distribution curves of the TiO₂ NPs, TiO₂ HSs, LDH, and TiO₂/LDH core–shell hybrid samples. According to the IUPAC classification,⁴⁴ the isotherm of the TiO₂ HSs (Fig. S7a) is a type IV isotherm with a H4 hysteresis loop, implying the existence of narrow slit-like pores. This interpretation is further supported by the corresponding BJH pore-size distribution curve (inset of Fig. S7a), which reveals that TiO₂ HSs exhibit a pore-size distribution in the range 2–14 nm, with a mean pore diameter of approximately 6.5 nm. This pore structure is consistent with the TEM results (Fig. 2d). Analogous to the TiO₂ HSs, the TiO₂/LDH core–shell hybrid displays a type IV isotherm with a H4 hysteresis loop (Fig. S7b). Meanwhile, the isotherm of LDH (Fig. S7c), classified as type IV with a H3 hysteresis loop, suggests the

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existence of slit-shaped mesopores. The measured Brunauer–Emmett–Teller (BET)₁spectratice Online surface area (S_{BET}), average pore diameter, and total pore volume of all of the prepared samples are summarized in Table 1. The results show that the S_{BET} of the TiO₂ HSs is much higher than that of the reference TiO₂ NPs (Fig. S7d). Notably, the S_{BET} of the TiO₂/LDH core–shell hybrid is greater than that of the TiO₂ HSs, consistent with results reported for other hybrid heterostructures associated with TiO₂ hollow spheres.^{41,45} Moreover, compared with the TiO₂ HSs, the TiO₂/LDH core–shell hybrid exhibits a relatively higher average pore diameter and greater total pore volume, possibly because of the introduction of LDH, which exhibits a high average pore diameter and total pore volume. Such good surface and porous properties of the TiO₂/LDH core–shell hybrid exhibits are exposure of active sites and ion transport channels, thereby improving photocatalytic performance.

The adsorption of CO₂ onto the catalyst surface is considered a prerequisite step in the photocatalytic CO₂ conversion reaction.¹⁵ Hence, the CO₂ adsorption capabilities of the synthesized catalysts were investigated using CO₂ adsorption isotherm studies; the results are presented in Fig. 6a. Clearly, more CO₂ adsorbs onto the TiO₂HSs than onto the reference TiO₂ NPs, perhaps because of the large exposed surface area of TiO₂ HSs, which favors CO₂ adsorption. Interestingly, after LDH nanoflakes were grafted onto the TiO₂ hollow sphere cores, the resulting TiO₂/LDH core–shell hybrid displayed improved CO₂ adsorption capacity (0.48 mmol/g) compared with the TiO₂HSs (0.30 mmol/g) and the reference TiO₂NPs (0.14 mmol/g) catalysts. The improved CO₂ adsorption capacity of the TiO₂/LDH core–shell hybrid is attributed not only to the improved specific surface area and porous structure but also to the existence of abundant basic hydroxyl (–OH) functional groups on the LDH surface, which can facilitate chemical adsorption of acidic CO₂ molecules.^{26,46} Therefore, the improved CO₂ adsorption capability certainly accounts for the enhanced CO₂ photoreduction performance of the TiO₂/LDH core–shell hybrid.

TGA was conducted to examine the thermal stabilities of the prepared TiO₂ HS₈, LDH^{vandele Online} TiO₂/LDH core–shell hybrid samples. The TGA curve in Fig. 6b indicates that TiO₂ HSs have good thermal stability, with a total mass loss of only ~3.2% in the temperature range 30–800 °C. The observed weight loss was attributed to the elimination of surface-adsorbed water and residual organic species.³⁷ The TGA plot of LDH shows two major mass-loss regions, where the first weight loss at 30–200 °C corresponds to the loss of surface-adsorbed and interlayer (chemisorbed) water molecules.^{30,47} The second mass loss between 200 and 375 °C is related to the loss of interlayer NO₃⁻ species and dehydroxylation of the brucite-like layers.³⁰ No obvious weight loss occurs at temperatures greater than 375 °C, likely because of the formation of metal oxides from the LDH.⁴⁸ Similar mass-loss regions related to LDH are also observed in the TGA plot of TiO₂/LDH core–shell hybrid. Nonetheless, we estimated the actual content of LDH in the TiO₂/LDH core–shell hybrid to be 18.5 wt% on the basis of its TGA curve.

On the basis of the aforementioned experimental results, we proposed a formation mechanism for the TiO₂/LDH core–shell hybrid, which is schematically depicted in Scheme 1. Carbon spheres, which serve as the templates, with an average diameter of ~320 nm were first prepared by a simple hydrothermal route using agarose as a saccharide precursor. The surface of these carbon spheres was quite hydrophilic because of the presence of OH and C=O functional groups, as confirmed in previous reports.^{49,50} Upon addition of a titanium precursor to the carbon sphere colloid solution, the titanium cations were easily bound with surface functional groups of carbon spheres via electrostatic or coordination interactions.⁴⁹ In the subsequent calcination treatment, the inner part of the solid carbon spheres gradually dissolved; meanwhile, the surface layers comprising the titanium ions were cross-linked and recrystallized to form TiO₂ HSs as replicas of the templates but with a slightly smaller size. During the calcination treatment, numerous narrow-sized pores were created between the surface TiO₂ nanoparticles, as confirmed by TEM observations and BET measurements (Figs. 2d and S7a).

In the next step, the obtained TiO_2 HSs served as nucleation sites for the in situ growth of $I_2VDH_{TAOD104J}^{UCH}$ In detail, Ni²⁺ and Al³⁺ ions from their respective precursors tended to bind to the surface of the TiO₂ HSs. Upon the addition of urea and ammonium fluoride to the reaction mixture, LDH nanoflakes perpendicularly grew throughout the TiO₂ hollow sphere cores under hydrothermal conditions. As a result, the TiO₂/LDH core–shell hybrid with intimate interactions between the TiO₂ hollow-sphere cores and the LDH shell was realized. Notably, deionized water was the only solvent used in the synthesis; the use of toxic solvents or surfactants was deliberately avoided.

3.2 Photocatalytic activity

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The photocatalytic activities of the synthesized TiO₂ HSs, LDH, and TiO₂/LDH core–shell hybrid catalysts were investigated in detail via a CO₂ reduction assay under simulated solarlight illumination. Figure 7a and b demonstrates the evolution of carbon-based products as a function of irradiation time over all of the fabricated catalysts. Because of their adequate conduction band-edge potentials (determined by valence-band XPS analysis discussed later) for the water reduction process, all of the synthesized catalysts also generated H₂ as a competitive water reduction product (Fig. 7c). Under our experimental conditions, CH₄ was found to be an exclusive carbon-based product of CO₂ reduction when P25 or TiO₂ NPs or TiO₂ HSs were used as the photocatalyst. The reference TiO₂ NPs catalyst showed minimal CH₄ production, with a total yield of 0.20 μ mol for 5 h. A total CH₄ production yield of 1.02 μ mol was attained over the TiO₂ HSs, which is 5.1 times greater than that attained for the reference TiO₂ NPs catalyst. This result clearly reveals the importance of the hollow-sphere structure of TiO₂ in achieving enhanced photocatalytic CO₂ reduction performance. However, the selectivity toward CH₄ production against the competitive H₂ production over TiO₂ HSs was only 78%. Among the tested catalysts, P25 exhibited poor CH₄ production because of its

previously discussed intrinsic drawbacks. Meanwhile, bare LDH generated a distinct carbon $T_{A00104J}$ based product, CO, with a total yield of 0.32 µmol, in accordance with our previous reports.^{30,38}

As envisioned, after the LDH nanoflakes were grafted throughout the TiO₂ hollow-sphere cores, the resultant hierarchical TiO₂/LDH core–shell hybrid displayed substantially enhanced photocatalytic activity for CO₂ reduction to CH₄ compared with its counterpart, TiO₂ HSs. This target TiO₂/LDH core–shell hybrid exhibits the highest CH₄ evolution among the tested samples, with a total yield of 5.14 µmol over 5 h, equating to a rate of 20.56 µmol g⁻¹ h⁻¹ (Fig. 7d), representing remarkable 25.7- and 5.0-fold improvements in CH₄ production compared with those of reference TiO₂ NPs and TiO₂ HSs, respectively. The activity results also indicate that the TiO₂/LDH core–shell hybrid produced a small amount of CO (2.48 µmol g⁻¹ h⁻¹), as an additional solar fuel.

To verify the feasibility of carbon-based CH₄ or CO production from surface organic residues, a control experiment in the absence of CO₂ or in the presence of Ar was carried out. No CH₄ or CO production was detected for the same TiO₂/LDH core–shell hybrid after 5 h of light illumination. A ¹³C isotope-labeled experiment was also conducted over TiO₂/LDH core–shell hybrid under the identical test conditions; the resultant products were analyzed via gas chromatography–mass spectrometry (GC–MS). The peak at 8.62 min in the GC spectrum (inset of Fig. S8) with a m/z value of 17 in the MS spectrum (Fig. S8) was attributed to ¹³CH₄.^{51,52} Moreover, the MS spectrum also displays signals with m/z values of 29 and 45, corresponding to ¹³CO (as the minor product) and ¹³CO₂, respectively.⁵³ These results demonstrate that the carbon source was merely derived from the input CO₂, ruling out the possibility of contamination from other carbon sources. In addition, control experiments in the dark or without a catalyst did not led to the production of hydrocarbon fuels, confirming that CO₂ conversion was triggered solely by light irradiation in the presence of a catalyst. Furthermore, the yield of H₂ over the TiO₂/LDH core–shell hybrid was only 0.52 µmol, which implies that

the selectivity toward CH_4 generation against H_2 reached almost 95%. Notably, the VCL4^{rtde Online} production yield and selectivity (against water reduction) of TiO₂ HSs were substantially improved via coupling with the LDH, even though LDH alone did not generate any detectable CH_4 in the CO₂ reduction reaction under identical test conditions. In addition, the TiO₂/LDH core–shell hybrid is far superior many of the reported TiO₂-based catalyst systems with respect to the rate of CH_4 production, as summarized in Table S1. Furthermore, the apparent quantum yield of TiO₂/LDH core–shell hybrid for the formation of CH_4 was calculated to be 0.92%, which is also higher than the other state-of-the-art TiO₂-based photocatalysts for CH_4 production.^{18,54-57}

The importance of the core–shell structure on the CO₂ reduction performance was investigated by comparing the solar fuel production rates of the target TiO₂/LDH core–shell hybrid with those of a similar TiO₂ NPs/LDH hybrid with a different structure. Because the TiO₂ HSs were substituted with TiO₂ NPs in the synthesis process (see the Experimental section), the obtained TiO₂ NPs/LDH hybrid does not possesses the core–shell morphology (Fig. S9). The FESEM image (Fig. S9) also illustrates poor contact between the components of the TiO₂ NPs/LDH hybrid. As a result, the productivity and selectivity toward CO₂ reduction of the TiO₂ NPs/LDH hybrid are inferior to that of the TiO₂/LDH hybrid with core–shell morphology. These results confirm that the core–shell geometric structure could enlarge the interfacial contact area and thus provide a broader platform for efficient charge transfer, which subsequently resulted in extraordinary photocatalytic CO₂ reduction activity of the TiO₂/LDH core–shell hybrid.

Because the durability and photostability are indispensable parameters for a photocatalyst with respect to its practical applications, four consecutive CO₂ reduction test runs were carried out using the TiO₂/LDH core–shell hybrid. Fig. 8a clearly shows that the TiO₂/LDH core–shell hybrid maintains its remarkable activity after four successive test runs, with no apparent

reduction in CH₄ or CO production. This result implies that the TiO₂/LDH core-shell hybrid acount maintains impressive durability during prolonged CO₂ reduction reactions. In addition, XPS and XRD analyses were conducted to assess the stability of the target catalyst after CO₂ reduction activity tests. Negligible changes were observed in the XPS spectra (Fig. S10a and b) of the TiO₂/LDH core-shell hybrid before and after the photocatalytic CO₂ reduction tests, affirming that its chemical structure was not altered during the reaction. Moreover, the lack of an apparent difference in the XRD patterns (Fig. S11) of the fresh and reused TiO₂/LDH core-shell hybrid further evidences the stability of its phase structure. In addition, the SEM and TEM images in Fig. S12a and b clearly illustrated that the core-shell geometry of the TiO₂/NiAl-LDH hybrid did not change after the photocatalytic CO₂ reduction reaction. Hence, the aforementioned results strongly imply that the present TiO₂/LDH core-shell hybrid, as a highly efficient and stable photocatalyst, holds great promise for practical hydrocarbon fuel generation.

3.3 Photocatalytic mechanism

To determine the underlying reasons for the extraordinary photocatalytic CO_2 reduction performance of the TiO₂/LDH core–shell hybrid, we conducted various experiments and carefully analyzed the results. The photocatalytic CO_2 reduction reaction is well known to primarily encompass the following fundamental processes: (i) photoabsorption; (ii) separation and migration of photoexcited charge carriers; and (iii) CO_2 adsorption and reduction.^{58,59} These factors are elucidated as follows. Journal of Materials Chemistry A Accepted Manuscript

The previously discussed UV–vis DRS results demonstrate that the TiO_2/LDH core–shell hybrid exhibited improved photoabsorption ability because of the presence of UV-lightresponsive TiO_2 HSs and visible-light-responsive LDH. This broad range of photoabsorption could generate the vast number of photoexcited charges necessary for the subsequent CO_2

reduction reaction. Hence, this property is likely one of the pivotal reasons for the improved Addite Online CO₂ reduction efficiency of the TiO₂/LDH core–shell hybrid system.

The separation-recombination rate of the photoexcited electrons and holes is one of the decisive factors affecting the photocatalytic CO₂ reduction efficiency because the low recombination rate or high separation rate can enable more electrons to participate in reducing adsorbed CO2 molecules.60 Hence, a comprehensive understanding of charge separation and transport processes within the TiO₂/LDH core-shell hybrid is critical. In this regard, photoluminescence (PL) spectroscopy, a powerful tool to characterize the recombination probability of photoexcited electrons and holes,⁶¹ was used to analyze the synthesized catalysts. As shown in Fig. 8b, the PL emission intensity of the TiO₂/LDH core-shell hybrid decreased dramatically compared with those of the TiO₂ HSs and the TiO₂ NPs, which implies that charge-carrier recombination was efficiently hindered. In addition, the PL emission intensity of the target TiO₂/LDH core-shell hybrid is inferior to that of the analogous TiO₂ NPs/LDH hybrid with a different morphology, consistent with its superior CO₂ photoreduction performance, as previously discussed. This result provides strong evidence that the core-shell architecture of the TiO₂/LDH hybrid could create large interfacial contact between TiO₂ HSs and LDH for fast charge transfer, effectively impeding the direct recombination of photogenerated charge carriers.

Transient photocurrent response studies were also conducted to further verify the separation and transport behaviors of photogenerated charge carriers in the TiO₂/LDH core–shell hybrid. Because the photocurrent is primarily generated by the diffusion of photogenerated electrons, a strong photocurrent response implies greater separation efficiency of electron–hole pairs.^{60,62} Figure 8c displays the transient photocurrent responses of the TiO₂ HSs, TiO₂/LDH core–shell hybrid, TiO₂ NPs/LDH, and reference TiO₂ NPs samples, as recorded during several on–off cycles of intermittent light irradiation. The photocurrent response of the TiO₂/LDH core–shell

hybrid is several times higher than that of the TiO_2 NPs, TiO_2 HSs, and the TiO_2 NPs/ tiO_2 TiO_2

To provide additional evidence for the efficient charge transfer in the TiO₂/LDH core-shell hybrid, we conducted EIS analysis. The arc diameter in the EIS profile reflects the chargetransfer resistance of the electrode material: the smaller the arc diameter, the greater the charge transfer efficiency.^{16,63} Figure 8d depicts the Nyquist plots for the TiO₂ NPs, TiO₂ HSs, TiO₂ NPs/LDH, and TiO₂/LDH core-shell hybrid samples. These Nyquist plots were fitted using the equivalent circuits displayed in Fig. S13. The Randles circuit (which containing Warburg element) was used for the fitting of the EIS curves of TiO2/LDH core-shell and TiO2 NPs/LDH hybrids where diffusion behaviour along with solution resistance and charge transfer resistance were observed. The simple charge transfer circuit was used for the EIS curves of TiO₂ NPs and TiO_2 HSs where only solution resistance and charge transfer resistance were observed. The charge transfer resistance values of TiO₂ NPs and TiO₂ HSs are about 14.8 and 10.6 k Ω , respectively, as estimated by fitting the EIS data with equivalent circuit. Notably, the TiO₂/LDH core-shell hybrid displayed a significant decrease in the charge transfer resistance (152 Ω) compared to TiO₂ NPs, TiO₂ HSs, and TiO₂ NPs/LDH (420 Ω). The diminished charge transfer resistance imparts the TiO2/LDH core-shell hybrid with increased electronic conductivity, facilitating the migration of photoinduced electrons and holes. Thus, the EIS results, together with the PL and photocurrent outcomes, demonstrate that the strong synergy between the TiO₂ HSs and LDH, induced by their efficient core-shell geometric structure, promotes interfacial charge-transfer processes. Furthermore, these processes impede the direct recombination of photoexcited charges, which eventually results in the exceptional $\sqrt[V]{O}_{2A00104J}$ reduction performance of the TiO₂/LDH core–shell hybrid toward the production of solar fuels.

In addition, the previously discussed BET analysis results demonstrate that the TiO₂/LDH core-shell hybrid maintains a high surface area and good pore structure, whereas the CO₂ adsorption isotherm analysis results confirm that the TiO₂/LDH core-shell hybrid exhibits excellent CO_2 adsorption capability, which is a prerequisite for the subsequent CO_2 reduction reaction by photoexcited charges. These results indicate that the enhanced surface area, pore structure, and CO₂ adsorption capability of the TiO₂/LDH core-shell hybrid are also important factors responsible for the extraordinary CO₂ photoreduction activity. To elucidate the transfer pathways of the photoinduced electrons and holes across the interface in the TiO₂/LDH coreshell hybrid, an investigation of the band-edge potentials of its constituents is essential. In this study, the VB edge potentials of TiO₂ and LDH were determined by VB-XPS from the intercept of the tangent to the density of states at the Fermi edge as 2.73 and 1.6 eV, respectively (Fig. S14), in good agreement with values reported previously.^{30,35,41,42} Meanwhile, the bandgap energies of TiO₂ HSs and LDH estimated from Tauc plots are 3.18 and 2.32 eV, respectively (Fig. S15). On the basis of these VB edge potentials and the bandgap energies obtained from Tauc plots (Fig. S15), the conduction band (CB) edge potentials were calculated to be -0.45and -0.72 eV for TiO₂ and LDH, respectively.

Because both the CB and VB potentials of TiO_2 are more positive than those of LDH, the charge transfer at the interface may follow the Z-scheme transfer or double-transfer route. If the Z-scheme transfer route is assumed for the present core–shell hybrid system, then the CO_2 reduction reaction and the water oxidation reaction would proceed on the CB of LDH and on the VB of TiO_2 , respectively. This behavior can be confirmed by evaluating the generation rate of spin-reactive hydroxyl radicals (•OH) and superoxide radicals ($O_2^{\bullet-}$) via the ESR technique. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO), a typical spin-trap molecule, was used for

trapping the 'OH and O₂⁻⁻ to form the DMPO-OH and DMPO-O₂⁻⁻ adducts, respectively divergence of the optime Figure 9a and 9b display typical DMPO-OH and DMPO-O2[•] peaks of the TiO2 HSs, LDH, and the TiO₂/LDH core-shell hybrid under simulated solar-light irradiation. The lack of a signal corresponding to DMPO-OH or DMPO-O2⁻ under the dark condition for all of the catalysts demonstrates that the spin-reactive species were indeed produced under stimulation of solar light. A strong ESR signal with a 1:2:2:1 quartet corresponding to the DMPO-'OH adduct was observed for the TiO₂ HSs. By contrast, no obvious signal was detected for LDH because of its unmatched VB potential to produce 'OH radicals. Surprisingly, the TiO₂/LDH core-shell hybrid displayed a substantial decrease in DMPO-'OH signal intensity compared with the TiO₂ HSs, perhaps because of the photoinduced hole transfer from the VB of TiO₂ to the VB of LDH. Meanwhile, a set of four peaks corresponding to the DMPO-O2⁺⁻ adduct was observed for all of the three catalysts; however, the intensity of the peaks for the TiO₂/LDH core-shell hybrid was much higher than that observed for TiO₂ HSs and LDH. The increased DMPO-O₂^{•-} signal intensity and the decreased DMPO-•OH signal intensity for the TiO₂/LDH core-shell hybrid indicate that the Z-scheme transfer route is not applicable to the present coreshell hybrid system. Therefore, the charge transfer in the TiO₂/LDH core–shell hybrid follows the conventional double-transfer route, where the CO₂ photoreduction process occurs on the CB of TiO₂ and the water oxidation reaction occurs on the VB of LDH. Notably, TiO₂ HSs and LDH exclusively produced CH₄ and CO, respectively, whereas the TiO₂/LDH core-shell hybrid produced CH₄ as the major product along with very small amount of CO, which also supports the aforementioned conclusion that the CO₂ reduction reaction occurs on the CB of TiO₂.

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The band alignment of the TiO_2/LDH core–shell hybrid and detailed conventional doubletransfer mechanism based on the previously discussed ESR results and band-structure analysis are schematically illustrated in Fig. 10. When the TiO_2/LDH core–shell hybrid is exposed to

light, both TiO₂ and LDH are excited, producing electron (e⁻) and hole (h⁺) charge carries discussion of the second s the CB and VB, respectively. Because of the well-matched band structure and inner electrical field established between TiO₂ and LDH, the excited electrons transfer from the CB of LDH to the CB of TiO₂; meanwhile, the photoinduced holes tend to transfer from the VB of TiO₂ to the VB of LDH. As a result, the direct recombination of photoexcited electrons and holes is substantially inhibited in both components. The charge transfer process also results in the accumulation of holes in the VB of LDH and electrons in the CB of TiO₂. The gathered holes in the VB of LDH are trapped by H₂O molecules to release protons (H⁺) and O₂. Meanwhile, under the assistance of the produced protons, the electrons accumulated in the CB of TiO₂ can react with CO₂ molecules adsorbed onto the surface of the catalyst to produce solar fuels such as CH₄ and CO. Thermodynamically, the generation of CH₄ from CO₂ reduction is indeed difficult compared with the generation of CO because the former requires 8 e⁻ and 8 H⁺, whereas the latter needs only 2 e⁻ and 2 H⁺. Nonetheless, the CB potential of TiO₂ (-0.45 eV vs. normal hydrogen electrode (NHE), pH = 7) is slightly lower than the standard reduction potential of CO/CO_2 (-0.53 eV vs. NHE, pH = 7) but is higher than the standard reduction potential of CH₄/CO₂ (-0.24 eV vs. NHE, pH = 7),¹⁰ suggesting that the electrons in the CB of TiO₂ are only capable of producing CH₄. In addition, the double transfer mechanism suggests that a substantial number of available electrons (required for CH₄ formation) exist in the CB of TiO₂, which could also explain why CH₄ was generated as a major product in the CO₂ reduction reaction by the TiO₂/LDH core-shell hybrid. The leftover electrons in the CB of LDH after charge transfer may be responsible for the observed production of a small amount of CO. The reactions that occur during the photocatalytic CO₂ conversion process to produce solar fuel are summarized by the following equations:

> TiO₂/LDH + hv→TiO₂/LDH (h_{VB}^+ + e_{CB}^-) TiO₂/LDH (h_{VB}^+ + e_{CB}^-)→TiO₂ (e^-) + LDH (h_{VB}^+)

 $LDH (h_{VB}^{+}) + 2H_{2}O \rightarrow O_{2} + 4H^{+} + 4e^{-}; E^{0} = +0.82 V$ View Article Online DOI: 10.1039/DOTA00104J TiO_{2}(8e^{-}) + 8H^{+} + CO_{2} \rightarrow TiO_{2} + CH_{4} + 2H_{2}O; E^{0} = -0.24 V (Major) $LDH (2e^{-}) + 2H^{+} + CO_{2} \rightarrow LDH + CO + H_{2}O; E^{0} = -0.53 V (Minor)$ TiO_{2} or LDH (2e^{-}) + 2H^{+} \rightarrow TiO_{2} or LDH + H_{2}; E^{0} = -0.41 V (Minor)

4 Conclusions

In summary, we successfully fabricated the TiO₂/LDH core–shell hybrid via ecologically friendly and economical synthesis route. Notably, compared with TiO₂ NPs, TiO₂ HSs, commercial P25, and TiO₂ NPs/LDH with different morphologies, the synthesized TiO₂/LDH core–shell hybrid displays substantially enhanced photocatalytic CO₂ reduction activity favoring CH₄ and CO production. The CO₂ reduction activity of the TiO₂/LDH core–shell hybrid in terms of CH₄ production is comparable, and in many cases superior, to that of the numerous reported TiO₂-based photocatalysts. This remarkable CO₂ reduction activity of the TiO₂/LDH core–shell hybrid toward solar fuel generation is predominantly attributed to its unique core–shell geometric structure, which provides an enhanced interfacial contact area for efficient charge transfer, together with other advantageous attributes such as good light-harvesting ability, a large surface area, porous structure, and outstanding CO₂ adsorption capability. Additionally, the TiO₂/LDH core–shell hybrid demonstrates high stability during successive test cycles, with no apparent change in the CO₂ reduction activity.

Conflicts of interest

There are no conflicts to declare.

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Figure captions

Fig. 1 (a, b) FESEM and (c, d) TEM micrographs of the prepared carbon spheres.

Fig. 2 (a) FESEM and (b) TEM images of the TiO_2/C sample. (c) FESEM and (d) TEM images (inset is the magnified-TEM image) of the TiO_2 HSs.

Fig. 3 (a) TEM, (b) magnified TEM, and (c) high-resolution TEM micrographs of the TiO_2/LDH core–shell hybrid. (d to h) STEM-HAADF elemental distribution maps of constituent elements in the TiO_2/LDH core–shell hybrid.

Fig. 4 (a) XRD and (b) UV-vis DRS spectra of the prepared samples.

Fig. 5 High-resolution XPS spectra of TiO_2 HSs, LDH, and TiO_2/LDH core–shell hybrid samples. (a) Ti 2p, (b) Ni 2p, (c) Al 2p, and (d) O 1s.

Fig. 6 (a) CO₂ adsorption isotherms and (b) TGA curves of the prepared samples.

Fig. 7 Time-dependent (a) CH_4 , (b) CO, and (c) H_2 yields produced in the presence of all the prepared samples. (d) Comparison of the photocatalytic CH_4 , CO, and H_2 production rates over the prepared samples upon 5 h of simulated-solar-light irradiation.

Fig. 8 (a) Recycling tests of CH_4 and CO evolution over the TiO_2/LDH core–shell hybrid. (b) PL, (c) photocurrent, and (d) EIS profiles of TiO_2 NPs, TiO_2 HSs, TiO_2 NPs/LDH, and TiO_2/LDH core–shell hybrid samples.

Fig. 9 DMPO spin-trapping ESR spectra of TiO_2 HSs, LDH, and TiO_2/LDH core–shell hybrid samples for (a) DMPO–'OH and (c) DMPO–O₂'– irradiated for 6 min.

Fig. 10 Schematic illustration of the proposed mechanism for photocatalytic CO_2 reduction in the TiO₂/LDH core–shell hybrid system.

Scheme 1 Schematic representation of the synthesis of TiO₂/LDH core–shell hybrid photocatalyst.

Photocatalyst	<i>S_{BET}</i> (m ² g ⁻¹)	Mean pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
TiO ₂ HSs	108.5	6.5	0.278
TiO ₂ /LDH core-shell	115.2	10.8	0.312
LDH	35.9	48.7	0.396
TiO ₂ NPs	47.3	38.4	0.354

Table 1 S_{BET}, average pore diameter, and total pore volume for TiO₂ HSs, TiO₂ NPs $I_{10,1039/D07A00104J}^{VOMPticle Online}$ and TiO₂/LDH core–shell hybrid samples.



Scheme 1 Schematic representation of the synthesis of TiO_2/LDH core-shell hybrid photocatalyst.



Fig. 1 (a, b) FESEM and (c, d) TEM images of the prepared carbon spheres.



Fig. 2 (a) FESEM and (b) TEM images of TiO_2/C . (c) FESEM and (d) TEM images (inset is the magnified-TEM image) of TiO_2 HSs.

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Fig. 3 (a) TEM, (b) magnified TEM, and (c) high-resolution TEM micrographs of the TiO_2/LDH core–shell hybrid. (d to h) STEM-HAADF elemental distribution maps of constituent elements in the TiO_2/LDH core–shell hybrid.



Fig. 4 (a) XRD and (b) DRS spectra of the prepared samples.



Fig. 5 High-resolution XPS spectra of TiO_2 HSs, LDH, and TiO_2/LDH core–shell hybrid samples. (a) Ti 2p, (b) Ni 2p, (c) Al 2p, and (d) O 1s.

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Fig. 6 (a) CO_2 adsorption isotherms and (b) TGA curves of the prepared samples.



Fig. 7 Time-dependent (a) CH_4 , (b) CO, and (c) H_2 yields produced in the presence of all the prepared samples. (d) Comparison of the photocatalytic CH_4 , CO, and H_2 production rates over the prepared samples upon 5 h of simulated-solar-light irradiation.



Fig. 8 (a) Recycling tests of CH_4 and CO evolution over the TiO_2/LDH core–shell hybrid. (b) steady-state PL spectra, (c) photocurrent responses, and (d) EIS profiles of TiO_2 NPs, TiO_2 HSs, TiO_2 NPs/LDH, and TiO_2/LDH core–shell hybrid samples.



Fig. 9 DMPO spin-trapping ESR spectra of TiO_2 HSs, LDH, and TiO_2/LDH core–shell hybrid samples for (a) DMPO–OH and (c) DMPO–O₂⁻⁻ irradiated for 6 min.



Fig. 10 Schematic illustration of the proposed mechanism for photocatalytic CO₂ reduction in the TiO₂/LDH core–shell hybrid system.

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A green approach is proposed to fabricate TiO_2/LDH core–shell hybrid as a potential catalyst for photoreduction of CO_2 to solar fuels with high activity and selectivity.

