Coupling Long-Range Facet Junction and Interfacial Heterojunction via Edge-Selective Deposition for High-Performance Z-Scheme Photocatalyst

Xuan Li, Shoaib Anwer, Qiangshun Guan, Dalaver H. Anjum, Giovanni Palmisano, and Lianxi Zheng*

The construction of photocatalytic systems that have strong redox capability, effective charge separation, and large reactive surfaces is of great scientific and practical interest. Herein, an edge-connected 2D/2D Z-scheme system that combines the facet junction and the interfacial heterojunction to achieve effective long-range charge separation and large reactive surface exposure is designed and fabricated. The heterostructure is realized by the selective growth of 2D-layered MoS₂ nanoflakes on the edge-sites of thin TiO₂ nanosheets via an Au-promoted photodeposition method. Attributed to the synergetic coupling of the facet junction and the interfacial heterojunction that assures the effective charge separation, and the tremendous but physically separated reactive sites offered by layered MoS₂ and highly-exposed (001) facets of TiO₂, respectively, the artificial Z-scheme exhibits excellent photocatalytic performance in photodegradation tests. Moreover, the junctional plasmonic Au nanoclusters not only act as electron traps to promote the edge-selective synthesis but also generate “hot electrons” to further boost photocatalytic performance. The Z-scheme charge-flow direction in the heterostructure and the roles of electrons and holes are comprehensively studied using in situ irradiated X-ray photoelectron spectroscopy and photodegradation tests. This work offers a new insight into designing high-performance Z-scheme photocatalytic systems.

1. Introduction

Two of the biggest challenges confronting the world today are the global crises of clean energy supply and environmental pollution. To address these concerns, one of the most promising and sustainable technologies is sunlight-assisted semiconductor-based photocatalysis, which uses free solar energy to produce clean energy and for the removal of environmental pollutants.[1] An ideal semiconductor photocatalyst should have strong redox capability, effective charge separation, and a large reactive surface area.[2] To boost the redox capability, constructing Z-scheme heterojunction has proven to be the most effective strategy because it could take the synergistic effects of two semiconducting components to keep the high-energy holes/electrons for redox reactions.[3] The effective charge separation could be realized by facet junctions[4] or heterojunctions,[5] with facet junctions having weak but relatively long-range charge separation while heterojunctions possessing strong but local charge separation. The large reactive surface area is commonly achieved by employing low-dimensional, especially 2D nanomaterials.[6] Irrespective of the progress made in each of these areas, it remains an extreme challenge to construct a 2D material-based Z-scheme photocatalytic system with a proper geometry so that all of the three merits exist in one unique catalytic system.

Interfacial design and selective synthesis are two major obstacles toward this goal. To obtain a Z-scheme heterojunction for...
high redox capability, two constituent semiconductors must have well-matched band alignment, intimate contact, and a dedicated charge transfer channel. However, interfacial defects, functional groups, adsorbents, etc., could easily alter these interfacial properties, resulting in the formation of a Type II rather than a Z-scheme heterojunction. In order to alleviate this uncertainty, minor differences between surface sites or crystal facets have been utilized for selectively constructing Z-scheme heterostructures. It was found that some sites of a material surface or some crystal facets of a semiconductor were more favorable for the accumulation of electrons while some were prone to act as hole traps. This difference could be an intrinsic feature of the materials or induced by surface modification via ion or particle decoration. For example, CdS was selectively deposited at the electron transfer sites of g-C₃N₄ to regulate the electron flow direction. Selective growth of CdS on (001) or (101) TiO₂ facets was controlled by attaching/detaching F⁻ ions. Core–shell heterojunctions were achieved by Au nanoparticle-mediated growth. TiO₂ hollow nanoboxes were utilized to force (101) facets to be exposed to the outmost of the cluster structures, forming TiO₂(101)/g-C₃N₄ contacted heterostructures. Cross-stacked TiO₂ nanostructures were used to expose (101) facets for fast and easy access to the precursors during photodeposition (PD) and to avoid the stacking growth of MoS₂ on (001) facets. These strategies demonstrate great success in constructing different types of Z-scheme heterojunctions, including randomly deposited, site-selectively deposited, and facet-selectively deposited Z-schemes, but still fall short of obtaining high-performance photocatalysts, both efficient charge separation and large reactive surface area. More specifically, in randomly or site-selectively deposited Z-scheme structures, the second semiconductor generally covers the surface of the first semiconductor in the format of nanoparticles or nanoclusters (NCs), so the increase of surface area for reduction (or oxidation) is at the expense of the decrease of the surface area for oxidation (or reduction). Furthermore, the spatial distance between these NCs is extremely short, which increases the charge recombination via environmental routes (e.g., backward redox in the liquid phase). Although the heterojunction itself has effective charge separation capability, the external recombination routes will compromise the overall charge separation efficiency. Consequently, such photocatalysts usually need sacrificial agents to guarantee their photocatalytic performance. In fact-selectively deposited Z-scheme structures, a complex morphology of the first semiconductor, which involves a complex fabrication process, is required to confine the access of precursors of the second semiconductor during the selective synthesis/construction. This confining mechanism, as well as the complex geometry, will also limit the access to the target molecules in photocatalytic applications, resulting in a significant decrease in the active surface area of the catalyst and thus the extent of its utilization.

Herein, we design a 2D material-based Z-scheme photocatalyst that constructively couples the facet junction and heterojunction to simultaneously achieve high redox capability, efficient charge separation, and large reactive surface area. 2D anatase TiO₂ nanosheets (TNSs) with highly-exposed (001) facets and layered MoS₂ nanoflakes (NFs) are employed as two-component materials. Au NCs are first decorated on the edge surfaces (i.e., (101) facets) of TNSs via a diffusion and spatial confinement strategy. MoS₂ is then selectively deposited on the Au NCs and TiO₂ edge surfaces via a simple PD method. The resultant structure not only takes advantages of the combinative effect from the facet junction and heterojunction to maximize the charge separation and form a Z-scheme structure but also physically separates the redox reactive surfaces, leaving the highly-exposed (001) facets of 2D TNSs for oxidation and MoS₂ for reduction reactions. While the Au NCs implanted between two semiconductors not only serve as a mediator to facilitate the fast migration of photogenerated electron holes at the heterointerface to ensure an effective Z-scheme charge transfer but also act as a source of “hot electron” injection to improve the photocatalytic performance. Such a photocatalyst system is extremely beneficial for photodegradation applications that have diverse and unknown pollutants.

2. Results and Discussion

2.1. Design and Edge-Selective Construction of MoS₂/Au/TiO₂ Heterogeneous Photocatalyst

The idea of junction coupling was realized by constructing an edge-connected MoS₂/Au/TiO₂ (MS/Au/T) heterogeneous photocatalyst. The schematic design and stepwise fabrication process are illustrated in Figure 1a. In the first step, rectangular-shaped anatase TNSs with highly-exposed (001) facets were prepared via a hydrothermal process. In the second step, Au atoms and fine nanoparticles were dispersed on the TNSs via solution phase synthesis. The dispersed Au particles were then turned into selectively deposited Au NCs on the edge-sites, that is, (101) facets of TNSs after controlled calcination treatment to obtain Au/TiO₂ (Au/T) heterostructures. Mechanistically, Au ions were first reduced into Au atoms or small particles that were randomly distributed over the TNSs surfaces and then transformed to NCs and selectively accumulated on (101) facets via diffusion and spatial confinement mechanism. In the last step, MoS₂ was selectively deposited via a modified PD method at room temperature. Au/T was initially mixed with an aqueous solution containing MoS₄²⁻ and then irradiated with simulated solar light. Interestingly, it was found that MoS₂, preferably grew on Au NCs first, then on (101) facets of TNSs to form ternary MS/Au/T heterostructures. Notably, Au played a critical role in the PD process, because it offered strong affinity with S²⁻ trapped electrons from TiO₂ (101) facets, and produced more electrons via localized surface plasmon resonance (LSPR). Therefore, it accumulated more electrons to amplify the potential difference between (001) and (101) facets of TNSs, and thus promoted the selective PD of MoS₂ on Au NCs and the edges of TNSs.

To illustrate the charge carrier’s migration principle, the energy band diagrams of TNSs, Au/T, and MS/Au/T are shown in Figure 1b–d. Under light irradiation, the photogenerated electrons and holes transfer to (101) and (001) facets of TNSs respectively, forming a facet junction (Figure 1b). Since the work function of Au is larger than that of TiO₂, the accumulated photogenerated electrons at the interface transfer from TiO₂ (101) facets to Au NCs, establishing a consecutive electron flow path: TiO₂ (001) facet → TiO₂ (101) facet → Au NCs (Figure 1c), which facilitates an efficient charge separation in Au/T heterostructure. In MS/Au/T, Au NCs act as the mediator to recombine the photoinduced electrons from the conduction band (CB) of TiO₂ (101) and MoS₂.
facets with the holes from the valence band (VB) of MoS$_2$, forming a Z-scheme charge transfer that leaves the electrons in CB of MoS$_2$ and holes in VB of TiO$_2$ (001) facets with higher energies for redox reactions (Figure 1d).\cite{10} This Z-scheme boosts the charge separation to have a higher photocatalytic efficiency and can be applied in various catalytic reactions with high redox potentials, owing to its well-retained strong redox ability. Particularly, in our system, the photoinduced holes mainly accumulate on the TiO$_2$ (001) facets with a large area, which offer highly-exposed oxidation sites and thus promote the photocatalytic reaction. In addition, the spatially separated reduction (MoS$_2$) and oxidation (TiO$_2$ [001] facets) active sites allow the photocatalyst system to participate in reduction and oxidation reactions simultaneously, beneficial for the photodegradation applications that have diverse and unknown pollutants.

The morphologies of TNSs, Au/T, and MS/Au/T were examined by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) analysis. As depicted in Figure 1e and Figure S1, Supporting Information, TNSs exhibited a 2D rectangular shape with a mean length of $\approx 60$ nm and thickness of $\approx 6$ nm. Indexed lattice spacing of 0.35 nm (see inset Figure 1f) from TNS surfaces and 0.235 nm (Figure S1b, Supporting Information) from the vertical cross-sectional image of TNSs were identified and correspond to the (101) and (001) planes of the crystalline anatase phase of TiO$_2$,\cite{13,16} respectively, confirming that the synthesized TNSs have highly-exposed (001) facets and thin (101) facets. Figure 1g,h and Figure S2a,b, Supporting Information, demonstrated that highly crystallized Au NCs were successfully deposited on the edge sites of TNSs with intimate contact. The observed lattice spacing of 0.235 nm (Figure S2c, Supporting Information) matched well with the (111) lattice plane of face-centered cubic (FCC) Au.\cite{17} The transmission electron microscopy (TEM) image in Figure 1i and the high-angle annular dark-field scanning TEM (HAADF-STEM) image in Figure 1j clearly displayed that MoS$_2$ NFs were intimately deposited in a layered manner via photo-assisted nucleation and growth process at room temperature. Red-dotted line in Figure 1k disclosed that MoS$_2$ NFs were thin and immature crystalline structures, but they formed the shell to cover the Au NCSs (yellow circle) pre-deposited on TiO$_2$ (101) facets. A clearer HAADF-STEM image showing two distinct interfaces of TiO$_2$/Au and Au/MoS$_2$ in MS/Au/T can be found in Figure S2d, Supporting Information.

The composition and crystal structure of the prepared photocatalysts were further investigated by powder X-ray diffraction (XRD) and Raman spectroscopy. The obtained patterns of TNSs, Au/T, and MS/Au/T are shown in Figure S3, Supporting Information. As shown in Figure S3a, Supporting Information, the XRD diffraction peaks at 25.1°, 38.1°, 47.9°, and 75° were obvious in the as-prepared three samples and could be respectively assigned to the (101), (004), (200), and (215) crystallographic planes of anatase TiO$_2$, which well matched the reference pattern (JCPDS 21–1272).\cite{13,16} Anatase TNSs were well-retained without any phase change even after the deposition of Au NCs and MoS$_2$ NFs. The diffraction peaks observed at 38.1°, 44.3°, 64.4°, and 77.5° in Au/T photocatalyst could be attributed to FCC Au (JCPDS 04–0784). The distinct (004) diffraction peak of TNSs indicates the dominant crystal growth along the (001) direction, which is typical for anatase TiO$_2$ with highly-exposed (001) facets.\cite{16} However, no obvious signals of MoS$_2$ were observed in the XRD pattern of the MS/Au/T photocatalyst. This
could be due to its amorphous-like structure or poor crystallinity and thin-layered 2D morphology or high dispersion on very small but crystalline Au NCs.\textsuperscript{[18]} The Raman studies further demonstrated this conjecture. As shown in Figure S3b, Supporting Information, the peaks at 143, 392, 511, and 632 cm\(^{-1}\) could be respectively assigned to \(E_g\), \(B_{1g}\), \(A_{1g}\), and \(E_g\) anatase tetragonal vibration modes of TiO\(_2\).\textsuperscript{[19]} The observed shift at 153 cm\(^{-1}\) corresponding to the \(E_g\) Raman mode of Au/T confirmed a strong interfacial contact and electronic interaction between TiO\(_2\) and Au.\textsuperscript{[19]} However, no characteristic peaks belonging to \(E_{1g}\) and \(A_{1g}\) of 2H-MoS\(_2\) were found in the MS/Au/T spectrum, which confirmed the amorphous-like structure and poor crystallinity of MoS\(_2\).\textsuperscript{[20]} As experimental evidence, the presence of MoS\(_2\) was proved by X-ray photoelectron spectroscopy (XPS). The XPS spectrum of MS/Au/T exhibited two characteristic peaks at 229.04 and 232.14 eV (Figure S4, Supporting Information), attributed to the binding energies (BEs) of Mo 3d\(_{5/2}\) and Mo 3d\(_{3/2}\) for Mo\(^{4+}\) species.\textsuperscript{[21]} The BEs of Mo\(^{4+}\) 3d doublet demonstrated that MoS\(_2\) was a semiconducting 2H phase.\textsuperscript{[22]} The S 2p\(_{3/2}\) and S 2p\(_{1/2}\) doublets, respectively at 161.88 and 163.08 eV, were assigned to S\(^2-\) ions.\textsuperscript{[21]} These XPS results confirmed the presence of 2H-MoS\(_2\) and supported the HRTEM investigations. Besides this, a contribution of Mo\(^{5+}\), Mo\(^{6+}\), and S\(^{2+}\) was also evident\textsuperscript{[21]} and summarized in Table S1, Supporting Information.

The chemical states of the key elements and the formation of heterojunctions were further investigated by XPS. As shown in Figure S5, Supporting Information, the BEs of Ti 2p displayed obvious differences among TNSs, Au/T, and MS/Au/T. For Au/T, the BEs of Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) were respectively 458.47 and 464.17 eV, with splitting energy of 5.7 eV, manifesting the presence of tetragonal Ti\(^{4+}\).\textsuperscript{[21]} But both peaks were 0.11 eV lower than those of TNSs. This negative shift suggests strong interfacial interaction between Au and TiO\(_2\).\textsuperscript{[24]} After depositing MoS\(_2\) on Au/T, the BEs of Ti 2p showed an obvious positive shift (0.35 eV) compared to those of Au/T, which also suggests the strong interfacial interaction and indicates electrons moving out from TiO\(_2\) (into Au NCs). The XPS spectra of O 1s in TNSs, Au/T, and MS/Au/T can all be de-convoluted into one major and two minor peaks (Figure S6, Supporting Information), assigned to the lattice oxygen (O\(_L\)), surface oxygen vacancy (O\(_V\)) and absorbed water molecules (O\(_W\)), respectively.\textsuperscript{[25]} The O\(_V\) peak in Au/T exhibited a negative and positive shift compared to that in TNSs and MS/Au/T, respectively, which is consistent with the analysis of Ti 2p spectrum as described above. According to the XPS peak area, the content of O\(_V\) in the proportion of three oxygen peaks in TNSs, Au/T, and MS/Au/T was 3.5%, 6%, and 10.1% (Table S2, Supporting Information), respectively, demonstrating that more oxygen vacancies were formed in Au/T and especially in MS/Au/T. Two isolated peaks in the spectrum of Au 4f in Au/T, centered at 83.0 (Au 4f\(_{7/2}\)) and 86.6 eV (Au 4f\(_{5/2}\)) (Figure S7, Supporting Information), confirmed the existence of Au\(^0\) in the prepared photocatalysts.\textsuperscript{[26]} Positive shifts were observed in the peaks of Au 4f for MS/Au/T compared to those for Au/T, owing to the transfer of free electrons to recombine with the holes from MoS\(_2\).\textsuperscript{[27]} The above results demonstrate the existence of a strong interfacial interaction and the Z-scheme heterojunction formed between MoS\(_2\), Au, and TiO\(_2\) in MS/Au/T photocatalyst, which are favorable for the charge carrier transport in photocatalysis.

2.2. Nucleation and Growth Mechanisms of MoS\(_2\) NFs on Au/T

Detailed morphological studies showed that the deposition of MoS\(_2\) on Au/T could be divided into three stages: i) MoS\(_2\) primarily nucleated on the Au NCs and grew up into small-size NFs, shown as small bumps or shells in Figure 2a (marked in the
yellow dotted circle); ii) then these MoS$_2$ NPs expanded their
growth to cover the (101) facets of TNSs, as shown in Figure 2b–d
(red dotted line); iii) once (101) facets were fully covered, the ex-
cess MoS$_2$ turned to deposit on the (001) facets of TNSs, as clearly
shown in the BF-HRTEM (green dotted circle in Figure 2e) and
HAADF-STEM (Figure 2f) images. This site-selective nucleation,
facet-selective extension, and random excess growth process are
 schematically illustrated in Figure 2g.

The mechanism of nucleation and growth of MoS$_2$ NPs can
tentatively be explained as follows: under UV–vis/solar light ir-
radiation, the photogenerated holes and electrons within TNSs
were separated under the internal electric field formed between
the (001) and (101) facets,\footnote{29} resulted in the accumulation of elec-
trons on (101) facets. Due to the intimate contact between Au
NCs and TNSs, as well as the lower Fermi level of Au compared
to TiO$_2$,\footnote{28} the electrons preferred to gather on the Au NCs (Fig-
ure 1c). In addition, MoS$_2$ was formed from the photoreduction of
MoS$_4^{2-}$ assisted by photo-electrons.\footnote{28} therefore, it is easy for
MoS$_2$ to nucleate and grow on the Au NCs that own enriched elec-
trons and have a strong affinity to S. However, due to the small
size of Au NCs, the growth of MoS$_2$ was subsequently limited.
MoS$_2$ extended the growth in the other electron-rich areas, that is,
(001) facets of TNSs. Because of this extended growth pattern,
a direct Z-scheme charge transfer (as illustrated in Figure S8a,
Supporting Information), in addition to the aforementioned Z-
scheme, will also form between TiO$_2$ (101) facets and MoS$_2$ due
to their intimate contact. However, due to the strong electron trap-
ping capability of Au NCs, TiO$_2$ → Au → MoS$_2$. Z-scheme pattern
still dominates the charge transfer process. After the surface of
(101) facets were fully covered (only ≈6 nm wide), further growth
of MoS$_2$ could only occur on the (001) facets. In short, the se-
lectivity of the growth is based on the electron density and the
availability of the exposed surface area. Experimentally, it is in-
teresting to note that the low initial concentration of MoS$_2^{2-}$
and shorter PD time are more favorable for selective and controlled
growth.

2.3. Optimization of MoS$_2$ in MS/Au/T System

In order to preserve the junction-coupled Z-scheme structure de-
signed in Figure 1d, the aforementioned excess growth of MoS$_2$
on (001) facets should be minimized because it decreases the ox-
idation surface area and forms a Type II structure (Figure S8b,
Supporting Information), which weakens the redox capability. Al-
though Au NCs greatly amplified the difference between (101)
and (001) facets, selective growth and random growth are still
competitive processes and the preference could be altered by other
growth dynamics and reaction kinetics. A further in-depth
study on the growth rate and time is highly needed to op-
timize the MS/Au/T heterostructures for high photocatalytic per-
formance.

Photocatalytic MB degradation experiments were then per-
formed for the optimization of MS/Au/T photocatalysts under UV
light illumination (360–370 nm) for 90 min. Catalyst sam-
ple were prepared at a fixed initial concentration of MoS$_4^{2-}$
but with different PD times. For clear guidance on the MoS$_2$ amount
and growth rate, the set of samples was named according to the
theoretical mass ratio of MoS$_2$ in the prepared sample, denoted as
(%) MS/Au/T. For example, 10% MS/Au/T represents the set of
samples synthesized at a fixed MoS$_4^{2-}$ concentration that yields
10% MoS$_2$, if all MoS$_4^{2-}$ are converted into MoS$_2$. Figure 3a dis-
played the time profiles of $C_t/C_0$ for 10% MS/Au/T catalysts with
PD = 1, 2, 4, 5, and 6 h, respectively, where $C_t$ is the MB con-
centration at irradiation time $t$, and $C_0$ is the concentration at absorp-
equilibrium of the photocatalyst samples before irradiation.
With the increase of PD time, the degradation rate increased first,
until reaching the maximum value of 70.3% at PD = 5 h, and then
decreased. The corresponding pseudo-first-order constant $k$
(calculated as Supporting Information) is shown in Figure 3b.
This trend could be explained by the aforementioned nucleation
and growth mechanism: For the samples with short PD time,
their photocatalytic performance depended on the amount of de-
posited MoS$_2$, which increased with PD time. As the PD time
approached to ≈5 h, MoS$_2$ fully covered the Au NCs and TiO$_2$
(101) facets to form the proposed Z-scheme that exhibited the
best photocatalytic performance. However, as the PD time fur-
ther increased, MoS$_2$ started to grow on TiO$_2$ (001) facets and
disturbed the Z-scheme charge transfer, leading to a decreased
photocatalytic efficiency.

In addition to the PD time, the initial concentration of MoS$_2^{2-}$
also had a large impact on the growth of MoS$_2$, and thus affected
the photocatalytic efficiency. As shown in Figure 3c, we compared
the rate constant $k$ of MS/Au/T samples with different mass ra-
tios of MoS$_2$, which were synthesized at different initial concen-
trations of MoS$_4^{2-}$ but for the same PD time. For PD = 4, 6, and
8 h, when MoS$_2$ was less than 10%, $k$ increased with the increase
of the MoS$_2$ mass ratio. However, as MoS$_2$ was greater than 10%,$k$ decreased with the increase of MoS$_2$. This observation could be
explained as: when MoS$_2$ was less than 10%, the photocatalytic
efficiency was limited by the amount of MoS$_2$ due to the insuffi-
cient growth of MoS$_2$ on Au NCs and active TiO$_2$ (101) facets.
On the other hand, when MoS$_2$ was larger than 10%, it was much
easier and faster to grow on TiO$_2$ (001) facets at a higher ini-
tial concentration of MoS$_2^{2-}$, which changed the charge transfer
mechanism from Z-scheme to Type II (formed between MoS$_2$
and TiO$_2$ [001] facets, as shown in Figure S8b, Supporting Infor-
mation). In Type II charge transfer mechanism, the photogener-
ated electrons gathered on CB of TiO$_2$ (101) facets and holes on
VB of MoS$_2$, respectively, both characterized by lower redox en-
ergy. Moreover, the excess growth of MoS$_2$ on TiO$_2$ (001) facets
covered the active sites of holes for the catalytic reaction, further
resulting in a low photocatalytic efficiency. However, at PD = 2 h,
the values of $k$ for 5% and 10% were almost the same, indicating
that the growth of MoS$_2$ was not enough, as explained before.
After examining the overall trend of these curves, we have de-
termined that 10% MoS$_2$ is the optimum value in our designed
experiment. This value could be affected by the morphology or
exposed area ratio between (101) and (001) facets. The optimal $k$
values for different mass ratios of MoS$_2$ were summarized and
shown in Figure 3d. Sample 10% MS/Au/T at PD = 5 h exhibited
the best $k$ (0.0144 min$^{-1}$).

2.4. Confirmation of Z-Scheme Charge Transfer in MS/Au/T

To validate the Z-scheme charge transfer mechanism, in situ
irradiated XPS (ISI-XPS) analysis of the prepared MS/Au/T
photocatalyst were conducted. As shown in Figure 4a, without light irradiation (dark), Ti in MS/Au/T exhibited two peaks at 458.82 eV (Ti 2p$_{3/2}$) and 464.52 eV (Ti 2p$_{1/2}$), assigned to the characteristics Ti$^{4+}$ species in TiO$_2$.[30] Under UV light irradiation, a positive shift of 0.1 eV was observed in the BEs of Ti 2p, indicating a decrease in electron density.[31] Based on the electrostatic shielding effect, more outer electrons resulted in a weaker BE,[32] illustrating that the photoinduced electrons were transferred out of TiO$_2$. Other two characteristic peaks for Mo$^{4+}$ species in MoS$_2$ at 229.04 eV (Mo 3d$_{5/2}$) and 232.14 eV (Mo 3d$_{3/2}$) were observed in the absence of light,[21b] which displayed a negative shift of 0.22 eV upon the light illumination, suggesting the increase of electron density on MoS$_2$ surface (Figure 4b). The opposite BE shifts for Ti and Mo elements indicate the pathway for photogenerated electrons transfer across the interfacial heterojunction in MS/Au/T photocatalyst, that is, TiO$_2$ → Au → MoS$_2$, consistent with Z-scheme mechanism.

To probe the charge separation behavior, photocurrent transients were performed for TNSs, Au/T, and MS/Au/T, respectively. As shown in Figure 4c, MS/Au/T displayed the highest photocurrent density, which is eight- and four-fold higher than that of TNSs and Au/T. This reveals the outstanding charge separation capability in our designed system. To further demonstrate the Z-scheme charge transfer, steady-state fluorescence (FL) spectra was measured for TNSs, Au/T, and MS/Au/T, respectively. As shown in Figure 4d, two emission peaks at 397 and 465 nm, respectively associated with band-edge emission and surface-trapped holes related emission of TiO$_2$,[33] are both exhibited for all of the three samples. Compared to TiO$_2$ and Au/T samples, MS/Au/T has an emission quenching effect at 397 nm but enhanced emission at 465 nm, suggesting a fast trapping or transfer process of free carriers and more surface-trapped holes in the hetero-structured catalyst. This is very consistent with the Z-scheme charge flow, in which the holes on TiO$_2$ are preserved but electrons are transferred. Since the photocatalytic reactions are relatively slow processes, the surface-trapped carriers are more important than free carriers. Time-resolved FL decay at the emission wavelength of 465 nm was then measured and fitted with a bi-exponential function[34] (Supporting Information) to reveal more dynamics of surface-trapped holes. As displayed in Figure 4e, MS/Au/T exhibited the slowest decay among the three samples, suggesting the longest lifetime for TiO$_2$ surface holes, which was confirmed by the calculated average lifetime $\tau$ in the inserted table. All of these results demonstrated the Z-scheme charge transfer mechanism.

To further investigate the photocatalytic mechanism of MS/Au/T, the reactive species in MB degradation under UV light were investigated by using specific reactants. Isopropanol (IPA), ammonium oxalate (AO), and benzoquinone (BQ) were
employed as the scavengers for hydroxyl radicals (•OH), holes (h+), and superoxide radicals (•O2−), respectively.\[^{[35]}\] After introducing IPA, AO, and BQ in MB solution, k decreased from 0.0144 min\(^{-1}\) to 0.005 min\(^{-1}\), 0.098 min\(^{-1}\), and 0.0135 min\(^{-1}\), respectively, as shown in Figure 4f. This highlighted the critical role of •OH and a modest role of h+ as well as the negligible effect of •O2− on MB degradation. As one of the major reactive species in photocatalytic reaction, •OH radicals are mainly formed via direct oxidation of OH− or H₂O by holes or via multiple reduction reactions from •O2− by electrons.\[^{[36]}\] Since •O2− had little impact on MB degradation, the oxidation of OH− or H₂O became the only way to produce •OH radicals. In the synthesized MS/Au/T photocatalyst, the photogenerated holes from the VB of MoS₂ (1.2 V vs NHE\[^{[37]}\]) are incapable of oxidizing OH− or H₂O due to their more negative potential than that of OH−/•OH (2.4 V vs NHE\[^{[38]}\]) or H₂O/•OH (2.64 V vs NHE\[^{[35a]}\]), as indicated in Figure 4g. Consequently, •OH radicals must be generated by the photoinduced holes on the VB of TiO₂ (2.87 V vs NHE, as measured and calculated in Figures S9–S11, Supporting Information).

Based on the charge-transfer measurements and reactive species experiments, we proposed a photocatalytic mechanism in Figure 4g. The electrons on VBs of TiO₂ and MoS₂ were both excited and transferred to their respective CBs under UV light irradiation. Due to the intimate heterointerface formed between the Au NCs and TNSs, along with the lower Fermi level of Au than that of TiO₂, the electrons from the CB of TiO₂ flowed into Au and then recombined with the holes from the VB of MoS₂. This unique structure preserved the holes with high oxidation ability in VB of TNSs and electrons with high reduction ability in the CB of MoS₂. As a result, a Z-scheme charge transfer mechanism was established.\[^{[10]}\]

In many site-selectively and randomly grown Z-scheme photocatalytic systems, the photogenerated electrons and holes are separated locally and have many routes to recombine, so a sacrificial agent is usually needed to consume one type of charges
(electrons or holes) to guarantee the effective photocatalytic performance of the other type of charges (holes or electrons). In our system, since the holes were proved as the charge carriers to participate in MB degradation, the addition of an electron sink was expected to further improve the photocatalytic activity. Hence, we chose oxygen ($O_2$) as an electron sink and performed a comparative test for MB degradation with an MS/Au/T sample in the presence of limited (dissolved $O_2$ in solution) and rich $O_2$ (under a continuous flow of $O_2$ during the test) environment. The results are shown in Figure 4h. It was surprisingly observed that MS/Au/T showed almost the same photodegradation rate under the two conditions, indicating that the excess electrons did not recombine with the holes due to the perfect spatial separation of charges originating from the constructively coupled junctions.

The photocatalytic activity of the optimal MS/Au/T catalyst (10% MS/Au/T) was further compared with pristine TNSs, Au/T, and 10% MS/T by MB degradation experiments. As indicated in Figure 4i, 10% MS/Au-T showed the highest degradation rate. This is apparently attributed to the synergistic effect among TiO$_2$, Au, and MoS$_2$, which achieved a high separation efficiency of photoinduced electron-hole pairs in the designed hetero-interfacial photocatalyst.

### 2.5. Roles of Electrons in the System

In the designed Z-scheme heterojunction, the role of holes with high oxidation ability was demonstrated in MB degradation. To investigate the role of electrons in the system, the photocatalytic degradation of 4-nitrophenol (4-NP) was performed, because 4-NP could be oxidized by $\bullet$OH and also be reduced by $\bullet$O$_2^{-}$ into intermediate molecules for further oxidative degradation.$^{[39]}$ The reactive species experiments were conducted with the same scavengers as employed in the MB degradation experiment. The corresponding rate constants were calculated and shown in Figure 5a and Figure S12, Supporting Information. After adding AO, $k$ slightly decreased, indicating the little effect of holes in the experiment. As IPA and BQ were introduced, $k$ dropped significantly, demonstrating that both $\bullet$OH and $\bullet$O$_2^{-}$ were the major reactive species. In general, $\bullet$O$_2^{-}$ could reduce pollutants directly or generate $\bullet$OH via multiple reactions to oxidize the pollutants.

Since $\bullet$OH radicals generated from multiple reactions from $\bullet$O$_2^{-}$ was very limited as proven by the above MB degradation, the impact of the BQ test suggested that $\bullet$O$_2^{-}$ could directly reduce electron-deficient compounds bearing nitro groups (4-NP) into intermediates, which was further oxidized by $\bullet$OH.$^{[39]}$

It is well known that the LSPR of Au could not only broaden the visible light absorption$^{[40]}$ but generate “hot electrons” participating in the chemical reactions$^{[41]}$ to improve the photocatalytic efficiency. To demonstrate this effect in our system, a comparison test for 4-NP degradation with 10% MS/Au/T photocatalyst was performed under UV and simulated solar light. As indicated in Figure 5b, within 7 h of irradiation, the degradation rate under simulated solar light exhibited a higher degradation rate (10.6% higher) than that under UV light. The enhanced photocatalytic performance was attributed to “hot electrons” originating from...
the LSPR of Au. As illustrated in Figure 5d, at a certain wavelength of irradiation, the electrons on the surface of Au NCs were excited and collectively oscillated with the incident electromagnetic field,\[^{[42]}\] generating “hot electrons” in the surface plasma (SP) state. These “hot electrons” were then transferred to the CBs of the neighboring TiO\(_2\) and MoS\(_2\), respectively. The extra electrons on the CB of MoS\(_2\) reacted with the dissolved O\(_2\) to generate more \(\cdot\)O\(_2\)\(^{-}\), promoting the overall degradation rate of 4-NP.

The described mechanism was proved by comparing the ISI-XPS patterns of Mo element under UV and solar simulated light, respectively. As shown in Figure 5c, the BE of Mo\(^{4+}\) 3d decreased by 0.11 eV under simulated solar light compared to the value measured under UV light. This negative shift demonstrated the increase in the electron density, indicating the injection of “hot electrons” from Au NCs to MoS\(_2\). Hence, Au NCs played dual functions, not only acting as charge mediators in the Z-scheme function to boost the interfacial charge recombination but also generating excess “hot electrons” to improve the photocatalytic performance.

In order to demonstrate the superiority of the designed system in the photodegradation of organic pollutants, we compared the photocatalytic degradation of 4-NP in the presence of TNSs, Au/T, and 10% MS/Au/T photocatalysts under simulated solar light. As indicated in Figure 5e, 10% MS/Au/T exhibited the best photocatalytic activity, followed by Au/T and TNSs. The excellent photocatalytic activity of MS/Au/T was mainly attributed to two factors: i) the coupled junctions in MS/Au/T, which provided a highly separation efficiency of photoinduced electron-hole pairs in the photocatalyst; and ii) the “hot electrons” injection induced by the LSPR effect of Au, which provided extra electrons to participate in the reaction. It was interesting to observe that Au/T only showed a slight improvement in the degradation rate than TNSs, which was opposite to the situation of MB degradation (no LSPR under UV). The possible reason could be as follows: under simulated solar light, there exist electron-flow pathways in Au/T. One is from TiO\(_2\) to Au NCS due to the potential difference between TiO\(_2\) and Au. The other one is from Au NCS to TiO\(_2\) due to the “hot electrons” injection. These two routes counteract each other, compromising the charge separation efficiency and leading to only a slight improvement of photocatalytic performance of Au/T than TNSs. This conjecture is evidenced by the nearly unchanged BEs of Ti 2p in ISI-XPS measurements under UV and solar light illumination (Figure S13, Supporting Information). In contrast, MS/Au/T heterostructures could take all the synergistic effects from spatial charge separation and LSPR by Z-scheme junctions, showing significant performance enhancement in both MB degradation (oxidation only) and 4-NP degradation (oxidation and reduction).

To further demonstrate the superiority of our photocatalytic system, we summarized the recent research work of 2D/2D Z-scheme photocatalysts in the photodegradation of dyes and phenols (Table S3, Supporting Information). By comparing the normalized rate constants, our system exhibited notable performance in the photodegradation of dyes (especially for MB) and comparable performance in the photodegradation of phenols compared to the other 2D/2D Z-scheme photocatalysts, which indicates the great potential of our system in the photodegradation of organic pollutants.

3. Conclusion

We have designed an efficient MoS\(_2\)/Au/TiO\(_2\) Z-scheme photocatalytic system by a novel Au-induced selective growth of MoS\(_2\) on the edge sites of 2D TNSs. The ternary structure was fabricated by the following steps: i) hydrothermal preparation of TNSs with highly-exposed (001) facets; ii) selective deposition of Au NCs on the edge-sites of TNSs; iii) selective PD of MoS\(_2\), NFs on Au NCS and (101) facets of TNSs. The edge-selective growth of MoS\(_2\) was realized and promoted by Au NCs, which could trap electrons from TNSs and generated excess electrons via the LSPR effect for efficient photoreduction, and offered strong affinity to S for effective MoS\(_2\) nucleation. The growth and morphological evolution of MoS\(_2\) could be categorized into three stages: site-selective nucleation (on Au NCS), facet-selective extension (along TiO\(_2\) (101) facets), and random growth (over TiO\(_2\) (001) facets). It was found that a high precursor concentration and a long PD time promoted random growth. The optimal conditions were found to be a 10% MoS\(_2\) mass ratio and a 5 h PD time, which could be associated with the morphology of TiO\(_2\).

ISI-XPS measurements validated that the photogenerated electrons in TNSs were transferred to Au NCS and recombined with the holes generated in MoS\(_2\), forming a Z-scheme charge transfer route. Photocurrent transients and PL measurements further demonstrated the proposed Z-scheme mechanism. Since this Z-scheme was built on the TNS (101) facets, a synergistic coupling of the facet junction and the heterojunction was achieved to separate the photogenerated charges in relays. This structure not only suppressed the charge recombination in the system but also maintained the highly exposed surface to the utmost extent. Consequently, the highly exposed surfaces of TNSs and MoS\(_2\) NFs offered tremendous active sites for redox reactions. The spatial separation of TNSs and MoS\(_2\) NFs endowed the bifunctional system to participate in different photocatalytic reactions simultaneously. Au NCs in the proposed system served two purposes: constructing the heterojunction and accelerating the redox reactions by supplying “hot electrons”. As a result, the system demonstrated its effectiveness and efficiency in the photodegradation of organic pollutants without involving any sacrificial agents. This work sheds new light on the possibility of designing and selectively fabricating other 2D/2D Z-scheme photocatalysts using this novel photocatalyst prototype in the future.

4. Experimental Section

Materials: Analytical grade tetrabutyl titanate (C\(_{16}\)H\(_{36}\)O\(_4\)Ti, >97%), hydrofluoric acid (HF, 48%), ammonium tetrathiomolybdate (H\(_4\)N\(_2\)MoS\(_4\), 99.97%), and 4-nitrophenol (C\(_{7}\)H\(_4\)NO\(_3\), >99.9%) were procured from Sigma Aldrich. Gold (III) chloride trihydrate (III) (HAuCl\(_4\)+H\(_2\)O, 99.99%), urea (H\(_2\)NCONH\(_2\), 99%), and methylene blue (C\(_{16}\)H\(_{18}\)ClN\(_3\)S) were purchased from Merck. All the reagents were used as received without further purification. The water used throughout the experiments was purified by a Milli-Q system.

Synthesis of TiO\(_2\) Nanosheets with Highly Exposed (001) Facets: Anatase TNSNs were synthesized by hydrothermal method proposed by Han et al.,\[^{[13]}\] in the typical synthesis, 10 mL of tetrabutyl titanate and 1.2 mL of HF solution were mixed in a 25-mL Teflon stainless-steel autoclave under ambient conditions, followed by hydrothermal treatment of the solution in a heating oven at 180 °C for 24 h. After cooling down to room temperature, the white precipitate was collected by centrifugation at 6000 rpm, washed with...
Randomly-deposited Au/TiO2 with 4 wt% of Au loading was obtained. After washing with ethanol and DI water followed by centrifugation several times, the collected powder was then calcinated from room temperature to 80 °C in an oil bath under robust stirring for 3 h. After washing with ethanol and DI water followed by centrifugation several times, the randomly-deposited Au/TiO2 with 4 wt% of Au loading was obtained. After drying the randomly-deposited Au/TiO2 in a vacuum oven at 90 °C for 3 h, the collected powder was then calculated from room temperature to 400 °C in an Ar atmosphere under a flow rate of 40 mL min⁻¹ with a heating rate of 3 °C min⁻¹ for 3 h to obtained the selectively edge-deposited Au/TiO2.

The photocatalysts were characterized by an XRD (Empyrean from PANalytical) using CuKα as an X-ray radiation source (1.5418 Å) and a confocal Raman microscopy spectrometer (WITec alpha300 R) under 532 nm laser light. The detailed morphologies of the samples were studied with a field emission scanning electron microscope (JEOL JSM-7610F FEG-SEM) and a TEM (FEI Tecnai TEM 200 kV). The presence and distribution of elements were examined by energy-dispersive X-ray spectroscopy (EDS) (results shown in Figures S16 and S17, Supporting Information). HRTEM (FEI Tecnai C2 F20 S-Twin working at 300 kV) was used to investigate the crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to chemical states of the synthesized samples were characterized via an XPS (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

Characterizations of the Photocatalysts: The crystalline structures of the photocatalysts were characterized by an XRD (Empyrean from PANalytical), using CuKα as an X-ray radiation source (1.5418 Å) and a confocal Raman microscopy spectrometer (WITec alpha300 R) under 532 nm laser light. The detailed morphologies of the samples were studied with a field emission scanning electron microscope (JEOL JSM-7610F FEG-SEM) and a TEM (FEI Tecnai TEM 200 kV). The presence and distribution of elements were examined by energy-dispersive X-ray spectroscopy (EDS) (results shown in Figures S16 and S17, Supporting Information). HRTEM (FEI Tecnai C2 F20 S-Twin working at 300 kV) was used to investigate the crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

The crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

Characterizations of the Photocatalysts: The crystalline structures of the photocatalysts were characterized by an XRD (Empyrean from PANalytical), using CuKα as an X-ray radiation source (1.5418 Å) and a confocal Raman microscopy spectrometer (WITec alpha300 R) under 532 nm laser light. The detailed morphologies of the samples were studied with a field emission scanning electron microscope (JEOL JSM-7610F FEG-SEM) and a TEM (FEI Tecnai TEM 200 kV). The presence and distribution of elements were examined by energy-dispersive X-ray spectroscopy (EDS) (results shown in Figures S16 and S17, Supporting Information). HRTEM (FEI Tecnai C2 F20 S-Twin working at 300 kV) was used to investigate the crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

The crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

Characterizations of the Photocatalysts: The crystalline structures of the photocatalysts were characterized by an XRD (Empyrean from PANalytical), using CuKα as an X-ray radiation source (1.5418 Å) and a confocal Raman microscopy spectrometer (WITec alpha300 R) under 532 nm laser light. The detailed morphologies of the samples were studied with a field emission scanning electron microscope (JEOL JSM-7610F FEG-SEM) and a TEM (FEI Tecnai TEM 200 kV). The presence and distribution of elements were examined by energy-dispersive X-ray spectroscopy (EDS) (results shown in Figures S16 and S17, Supporting Information). HRTEM (FEI Tecnai C2 F20 S-Twin working at 300 kV) was used to investigate the crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

The crystallinity, phase purity, and interfacial lattice. Optical absorbance and reflectance of the prepared samples were measured by UV–vis spectrophotometer (PerkinElmer LAMBDA 1050) to obtain the optical bandgap (results shown in Figures S10 and S11, Supporting Information). The surface chemical states of the synthesized samples were characterized via an XPS equipped with an Al Kα radiation hemispherical electron energy analyzer (Thermo Fisher ESCALAB 250Xi). The BE of C 1s (284.6 eV) was used to characterize the chemical states of the synthesized samples.

Supporting Information: Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This work was supported financially by the Khalifa University Competitive Internal Research Awards CIRA-2018-03 (8474000077) and CIRA-2020-024 (8474000278).

Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 2D material, facet junction, heterojunction, photocatalyst, photodegradation, selective growth, Z-scheme
