Spatial Heterojunction in Nanostructured TiO$_2$ and Its Cascade Effect for Efficient Photocatalysis

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ABSTRACT: A highly efficient photoenergy conversion is strongly dependent on the cumulative cascade efficiency of the photogenerated carriers. Spatial heterojunctions are critical to directed charge transfer and, thus, attractive but still a challenge. Here, a spatially ternary titanium-defected TiO$_2$@carbon quantum dots@reduced graphene oxide (denoted as V$_{Ti}$@CQDs@rGO) in one system is shown to demonstrate a cascade effect of charges and significant performances regarding the photocurrent, the apparent quantum yield, and photocatalysis such as H$_2$ production from water splitting and CO$_2$ reduction. A key aspect in the construction is the technologically irrational junction of Ti-vacancies and nanocarbons for the spatially inside-out heterojunction. The new “spatial heterojunctions” concept, characteristics, mechanism, and extension are proposed at an atomic-/nanoscale to clarify the generation of rational heterojunctions as well as the cascade electron transfer.

KEYWORDS: Ti-vacancy, spatial heterojunction, cascade effect, seawater splitting, carbon dioxide reduction

Heterojunctions dictate the performance of semiconductors as photocatalysts and solar fuel technologies. A high efficiency of the photoenergy conversion is strongly dependent on the cumulative efficiency of the cascade effect of photogenerated carriers during separation, transfer, collection, and utilization. Generally, the electron transfer at the single nanocrystal or interface of nanocrystals is random. The electron dissipation and/or recombination often occurs before the electrons reach the surface of photocatalysts for the redox reaction. Photosynthesis is a cascade photosystem of inside-out light harvesting and inside-out directed transferring of charge, and it therefore inspires the search for the design of heterojunctions of semiconductors for anticipated performance in photocatalysis. Note that the junction between individual bioentities is a key to directed transfer of energy in natural system. Such oriented transfer could be the most efficient way to utilize the solar energy in the cascade photosystem. Currently, there are very rare synthetic routes able to control either the atomic/nanoscale spatial directed junctions distributed from inner lattice to outer layer surface (denoted as spatially inside-out heterojunction) or the cascade transfer between individual compositions within multiple heterojunctions of semiconductors.

Titanium dioxide (TiO$_2$), one of the widely used models of semiconductor, and nanocarbon is also one of the most efficient dopants to promote charge separation/transfer/utilization and significantly improve the photocatalytic performance of semiconductors. Metal vacancies at the surface/interface are acceptor-type centers for separation of inner charges, and thus a heterojunction of nanocarbons and titanium vacancies (Ti-vacancies) is theoretically a cascade nanostructure: separation by Ti-vacancies and transportation of the photogenerated charges from the inside by the nanocarbons. However, finding Ti-vacancies in the presence of carbon is theoretically as well as technologically irrational, because carbon is considered as a reductant capturing oxygen atoms from the TiO$_2$, resulting in oxygen irreversible.

Carbon quantum dots (CQDs), a new generation of nanocarbon, not only possess nice light absorptivity and carrier conductivity but also show bulky-molecular features, which can easily be doped into the TiO$_2$ nanocrystals. A heterojunction of Ti-vacancies and CQDs is theoretically possible, because the migrating oxygen from the rich oxygen-containing groups of CQDs can be used to form spatially inside-out cascade electron transfer.
an O-rich interface for producing Ti-vacancies. Ti-vacancies create a cascade bridge of photogenerated charges between the inner part and the surface/interface of the TiO2/carbon, which is the so-called “cascade effect”. Cascade systems are a sequential and directed energy transformation-utilization system in which the starting charges undergo a separation by transfer to the next collection, and so on, until a maximal utilization is reached. The cascades thus offer great advantages with respect to economizing on charges and time and hinder the possibility of undesired interface energy losses. Such highly desirable “directed charge-transfer” cascades therefore necessitate a spatial separation of the photogenerated charges. For the photoenergy conversion efficiency ($\eta_{\text{cs}}$) of our cascade photoconversion system, charge separation efficiency ($\eta_{\text{cs}}$) depends on the charge separation from the inner lattice to the Ti-vacancies, charge separation efficiency ($\eta_{\text{cs}}$) depends on the charge transfer from the Ti-vacancies to the CQDs, and charge utilization efficiency ($\eta_{\text{cu}}$) depends on the charge collection and utilization from the CQDs and TiO2 nanocrystals to the rGO sheets.

Core–Shell nanostructures are perfectly in accordance with, for example, photosynthesis in cells with outside-in energy mass absorbing and inside-out cascade energy transfer/utilization.33–35 In this work, a one-pot hydrothermal method was used to obtain a spatial distribution of titanium-defected TiO2@CQDs@reduced graphene oxide (denoted as $V_{\text{T}i}$) with a core–shell structure. To the best of our knowledge, the induction of Ti-vacancies by CQDs has rarely been reported, and the studies on Ti-vacancy are emerging. This ternary heterojunction provides an ideal model of producing spatially inside-out heterojunctions, resulting in a cascade effect for significant photocatalytic and photoelectrochemical performances. Such a mechanism has been investigated and preliminarily expanded to a $V_{\text{T}i}$@CQDs@rGO@Pt quaternary composite.

The spatial distribution of the inside CQDs and TiO2 nanoparticles with respect to the outer rGO layer is verified by scanning electron microscope (SEM), transmission electron microscope (TEM), high-resolution transmission electron microscope (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Note S1). The $V_{\text{T}i}$@CQDs@rGO are disperse mesostructured beads (∼500 nm in diameter) composed of TiO2 nanoparticles of ∼12 nm, CQDs of ∼5–8 nm, and outer layers of thin rGO sheets of 2–5 nm (Figure 1a & Figure S1a,b). The C distribution is continuous and clearly divided into two parts with increased C content. In particular, the green dots in Ti/C EDS maps clearly display around most of the surface of the TiO2 bead, indicating an intimate coating of rGO (Figure 1b,c; Figures S2 & S3). To distinguish the carbon from the CQDs and the rGO, covalent-N doped CQDs are used; the N-distribution is relatively uniform (Figure 1d) due to the spatial inside-out distribution of CQDs@rGO (left) and rGO (right). The $V_{\text{T}i}$@CQDs@rGO shows a slight decrease of the specific surface area and pore size in comparison with mesoporous TiO2 beads (Figure S4 and Table S1).

The clear lattice fringes of TiO2 and CQDs agree with the anatase TiO2 (101) planes and (110) lattice fringes of graphite, respectively (Figure 1e and Figures S5–S8).36–38 The uniform distribution of CQDs in overall mesostructured TiO2 nanocrystals and outer coating of rGO could be clearly seen by the combination analysis of all TEM images, STEM images, and EDS elemental maps (Figure S1c–f & Figure S5a). In contrast, without preassembly of CQDs and TiO2, the CQDs are only absorbed and agglomerated on the surface of the TiO2 bead, forming the surface heterojunction around the TiO2 beads (Figure S5b). Furthermore, the TiO2 nanocrystals are bonded to the CQDs and rGO layers by a nanofusion interface; this interface has a thickness of less than 1 nm from the HRTEM images as well as from the inverse fast Fourier transformation (FFT) images (Figure 1f,g). This crystalline/nanofusion/crystalline phase shows a disordered atomic arrangement and lattice distortions, making the ballistic transport of quantized electrical conductance.39–41 The heterojunctions of TiO2 nanocrystals and CQDs at an atom level, forming spatial junctions, results in minimum degradation of the carrier mobility and minimum interface-losing energy, therefore causing a high efficiency to cascade charge carriers.42,43

To obtain information about the Ti-vacancies, titanol (Ti–OH) sites can act as probe species to detect the Ti-vacancies by NMR. Ti–OH groups in Ti–OH nests are stabilized by hydrogen bonds, and the formation of Ti–OH nests can effectively stabilize clusters with negative oxygen atoms. The hydrogen-bond network can exert a large influence on the 1H NMR chemical shift of Ti–OH and give rise to a low-field shift of the resonance lines.44 To determine and understand the defects in TiO2, we performed highly sophisticated pulse techniques such as one-dimensional and two-dimensional 1H triple-quantum–single-quantum (TQ-SQ) magic angle spinning (MAS) NMR methods, which are not affected by the water signal. Note that a cluster of three protons is mandatory for the occurrence of a TQ coherence. Pairs of off-diagonal peaks at ($\delta_h, \delta_a + \delta_b + \delta_c$), ($\delta_b, \delta_a + \delta_b + \delta_c$), and ($\delta_c, \delta_a + \delta_b + \delta_c$) correspond to correlations between three protons with different chemical shifts. Generally, the signal of Ti–OH groups assigned to broken Ti–O–Ti bonds in the bulk phase.
appears in the range from 6.5 to 8.9 ppm; the location of Ti—OH groups at the surface appears in the range from 1.2 to 3.5 ppm.\textsuperscript{15} Compared to TiO\textsubscript{2}, direct surface/interface binary and/or ternary surface junctions (such as TiO\textsubscript{2}—rGO, TiO\textsubscript{2}—CQDs, TiO\textsubscript{2}—CQDs-rGO, the so-called “random surface heterojunctions”) and spatial junctions (\(V_{\text{Ti}}\@\text{CQDs}\)), Ti—OH nests with pairs of off-diagonal peaks at (5.3,5.3 + 5.3 + 5.3) and (5.5,5.5 + 5.5 + 5.5) appear only in \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) and \(V_{\text{Ti}}\@\text{CQDs}\) (Figure 2a and Figure S9), which is attributed to Ti—OH nests referring to the Ti-vacancies, and almost no other Ti—OH species are present.\textsuperscript{15} These indicate that the CQDs introduced into the TiO\textsubscript{2} lattice are the direct reason to produce Ti-vacancies at the interface between the CQDs and TiO\textsubscript{2}, not the individual present at the surface of TiO\textsubscript{2}. This is a definite first-step success of a spatial cascade to charge separation from the inner lattice to the Ti-vacancies and to the CQDs.

Electron paramagnetic resonance (EPR) spectra were recorded (Figure 2b) for the charge transfer from the Ti-vacancies to the CQDs. Obviously, a strong signal centered at \(g = 1.999\) can be observed for \(V_{\text{Ti}}\@\text{CQDs}\) and \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\), which is attributed to the Ti-vacancies.\textsuperscript{20,48} At the same time, the EPR signal at \(g = 2.002\) for CQD has disappeared.\textsuperscript{46,47} These results suggest that the Ti-vacancies are caused by the CQDs and directly bind to the CQDs, meaning that the charges of the Ti-vacancies can directly be transported to the CQDs as a second step of the spatial cascade.

Chemical connection such as Ti—C, Ti—O—C among the CQDs, TiO\textsubscript{2} nanocrystals, and rGO sheets are analyzed by X-ray photoelectron spectroscopy (XPS) (Figure 2c & Figure S10), providing more evidence for the cascade pathway of the charge transfer (Note S2). Note that the positive shifts of the Ti 2p core level suggest an increase of the electron–electron repulsion around the Ti atoms by strong interactions including both of the Ti—O—C and Ti—C bonds. In corresponding C 1s spectra, the new peaks at 283.9 eV in both \(V_{\text{Ti}}\@\text{CQDs}\) and \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) are assigned to Ti—C bond, and the peaks at 286.3 eV may be composed of Ti—O—C (Figure S10c).\textsuperscript{48—50} Moreover, clear pyrrolic N and pyridinic N and a very weak signal of Ti—N suggests almost no N-doping into TiO\textsubscript{2} possibly due to the relatively strong conjugate and/or covalent C—N bonding of CQDs (Figure S10g).\textsuperscript{51,52} Meanwhile, the Ti-vacancies in \(V_{\text{Ti}}\@\text{CQDs}\) and \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) can be deduced from the relatively high O/Ti ratio on the surface of the samples (Table S2). Two electron-transfer pathways are formed, namely, surface heterojunction and inside-out directed directional electron transfer (Figure S11).

Under UV—vis light (\(\lambda = 320–780\) nm) irradiation, the \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) exhibits the highest photocurrent intensity, which is twofold, fourfold, and eightfold higher compared to \(V_{\text{Ti}}\@\text{CQDs},\) TiO\textsubscript{2}—CQDs—rGO, and TiO\textsubscript{2}, respectively (Figure 2d). This means that the spatial inner-lattice-CQDs—rGO charge mobilities in \(V_{\text{Ti}}\@\text{CQDs}\) and \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) are better than only the surface/interface charge mobilities among TiO\textsubscript{2}, CQDs, and rGO. The calculated charge density difference shows that the neighboring O and Ti atoms of the Ti-vacancy lose electrons and that the electrons migrate to the Ti-vacancy compared to the normal TiO\textsubscript{2} model (Figure 2e,f),\textsuperscript{53} which theoretically suggests that Ti-vacancies act as charge transfer bridge in addition to as traps.

The charge transfer process is evaluated by electrochemical impedance spectroscopy (EIS), photoluminescence spectra (PL), and time-resolved photoluminescence (TRPL) measurements. The semicircle in the EIS Nyquist plots denotes resistance (\(R_{\text{ct}}\)) of the charge transfer at the electrode/electrolyte interfaces. The obvious decrease of \(R_{\text{ct}}\) after CQDs and rGO are loaded on TiO\textsubscript{2} shows a better interfacial charge transfer than pure TiO\textsubscript{2} (Figure S12a), indicating that nanocarbons are available to the charge transfer. Very interestingly, after irradiation with UV—vis light, the \(R_{\text{ct}}\) of \(V_{\text{Ti}}\@\text{CQDs}\) has significantly decreased, suggesting that photo-generated charges can enhance the interfacial transfer, possibly due to the inner-out potential difference. \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) shows the smallest semicircle among all samples, especially a clear decrease compared to \(V_{\text{Ti}}\@\text{CQDs}\), meaning a higher efficiency of the spatially inside-out electron transfer and the charge collection on the surface rGO.\textsuperscript{54,55} The electron transfer from different states of \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) is shown in Figure S12b. Compared to TiO\textsubscript{2} and TiO\textsubscript{2}—CQDs—rGO, the partial quenching of PL intensity of \(V_{\text{Ti}}\@\text{CQDs}\) can be attributed to the separation effect from the lattice to the Ti-vacancies and to the CQDs. \(V_{\text{Ti}}\@\text{CQDs}\@\text{rGO}\) shows the lowest PL signal; this is indicative of the collection effect from the inner to the outer
layer. More direct evidence is performed by the TRPL measurements (Figure S12c); TiO₂ shows the shortest decay time (1.55 ns) due to the fast charge recombination, after composite with CQDs and rGO. Photogenerated carriers in TiO₂−CQDs−rGO will separate through surface charge transfer, leading to a longer lifetime of the PL signal (1.74 ns). Both V_Ti@CQDs and V_Ti@CQDs@rGO exhibit a slower PL decay (2.45 ns and 2.81 ns, respectively), which again suggests that our spatially inside-out electron transfer and the charge collection effect on the surface play a key role in promoting the hole transfer. Similar evidence is also shown in the Fermi level measurements by UV-vis DRS, XPS valence band spectra, and Mott–Schottky plots (Figure S14). The negative shift of the conduction band minimum and the Fermi level (E_f = −0.15 eV) suggest the highest efficiency of spatial heterojunction and better charge separation in V_Ti@CQDs@rGO in comparison with TiO₂−CQDs−rGO and TiO₂ (Figure 2g).

The photocatalytic and photoelectrochemical performances on our samples are studied. We find that inadequate or excessive CQDs causes a lowered H₂ yield efficiency and optimized the initial content of 4 wt% of the CQDs in V_Ti@CQDs@rGO (Figure S15, CQDs and rGO weight ratio in final sample: 1.0 wt% from thermogravimetric analysis (TGA) in Figure S13b). Note that the absorbance and photoactivity of each component in heterojunction materials is a critical factor to the photocatalytic performance and thus may hinder the accurate evaluation of photocatalysts.36,57 To better understand the comparison of photocatalytic activity, we synthesized the core−shell structured reference sample without Ti-vacancy (random surface heterojunction, denoted as TiO₂−CQDs−rGO) by direct coating. Note that all the samples showed nearly no photocatalytic activity at visible light region and that all the TiO₂ and the composites of TiO₂−CQDs, and rGO show photocatalytic activity only at ultraviolet region (Figure S13a and Table S3). The experiment shows that the integrated V_Ti@CQDs@rGO exhibits a superior H₂ production rate of 31.9 μmol h⁻¹, more than V_Ti@CQDs (21.8 μmol h⁻¹), which is over 12.3-fold, 5.5-fold, and 3.2-fold the value of TiO₂ (2.6 μmol h⁻¹), TiO₂−CQDs (5.8 μmol h⁻¹), and TiO₂−CQDs−rGO (9.8 μmol h⁻¹), respectively. Even V_Ti@CQDs@rGO (1 wt% of CQDs) show higher photocatalytic activity than TiO₂−CQDs−rGO. The apparent quantum yields (AQY) of TiO₂−CQDs−rGO will separate through surface charge collection (2.45 ns and 2.81 ns, respectively), which again promotes the hole transfer. Similar evidence is also shown in Mott–Schottky measurements by UV−vis DRS, XPS valence band spectra, and Mott–Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14). The Schottky plots (Figure S14).

Because of the excellent corrosion resistance of seawater of the TiO₂ and nanocarbons, our spatial heterojunction is studied under seawater condition for potential marine applications, which demonstrates 4.4-fold higher than random surface heterojunction toward photocatalytic H₂ production from seawater splitting (Figure 3c) and 1.7-fold (from −370 to −610 mV) of corrosion potential than random surface heterojunction toward photo-electrochemical anticrosion of seawater (Figure 3d and Table S4). These remarkable performances (Tables S5 & S6) in seawater are mainly attributed to the nature of stability of our sample and readily accessible electron in V_Ti@CQDs@rGO, which reduces the distraction from the various ionic components and impurities in seawater. Notably, the directed charge transfer is key to the great improvement of the performances, because the only difference is the spatial junction and the random junctions of the same compositions. These results thus indicate that the spatial heterojunction of V_Ti@CQDs@rGO facilitates the spatial inside-out photogenerated electron transfer cascade and improves the electronic conductivity for better charge transfer kinetics, and it thus gives the significant rise to photocatalytic and photoelectrochemical performances.

On the basis of the above discussion, a formation mechanism of the ternary V_Ti@CQDs@rGO can be proposed (Figure 4). The CQDs act as bulky molecules with a high oxygen content (Figure S17) and are doped into the primary titanium oligomers under the assist of hexadecylamine (Figure 4Aa,Ab); then a core−shell structure TiO₂−CQDs@rGO can
Figure 4. Proposed mechanism. (A) Schematic illustration of the formation mechanism of the ternary V_{Ti}@CQDs@rGO composite, (a–c) in situ synthesis of TiO_{2}/CQDs precursor, (d–f) formation of the V_{Ti}@CQDs@rGO by hydrothermal and thermal treatment, (g, h) the simulated interfacial atom migration and the formation of Ti-vacancies during calcination; O_{ad} refers to migrating oxygen. (B) Schematic description of the spatial electron-transfer cascade pathway and the proposed mechanism.

be formed during a further hydrolysis-condensation-assembly (Figure 4Ac,Ad). After the following hydrothermal and thermal treatment, the TiO_{2}@CQDs@rGO allows a controlled interface and nanocrystal growth (Figure 4Ac,Af). Meanwhile, O atoms (in oxygen-containing groups) from the CQDs often tend to migrate to interfacial TiO_{2} nanocrystals (Figure 4Ag).58,59 The O-rich interface produces distortions and concomitant Ti vacancies (Figure 4Ah). The formation of titanium vacancies can be described as

$$2O_M^+ \rightarrow V_{Ti}^{m^+} + 2O + 4h^*$$  \hspace{1cm} (1)

where $O_M^+$ refers to migrating oxygen, $V_{Ti}^{m^+}$ stands for the Ti-vacancy, and $h^*$ represents the hole. Finally, a spatial inside-out structure forms at an atomic/nanoscale, and multiple heterojunctions are formed from the inner lattice to the Ti-vacancies to the CQDs to the rGO. The spatial heterojunction (center of Figure 4B) shows the cascade effect of generated charge, wherein the electron transfers from the inner lattice to the Ti-vacancies ($\eta_{Ti}$), from the Ti-vacancies to the CQDs ($\eta_{CQDs}$), and then passes along the uniform distribution of CQDs as a bridge that carries the conductor to the rGO sheets ($\eta_{rGO}$). The outer part of Figure 4B promotes the idea that the CQDs may act as a bridge in the spatial cascade to cover the interface energy transfer from the inner particles to the outer particles, and rGO sheets act as a net to collect the inside-out photoenergy. To further evaluate the spatial junctions mechanism for our proposed cascade effect, the quaternary $V_{Ti}@CQDs@rGO@Pt$ heterojunction is synthesized and achieves the significant performances of the H_{2} yield (67.8 mmol h^{-1} g^{-1}) and AQY (33.9%).

In summary, our spatial $V_{Ti}@CQDs@rGO$ heterostructure outperforms random surface heterojunction (such as TiO_{2}/CQDs-rGO) in terms of H_{2} production from water and seawater splitting, CO_{2} reduction reaction, and photoelectrochemical anticorrosion. Crucially is that the ideal heterojunction is able to produce a cascade effect of charges in one system. The ability to control the ternary heterostructure within a spatially inside-out distribution leads to unique and flexible properties of the resulting materials. This is critical for the development of, for example, an electron separation-transfer-collection-utilization cascade, in which the energy loss of the interfacial migration is controlled by a $V_{Ti}@CQDs@rGO$ spatial heterojunction. Our findings provide a rational design of high-performance semiconductors featuring low cost, high efficiency, and high stability.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b05121.

Methods, characterization, DFT calculations, photocatalytic and photoelectrochemical experiments, SEM and TEM images, N_{2} adsorption, XRD, ¹H TQ-SQ MAS NMR spectra, XPS, EIS, PL, TRPL, UV–vis DRS, XPS valence band spectra, Mott–Schottky plots, TGA, comparison of photocatalytic activity, OCP, FTIR measurements, and detailed notes (PDF)

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Author Contributions

Y.L. carried out all the experiments. X.Y.Y. conceived the project, provided the idea, and designed and guided the experiments. B.L.S. is chief leader of scientific and technological platform. L.H. and X.C. helped with the measurements. B.L.S., L.Y.W., and J.W.L. helped with the NMR measurements and corresponding analysis. X.L.L., L.Y.W., and J.W.L. helped with the CO2 reduction measurement. Y.X.Z. performed the DFT calculations and analysis. Z.Y.H. and G.T. performed the TEM and EDS characterizations. S.M.W., Y.Z.L., G.G.C., and W.H.L. helped analyze the results and gave helpful discussions. Y.L. and X.Y.Y. wrote and revised the paper. C.J. and G.V.T. revised the paper. All the authors discussed results and analyzed the data, and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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