***In-situ* synthesis of C-doped TiO₂@g-C₃N₄ core-shell hollow nanospheres with enhanced visible-light photocatalytic activity for H₂ evolution**

Yajun Zou^a, Jian-Wen Shi^{a,*}, Dandan Ma^a, Zhaoyang Fan^a, Lu Lu^b, Chunming Niu^a

^a*Center of Nanomaterials for Renewable Energy, State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China.*

^b*School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

Corresponding author:

Jian-Wen Shi

Center of Nanomaterials for Renewable Energy

State Key Laboratory of Electrical Insulation and Power Equipment

School of Electrical Engineering

Xi'an Jiaotong University, Xi'an 710049, China.

E-mail: jianwen.shi@mail.xjtu.edu.cn

Abstract

Developing photocatalysts with high charge separation and transfer efficiency remains a key challenge for photocatalytic water-splitting reaction. In this work, a facial approach was explored to successfully realize the *in-situ* growth of g-C₃N₄ on the surface of C-doped TiO₂ hollow nanospheres (C-TiO₂). The as-obtained heterogeneous photocatalyst, C-TiO₂@g-C₃N₄ (TCN), presented core-shell hollow nanosphere structure. Systematic studies disclose that the TCN photocatalysts exhibit remarkably enhanced visible-light photocatalytic activity for water splitting to produce H₂ compared with the pristine C-TiO₂ and g-C₃N₄. The TCN-2 photocatalyst (the weight ratio of initial urea and C-TiO₂ is 2:1) presents the highest H₂ generation rate of 35.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$, which is 22.7 and 10.5 times higher than that of C-TiO₂ and g-C₃N₄, respectively. The enhanced photocatalytic performance can be attributed to the formation of the heterojunction between the two semiconductors, which effectively promotes the separation of photo-generated carriers. Meanwhile, the intimate contact between the C-TiO₂ and g-C₃N₄ resulted from the *in-situ* growth greatly improves the separation and transfer efficiency of photo-generated carries. Besides, the enhancement in the utilization efficiency of light energy due to the unique hollow structure also exhibits a positive contribution.

Keywords: Photocatalysis; g-C₃N₄; visible-light; water splitting; H₂ evolution

1. Introduction

Solar energy is one of the most abundant, clean and renewable natural energy resources on the earth. The conversion from solar energy to valuable chemical resources has provided an ideal solution to mitigate global energy and environmental issues [1]. Hydrogen has been acknowledged as an alternative form of storable and clean energy for the future. Since Fujishima and Honda [2] first reported the photocatalytic splitting of water on TiO_2 electrodes in 1972, a variety of semiconductors based on metal oxide [3-5], metal (oxy) nitrides [6-8], and metal (oxy) sulfides etc. have been explored as photocatalysts for water splitting [9-11]. Among various semiconductors, TiO_2 is most widely used due to its favorable electronic energy band structure and high photo-chemical stability [12-13]. Moreover, TiO_2 photocatalytic water-splitting technology has great potential for low-cost and environmentally friendly solar-hydrogen conversion [14,15]. Nevertheless, the narrow light-response range and high recombination rate of photo-induced electrons and holes restrict its practical application [16-18]. Therefore, it is highly desired to develop visible-light-responsive TiO_2 -based photocatalysts with excellent photogenerated charge separation, and many strategies have been tried, such as metal deposition [12,19,20], impurity doping [21-23], coupling with binary composites [24-26], and structure modifications [27-29].

Among all the strategies, coupling TiO_2 with other visible-light-responsive semiconductors to form heterojunction structure is proved to be highly efficient [30,31]. Carbon nitride ($\text{g-C}_3\text{N}_4$) has recently received a lot of interest as a promising photocatalyst since Wang and coworkers' report [32]. As a metal-free polymeric semiconductor, $\text{g-C}_3\text{N}_4$ with a moderate band gap of 2.7 eV has attracted more and more attentions for its inherent chemical and thermal stability [33,34]. Also, $\text{g-C}_3\text{N}_4$ composed of two-dimensional layered structures can be synthesized through facile thermal

condensation by precursors such as melamine, urea, cyanamide and thiourea [35]. Moreover, the delocalized conjugated π structure of g-C₃N₄ allows a relatively slow charge recombination during the charge transfer process [36], making itself a sensitizer candidate for the fabrication of efficient visible-light-driven photocatalyst. Recently, Yu et al. [37] fabricated a direct g-C₃N₄-TiO₂ Z-scheme photocatalyst, which achieved an efficient space separation of the photo-generated electron-hole pairs. Wang et al. [38] synthesized TiO₂/g-C₃N₄ composites by calcining the mixture of melamine and TiO₂ precursor, and found the absorption in UV and visible-light region was enhanced due to the synergic effect between TiO₂ and g-C₃N₄. Li et al. [39] reported on brookite TiO₂ hybridized with g-C₃N₄ via a facile calcination in air, showing an activity superior to g-C₃N₄ or TiO₂ for hydrogen generation from water splitting under visible light. Yan et al. [40] synthesized TiO₂/g-C₃N₄ heterojunctions by a one-step hydrothermal process for photocatalytic water splitting, and found that the layered g-C₃N₄ structure provided the heterogeneous nucleation template for anatase TiO₂ nanoparticles with (001) facet exposure, which was beneficial to the interface transfer of photogenerated charge carriers. Jiang et al. [41] fabricated g-C₃N₄ hybridized hierarchical yolk-shell TiO₂ spheres via a solvothermal method, and found that the charge separation was improved due to the heterojunction between TiO₂ and g-C₃N₄, facilitating the enhanced photocatalytic efficiency. Tang et al. [42] designed spindle-shaped nanoporous TiO₂ coupled g-C₃N₄ nanosheets, which exhibited higher photocatalytic activity under visible light irradiation compared to pure g-C₃N₄ or TiO₂. Besides, some strategies, such as doping, were also used in the development of TiO₂/g-C₃N₄ composites. Lu et al. [43] combined g-C₃N₄ with Ti³⁺-TiO₂ photocatalyst with co-exposed {0 0 1} and {1 0 1} facets via a hydrothermal-sonication assisted strategy, and found that the synergic effect between Ti³⁺-TiO₂ and g-C₃N₄ contributed to

the photocatalytic activity. Li et al. [44] constructed g-C₃N₄/rutile-brookite TiO_{2-x}N_y as a Z-scheme photocatalytic system, which showed improvement on the photocatalytic activity than g-C₃N₄/single brookite TiO_{2-x}N_y due to the excellent transfers of electrons and holes. Li et al. [45] synthesized P-doped g-C₃N₄/TiO₂ heterostructure by a solvent-thermal method, and found that the enhanced photocatalytic performance could be attributed to both phosphorus doping and the surface heterojunction.

Though the construction of TiO₂-g-C₃N₄ heterojunction structure has been proved effective for promoting photocatalytic activity, it still remains a challenge to synthesize a heterostructure in which TiO₂ and g-C₃N₄ are uniformly composited and well connected. The poor interfacial connection can form barriers on the interface of the heterojunction, which may block the migration of charge carriers, leading to a fast recombination of photogenerated charge carriers [46]. In addition, it has been demonstrated that hollow structure can endow photocatalysts with several excellent properties, such as low density, high light-harvesting efficiency, facilitated diffusion and migration of molecules. Therefore, it can be predicted that the catalytic activity of TiO₂/g-C₃N₄ composite can be significantly improved if the intimate contact between the two semiconductors can be realized and the morphology of TiO₂/g-C₃N₄ composite can be adjusted into hollow structure. Unfortunately, it has never been reported so far.

In present work, we successfully synthesized C-TiO₂@g-C₃N₄ core-shell hollow nanospheres by a facile two-step approach. Firstly, C-doped TiO₂ hollow spheres were prepared by using carbon spheres as templates. Then, g-C₃N₄ was coated on the surface of C-TiO₂ hollow spheres via the *in-situ* growth of g-C₃N₄ on C-TiO₂ hollow spheres, which well realized the intimate contact between the two semiconductors. The obtained C-TiO₂@g-C₃N₄ photocatalysts showed

highly enhanced photocatalytic activities for H₂ evolution under visible light irradiation in comparison with pure C-TiO₂ and g-C₃N₄.

2. Experimental section

2.1 Preparation of g-C₃N₄

The g-C₃N₄ was obtained by the calcination of urea. Briefly, 5 g of urea was put into a covered ceramic crucible and heated in a muffle furnace at 550 °C for 2 h with a heating rate of 10 °C·min⁻¹. After cooling to room temperature, the obtained g-C₃N₄ was ground into powder.

2.2 Preparation of C-doped TiO₂ hollow spheres

C-TiO₂ hollow spheres were prepared by using carbon sphere as template, as reported in our previous paper [47]. In a typical synthesis procedure, 0.8 g of carbon spheres with a diameter of about 200 nm were added to 20 mL of ethanol and stirred vigorously for 30 min in a sealed beaker. Then another solution including 5 mL of titanium isopropoxide (TIPT) and 20 mL of ethanol was added dropwise into the beaker under vigorous stirring. The mixture was stirred vigorously for another 1 h. After being centrifuged and washed with water and ethanol for several times, the products were dried at 80 °C for 4 h in an oven, resulting in the TiO₂-carbon composite spheres. Finally, the TiO₂-carbon composite spheres were calcined at 500 °C in nitrogen atmosphere for 1 h, and then calcined at 500 °C in air for 4 h, resulting in C-TiO₂ hollow spheres. For comparison, C-TiO₂ without hollow structure was prepared by milling the C-TiO₂ hollow spheres in an agate mortar and then treating the sample for 30 min in an ultrasonic cell disruptor. The resulted C-TiO₂ was denoted as C-TiO₂-R.

2.3 Preparation of C-TiO₂@ g-C₃N₄ composites

C-TiO₂@g-C₃N₄ composites (TCN) were achieved by the *in-situ* growth of g-C₃N₄ on C-TiO₂

hollow spheres. In a typical procedure, a certain amount of urea was completely dissolved in 5 mL of methanol to form clarified solution. Then, 50 mg of C-TiO₂ hollow spheres were added into the solution and well dispersed by ultrasonic treatment. In this process, the precursor of g-C₃N₄ was intimately coated on the surface of C-TiO₂ hollow spheres, resulting in the *in-situ* growth of g-C₃N₄ on C-TiO₂ in the subsequent heat-treatment (550 °C for 2 h). The obtained products with different initial urea and C-TiO₂ weight ratios of 1:1, 2:1, 3:1 were denoted as TCN-1, TCN-2, TCN-3, respectively. The whole preparation process of C-TiO₂@g-C₃N₄ composites is illustrated in **Fig. 1**.

2.4 Characterization

X-ray diffraction patterns were obtained from a Bruker D2 Phaser using Cu/K α radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were obtained by FEI Quanta 250 equipment. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were obtained on a JEOL JEM2100 TEM. The elemental composition over the selected region was analyzed by an energy dispersive X-ray spectrometer (EDS) attached to a JEM ARM200F TEM. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI5300 analyzer with aluminum K α radiation. N₂ adsorption-desorption isotherms were conducted on a Quantachrome at liquid N₂ temperature. The specific area was determined from the linear portion of the BET plot. Ultraviolet–visible (UV-vis) diffuse reflectance spectroscopies (DRS) were recorded by a V-670 spectrophotometer equipped with an integrating sphere. Photoluminescence (PL) spectra were measured on a FLS980 spectrometer at room temperature using a 350 nm excitation wavelength.

2.5 Photocatalytic measurements

The photocatalytic water splitting was carried out in a top-irradiation quartz cell connected to a closed glass gas circulation system (GEL-SPH2N, Beijing). In a typical photocatalytic reaction, 10 mg of sample was dispersed in a 40 ml of aqueous solution containing 10% methanol. The suspension was thoroughly evacuated and then irradiated by a 300 W Xe lamp (PLS-SXE300) equipped with a 420 nm cutoff filter. The temperature of the reaction solution was maintained at 6 °C by a flow of cooling water during the photocatalytic reaction. The gases evolved were analyzed with an on-line TCD gas chromatograph (GC-9720, nitrogen carrier).

2.6 Photoelectrochemical measurements

The photocurrent and electrochemical impedance spectroscopy (EIS) measurements were carried out using an electrochemical station (Autolab PGSTAT 302N) in a standard three-electrode quartz cell equipped with a working electrode, a platinum sheet as the counter electrode and a saturation calomel electrode (SCE) as the reference electrode. To obtain the working electrode, 5 mg of samples were suspended in 0.5 mL of deionized water with 0.05 mL of 5 wt% Nafion D-520 dispersant, and then the mixture was treated with ultrasound for 30 min and spread onto the FTO glass. After being dried naturally, the FTO glass was heated at 120 °C for 1 h to evaporate the solvent. 0.1 M of Na₂SO₄ aqueous solution was used as the electrolyte. A 300 W Xe lamp (PLS-SXE300) equipped with a 420 nm filter was used as light source.

3. Results and discussion

3.1 Morphology and structure characterization

The morphology of C-TiO₂ and TCN-2 samples was investigated by SEM, TEM and HRTEM. Fig. A1 (Appendix) shows the SEM image of C-TiO₂ nanospheres, from which some broken hollow spheres could be observed, clearly indicating the hollow sphere structure of C-TiO₂. As

exhibited in **Fig. 2a**, C-TiO₂ hollow nanospheres with an approximate average diameter of 100 nm were formed by the packing of TiO₂ nanoparticles with a diameter of about 10 nm. **Fig. 2b** shows that the rough surface of C-TiO₂ hollow nanospheres became smooth after coated with g-C₃N₄, indicating the *in-situ* growth of g-C₃N₄ on C-TiO₂ was successfully realized. As shown in the corresponding HRTEM images in **Figs 2c and d**, the well-ordered lattice fringes with interplanar spacing of 0.35 nm can be observed, which can be assigned to the (101) facet of anatase TiO₂. **Fig. 2d** further reveals that C-TiO₂ hollow nanospheres were successfully coated by g-C₃N₄ nanosheets with a thin thickness of 2-3 nm. Moreover, it can be seen from **Fig. 2d** that the interfacial contact between C-TiO₂ hollow nanospheres and g-C₃N₄ nanosheets was very intimate, which is very helpful for interface migration of the carriers, thus enhancing the photocatalytic efficiency to a large extent [48]. From the EDS elemental mapping images shown in **Fig. 3**, the elements Ti (blue) and O (yellow) are mainly distributed on the wall of the nanosphere, further suggesting a hollow sphere structure of the C-TiO₂ core, while the elements C (green) and N (red) are uniformly scattered on the C-TiO₂ and wrapping the whole nanosphere, indicating that C-TiO₂ and g-C₃N₄ formed a closely contacted core-shell structure. XRD patterns of C-TiO₂, g-C₃N₄ and TCN are shown in **Fig. 4**. The distinct diffraction peaks at 13.0° and 27.4° in the g-C₃N₄, corresponding to the in-plane structural packing motif and interlayer stacking of aromatic segments, can be indexed to the (100) and (002) peaks for graphitic materials, respectively. The main diffraction peaks of C-TiO₂ located at 2θ values of 25.3°, 37.8°, and 48.0° can be well indexed to (101), (004), and (200) crystal planes of anatase (JCPDS, No. 21-1272), respectively. For TCN, the diffraction peaks corresponding to anatase TiO₂ can be observed in all samples, and the diffraction peaks consistent with g-C₃N₄ gradually became obvious from inconspicuous with the increasing amount

of g-C₃N₄. Moreover, compared with the pristine C-TiO₂, the diffraction peaks originating from TiO₂ in TCN showed a stronger intensity, in accordance with the improved crystallinity due to the calcination at 550 °C.

To determine the surface area of the as-synthesized samples, N₂ adsorption-desorption isotherms were measured. As displayed in **Fig. 5a**, all the samples exhibited a type IV isotherm with a H3 hysteresis loop, indicating the presence of mesopores. The BET surface area (S_{BET}) and pore volume of samples showed a similar changing trend (**Table 1**). The S_{BET} of C-TiO₂ hollow spheres was 80.7 m²·g⁻¹, while g-C₃N₄ exhibited a large S_{BET} of 275.8 m²·g⁻¹ due to its porous and sheet-like structure. After g-C₃N₄ was wrapped on C-TiO₂ hollow spheres, the S_{BET} of TCN-1 and TCN-2 decreased to 67.0 and 53.4 m²·g⁻¹, respectively. This can be explained by the growth of g-C₃N₄ on the surface of C-TiO₂ hollow spheres, which could cover or fill some of the mesopores formed by the packing of the TiO₂ nanoparticles, thus leading to the decrease of S_{BET} . When the amount of g-C₃N₄ loading became higher, however, the S_{BET} of TCN-3 increased to 121.1 m²·g⁻¹. Since g-C₃N₄ possesses a large specific surface area, the excessive g-C₃N₄ accumulated on the surface of the C-TiO₂ hollow spheres would contribute to the increase of the S_{BET} . For the C-TiO₂ and TCN samples, there is a main pore distribution between 2 nm and 20 nm (**Fig. 5b**), which can be ascribed to the mesopores formed by the packing of TiO₂ nanoparticles with an average size of 10 nm. The average pore size of g-C₃N₄ is 3.72 nm, resulting from the thermal treatment process of urea. TCN presented a pore size distribution curve combined C-TiO₂ with TCN.

To investigate the surface chemical composition and chemical status of elements, XPS analysis was carried out on TCN-2. As shown in **Fig. 6a**, the binding energies at 284.8 eV and 288.7 eV on the C 1s core-level spectrum can be ascribed to the sp² C–C bonds of graphitic carbon and

sp^2 -bonded carbon (N=C=N) in the s-triazine rings [30,49], respectively, and the peak at 286.0 eV can be attributed to the oxygen bound species C-O [50]. The peak at 283.9 eV is close to the C1s peak of TiC (283.0 eV) [51], indicating the formation of O-Ti-C bonds [52]. In the XPS spectrum of N 1s shown in **Fig. 6b**, the peaks located at 399.5 eV, 400.0 eV and 400.9 eV can be ascribed to the sp^2 -bonded N (C=N=C), tertiary nitrogen N-(C)₃ groups, and amino groups (C-N-H) [49,53,54], respectively. The peak at 404.9 eV could be caused by the charging effects [55]. The two distinguished peaks of Ti 2p in **Fig. 6c** at 458.8 eV and 464.6 eV correspond to the Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbital splitting photoelectrons [56], respectively. The XPS spectrum of the O1s consists of two peaks at 530.0 eV and 531.3 eV (**Fig. 6d**), which can be assigned to Ti-O bond and O-H bond, respectively [57].

3.2 Optical absorption properties

The optical absorption properties of all samples were investigated by UV-vis diffuse reflectance spectroscopy. As shown in **Fig. 7**, the C-TiO₂ exhibited an absorption edge at 400 nm, while the pure g-C₃N₄ was able to absorb light with a wavelength up to 480 nm. After they were combined with each other, the obtained TCN composites exhibited an enhanced optical absorption both in UV and visible light region. With the increasing ratio of g-C₃N₄ in the TCN composites, the absorption in the UV region was improved and the absorption edge was shifted towards longer wavelength as compared to the C-TiO₂. This can be ascribed to the presence of g-C₃N₄, which displayed a strong absorption in the region of 350-400 nm. However, when the urea/C-TiO₂ ratio increased from 2:1 (TCN-2) to 3:1 (TCN-3), the optical absorption at wavelength longer than 400 nm was weakened. As evidenced by previous report [38], too much g-C₃N₄ would agglomerate on the surface of C-TiO₂, thus leading to a lower optical absorption. Therefore, the content of g-C₃N₄

in the TCN composites plays an important role in the light response both in UV and visible light region.

3.3 Photocatalytic hydrogen production activity

The actual photocatalytic activities for hydrogen production of the C-TiO₂-R, C-TiO₂, g-C₃N₄, and TCN composites were evaluated in aqueous solution with methanol as sacrificial agent under visible light. The average rate of hydrogen production within 5 h is illustrated in **Fig. 8a**. The C-TiO₂ presented a H₂ generation rate of 1.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$, while the C-TiO₂-R displayed a H₂ generation rate of 1.2 $\mu\text{mol g}^{-1}\text{h}^{-1}$, which decreased by 20% compared with that of C-TiO₂, indicating the superiority of the hollow sphere structure. The pure g-C₃N₄ only showed a H₂ generation rate of 3.1 $\mu\text{mol g}^{-1}\text{h}^{-1}$ due to the rapid recombination of electrons and holes. It is obvious that the photocatalytic activity of TCN was greatly enhanced, and the H₂ generation rate of the TCN composites increased with the increasing urea/C-TiO₂ ratio from 1:1(TCN-1) to 2:1(TCN-2), and then decreased when the ratio was up to 3:1. The TCN-2 photocatalyst presented the highest H₂ generation rate of 35.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$, which was 22.7 and 10.5 times higher than that of C-TiO₂ and g-C₃N₄, respectively. The enhanced H₂ generation performance of TCN composites can be ascribed to visible light response from g-C₃N₄ and the improved charge separation efficiency due to the strong interactions between g-C₃N₄ and C-TiO₂. Moreover, the structure of TiO₂ hollow spheres could result in the reflections of light within the interior cavity, thus increasing the utilization of the light energy. However, too much g-C₃N₄ covering the surface of C-TiO₂ would reduce the density of active sites and create a light screening effect [58]. Besides, excessive g-C₃N₄ accumulated on the C-TiO₂ surface may encourage the recombination of charge carriers, which will decrease the photocatalytic efficiency [59]. To test the stability of TCN

samples, the recycling experiment of hydrogen evolution rate over TCN-2 was carried out. As shown in **Fig. 8b**, no obvious hydrogen evolution rate decrease was observed within four cycles in 16 h, which demonstrates the photostability of TCN samples.

3.4 Photoluminescence spectroscopy

To investigate the separation of photogenerated electrons and holes, photoluminescence spectroscopy was performed with an excitation wavelength of 350 nm. As shown in **Fig. 9**, the pure g-C₃N₄ exhibits strong photoluminescence with an emission peak at about 460 nm, which is consistent with UV-vis analysis. This strong peak is attributed to the band-band PL phenomenon with the energy of light approximately equal to the band gap energy of g-C₃N₄ [60]. The wide PL spectrum of C-TiO₂ in the wavelength range of 400-550 nm is due to the emission of bandgap transition and excitonic PL resulting from surface oxygen vacancies and defects [61]. After the formation of TCN composites, the emission peak in the PL spectra of TCN was similar to that of the C-TiO₂, but the emission intensity grew weaker with the increasing loading of g-C₃N₄, indicating that the recombination of photogenerated electrons and holes was restricted. The low photoluminescence intensity of TCN confirmed that the formation of the C-TiO₂@g-C₃N₄ heterostructure remarkably promoted charge transfer efficiency, thereby favoring the photocatalytic reactions.

3.5 Photocurrent and electrochemical impedance spectroscopy

Photocurrent measurements carried out on C-TiO₂, g-C₃N₄ and TCN-2 under visible light were shown in **Fig. 10a**. Pure g-C₃N₄ showed a low photocurrent response due to the quick recombination of photo-generated electrons and holes. Compared with g-C₃N₄ and C-TiO₂, TCN-2 exhibited a higher photocurrent response, which can be ascribed to the enhanced absorption of

visible light as well as the improved charge separation and migration efficiency resulting from the heterojunction between g-C₃N₄ and C-TiO₂. Electrochemical impedance spectroscopy (EIS) was also studied on C-TiO₂, g-C₃N₄ and TCN-2. As presented in **Fig. 10b**, the impedance arc radius of TCN-2 was smaller than that of g-C₃N₄ and C-TiO₂, suggesting a less interface electron resistance due to the intimate contact between the two semiconductors. Therefore, it can be concluded that the heterojunction between g-C₃N₄ and C-TiO₂ not only promoted the separation efficiency of photo-induced electrons and holes but also enhanced their transfer efficiency, thus favoring the photocatalytic reactions.

3.6 Photocatalytic mechanism of TCN composites

On the basis of the experimental results, a reasonable mechanism for the enhanced visible-light photocatalytic performance of the C-TiO₂@g-C₃N₄ heterostructure is proposed. As shown in **Fig. 11a**, under the excitation of visible light, the photogenerated electrons can be produced both by C-TiO₂ and g-C₃N₄ (C-TiO₂ can respond visible light due to C-doping [47]). There are three ways for photo-induced electrons to be consumed: (a) recombine with holes inside the photocatalysts (bulk recombination); (b) recombine with holes outside the photocatalysts (surface recombination); (c) migrate to the surface of the photocatalysts and react with protons (or H₂O) for H₂ evolution. The recombination step between photo-induced electrons and holes is ineffective for water splitting and largely limits the quantum efficiency of the photocatalysts. Thus, only a small fraction of the photoinduced charge carriers can contribute to photocatalytic reactions [62]. Therefore, the key for the high-efficiency water splitting is to promote the separation of photo-induced electrons and holes and fast charge carrier transport. In this case, the coupling of C-TiO₂ and g-C₃N₄ can serve as a contributor to wide charge separation and fast electron transfer.

The conduction band (CB) of g-C₃N₄ is -1.14, which is more negative than that of C-TiO₂. Meanwhile, the valence band (VB) of C-TiO₂ is more positive than that of g-C₃N₄ (+1.54 eV) [63]. Therefore, a typical type-II heterostructure can be formed between C-TiO₂ and g-C₃N₄ [64]. The photoinduced electrons resulted from g-C₃N₄ will transfer to the conduction band of C-TiO₂ and reduce H⁺ to H₂. Meanwhile, the photoinduced holes resulted from C-TiO₂ will migrate to the valence band of g-C₃N₄ and oxidize the sacrificial agent (CH₃OH) to products, such as CO₂, CO and H₂O. Therefore, effective charge separation can be achieved by the C-TiO₂@g-C₃N₄ heterostructure, resulting in a longer life time of the photogenerated charge carriers, which is in accordance with the results of PL spectroscopy (**Fig. 9**). Meanwhile, the EIS and photocurrent results (**Fig. 10**) indicate that the intimate contact between C-TiO₂ and g-C₃N₄ can effectively reduce the migration resistance of photo-generated carries, resulting in a faster carriers transfer. Moreover, the unique hollow structure can effectively enhance the utilization efficiency of light energy via the multiply reflection of light within the inner cavity (**Fig. 11b**), resulting in more photogenerated electron-hole pairs [41]. All these positive factors effectively enhance the visible-light photocatalytic performance of C-TiO₂@g-C₃N₄ core-shell hollow nanospheres.

4. Conclusions

In summary, C-TiO₂@g-C₃N₄ core-shell hollow nanospheres with different mass ratios of g-C₃N₄ to C-TiO₂ were fabricated by an *in-situ* growth method. The TCN composites showed much superior photocatalytic performance to the C-TiO₂ and the pure g-C₃N₄. Among the TCN samples, TCN-2 exhibited the highest H₂ generation rate of 35.6 μmol g⁻¹ h⁻¹, which was 22.7 times and 10.5 times higher than that of C-TiO₂ and pure g-C₃N₄, respectively. The enhanced photocatalytic activities of the TCN composites can be primarily attributed to the formation of a

type-II heterojunction and the intimate contact between the two semiconductors. The former effectively promoted the separation of photogenerated electrons and holes, and the latter effectively improved the migration velocity of photo-generated carries. Besides, the enhancement in the utilization efficiency of light energy resulted from the unique hollow structure can also be counted as one positive factor. This work may shed light on the deliberately designed photocatalysts for more efficient visible-light activity.

Acknowledgements

This work was sponsored by the National Natural Science Fund Committee-Baosteel Group Corporation Steel Joint Research Fund (U1460105), the National Science Foundation of China (51521065), the Natural Science Foundation of Shaanxi Province (2015JM2055), and the Fundamental Research Funds for the Central Universities (2015gjh06). SEM was carried out at the Center for Advancing Materials Performance from the Nanoscale (CAMP NANO). TEM was carried out at International Center for Dielectric Research (ICDR). We thank Dr. C. Guo and Mr. C. Ma for their help in using SEM and TEM, respectively.

References

- [1] Z. Xu, J.F. Han, B. Seger, H.J. Chen, G.Q. Lu, C. Li, L.Z. Wang, An integrated photoelectrochemical-chemical loop for solar-driven overall splitting of hydrogen sulfide, *Angew. Chem. Int. Ed.* 53 (2014) 4399-4403.
- [2] A. Fujishima, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37-38.
- [3] Z.G. Zou, J.H. Ye, K. Sayama, H. Arakawa, Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst, *Nature* 414 (2001) 625-627.

- [4] H.G. Kim, D.W. Hwang, J.S. Lee, Single-phase oxide photocatalyst working under visible light, *J. Amer. Chem. Soc.* 126 (2004) 8912-8913.
- [5] J. Huang, S. Wang, Y.Q. Zhao, X.Y. Wang, S.P. Wang, S.H. Wu, S.M. Zhang, W.P. Huang, Synthesis and characterization of CuO/TiO₂ catalysts for low-temperature CO oxidation, *Chem. Commun.* 7 (2006) 1029-1034.
- [6] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, GaN: ZnO solid solution as a photocatalyst for visible-light-driven overall water splitting, *J. Amer. Chem. Soc.* 127 (2005) 8286-8287.
- [7] W.J. Luo, Z.S. Li, X.J. Jiang, T. Yu, L.F. Liu, X.Y. Chen, J.H. Ye, Z.G. Zou, Correlation between the band positions of (SrTiO₃)_{1-x}•(LaTiO₂N)_x solid solutions and photocatalytic properties under visible light irradiation, *Phys. Chem. Chem. Phys.* 10 (2008) 6717-6723.
- [8] R. Abe, T. Takata, H. Sugihara, K. Domen, Photocatalytic overall water splitting under visible light by TaON and WO₃ with an IO³⁻/I⁻ shuttle redox mediator, *Chem. Commun.* 30 (2005) 3829-3831.
- [9] I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, Photocatalytic H₂ evolution reaction from aqueous solutions over band structure-controlled (AgIn)_xZn_{2(1-x)}S₂ solid solution photocatalysts with visible-light response and their surface nanostructures, *J. Amer. Chem. Soc.* 126 (2004) 13406-13413.
- [10] I. Tsuji, Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, Novel stannite-type complex sulfide photocatalysts Al₂-Zn-AIV-S₄ (Al= Cu and Ag; AIV= Sn and Ge) for hydrogen evolution under visible-light irradiation, *Chem. Mater.* 22 (2010) 1402-1409.
- [11] K. Ikeue, Y. Shinmura, M. Machida, Ag-doped Mn-Cd sulfide as a visible-light-driven

- photocatalyst for H₂ evolution, *Appl. Catal. B* 123 (2012) 84-88.
- [12] N.L. Wu, M.S. Lee, Enhanced TiO₂ photocatalysis by Cu in hydrogen production from aqueous methanol solution, *Int. J. Hydrogen Energy* 29 (2004) 1601-1605.
- [13] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. A* 1 (2000) 1-21.
- [14] E.P. Melián, O.G. Díaz, A.O. Méndez, C.R. López, M.N. Suárez, J.M.D. Rodríguez, J.A. Navío, D.F. Hevia, J.P. Peña, Efficient and affordable hydrogen production by water photo-splitting using TiO₂-based photocatalysts, *Int. J. Hydrogen Energy* 38 (2013) 2144-2155.
- [15] Z.F. Jiang, W.M. Wan, W. Wei, K. M. Chen, H.M. Li, P.K. Wong, J.M. Xie, Gentle way to build reduced titanium dioxide nanodots integrated with graphite-like carbon spheres: From DFT calculation to experimental measurement, *Appl. Catal. B* 204 (2017) 283-295.
- [16] S.S. Soni, M.J. Henderson, J.F. Bardeau, A. Gibaud, Visible-Light Photocatalysis in Titania-Based Mesoporous Thin Films, *Adv. Mater.* 20 (2008) 1493-1498.
- [17] D.G. Shchukin, R.A. Caruso, Inorganic macroporous films from preformed nanoparticles and membrane templates: synthesis and investigation of photocatalytic and photoelectrochemical properties, *Adv. Funct. Mater.* 13 (2003) 789-794.
- [18] W. Ho, C.Y. Jimmy, S. Lee, Synthesis of hierarchical nanoporous F-doped TiO₂ spheres with visible light photocatalytic activity, *Chem. Commun.* 10 (2006) 1115-1117.
- [19] G.L. Chiarello, M.H. Aguirre, E. Selli, Hydrogen production by photocatalytic steam reforming of methanol on noble metal-modified TiO₂, *J. Catal.* 273 (2010) 182-190.
- [20] A.A. Ismail, Mesoporous PdO-TiO₂ nanocomposites with enhanced photocatalytic activity,

Appl. Catal. B 117 (2012) 67-72.

- [21] C. Siriwong, N. Wetchakun, B. Inceesungvorn, D. Channei, T. Samerjai, S. Phanichphant, Doped-metal oxide nanoparticles for use as photocatalysts, *Prog. Cryst. Growth Charact. Mater.* 58 (2012) 145-163.
- [22] H. Park, Y. Park, W. Kim, W. Choi, Surface modification of TiO₂ photocatalyst for environmental applications, *J. Photochem. Photobiol. C* 15 (2013) 1-20.
- [23] J.S. Jang, H.G. Kim, J.S. Lee, Heterojunction semiconductors: A strategy to develop efficient photocatalytic materials for visible light water splitting, *Catal. Today* 185 (2012) 270-277.
- [24] Q.Z. Wang, N. An, Y. Bai, H.H. Hang, J.J. Li, X.L. Lu, Y.H. Liu, F.P. Wang, Z.M. Li, Z.Q. Lei, High photocatalytic hydrogen production from methanol aqueous solution using the photocatalysts CuS/TiO₂, *Int. J. Hydrogen Energy* 38 (2013) 10739-10745.
- [25] Q.Z. Wang, G.X. Yun, Y. Bai, N. An, Y.T. Chen, R.F. Wang, Z.Q. Lei, W.F. Shangguan, NiS as co-catalyst for enhanced photocatalytic hydrogen evolution over TiO₂, *Int. J. Hydrogen Energy* 39 (2014) 13421-13428.
- [26] X.Y. Zhang, H.P. Li, X.L. Cui, Y. Lin, Graphene/TiO₂ nanocomposites: synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting, *J. Mater. Chem.* 20 (2010) 2801-2806.
- [27] J. Jitputti, Y. Suzuki, S. Yoshikawa, Synthesis of TiO₂ nanowires and their photocatalytic activity for hydrogen evolution, *Catal. Commun.* 9 (2008) 1265-1271.
- [28] J. Zhu, M. Zäch, Nanostructured materials for photocatalytic hydrogen production, *Curr. Opin. Colloid Interface Sci.* 14 (2009) 260-269.
- [29] C. Han, Y.D. Wang, Y.P. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, In situ synthesis of

- graphitic-C₃N₄ nanosheet hybridized N-doped TiO₂ nanofibers for efficient photocatalytic H₂ production and degradation, *Nano Res.* 8 (2015) 1199-1209.
- [30] B. Chai, T.Y. Peng, J. Mao, K. Li, L. Zan, Graphitic carbon nitride (g-C₃N₄)-Pt-TiO₂ nanocomposite as an efficient photocatalyst for hydrogen production under visible light irradiation, *Phys. Chem. Chem. Phys.* 14 (2012) 16745-16752.
- [31] M.N. Huang, J.H. Yu, Q. Hu, W.L. Su, M.G. Fan, B. Li, L.H. Dong, Preparation and enhanced photocatalytic activity of carbon nitride/titania (001 vs 101 facets)/ reduced graphene oxide (g-C₃N₄/TiO₂/rGO) hybrids under visible light, *Appl. Surf. Sci.* 389 (2016) 1084-1093.
- [32] X.C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, *Nat. Mater.* 8 (2009) 76-80.
- [33] D.G. Gong, J.G. Highfield, S.Z.E. Ng, Y.X. Tang, W.C.J. Ho, Q.L. Tay, Z. Chen, Poly tri-s-triazines as visible light sensitizers in titania-based composite photocatalysts: promotion of melon development from urea over acid titanates, *ACS Sustainable Chem. Eng.* 2 (2013) 149-157.
- [34] S.W. Cao, J.G. Yu, g-C₃N₄-based photocatalysts for hydrogen generation, *J. Phys. Chem. Lett.* 5 (2014) 2101-2107.
- [35] W.L. Yu, D.F. Xu, T.Y. Peng, Enhanced photocatalytic activity of g-C₃N₄ for selective CO₂ reduction to CH₃OH via facile coupling of ZnO: a direct Z-scheme mechanism, *J. Mater. Chem. A* 3 (2015) 19936-19947.
- [36] Y.J. Wang, R. Shi, J. Lin, Y.F. Zhu, Enhancement of photocurrent and photocatalytic activity

- of ZnO hybridized with graphite-like C₃N₄, *Energ. Environ. Sci.* 4 (2011) 2922-2929.
- [37] J.G. Yu, S.H. Wang, J.X. Low, W. Xiao, Enhanced photocatalytic performance of direct Z-scheme g-C₃N₄-TiO₂ photocatalysts for the decomposition of formaldehyde in air, *Phys. Chem. Chem. Phys.* 15 (2013) 16883-16890.
- [38] J.X. Wang, J. Huang, H.L. Xie, A.L. Qu, Synthesis of g-C₃N₄/TiO₂ with enhanced photocatalytic activity for H₂ evolution by a simple method, *Int. J. Hydrogen Energy* 39 (2014) 6354-6363.
- [39] Y.P. Zang, L.P. Li, Y.S. Xu, Y. Zuo, G.S. Li, Hybridization of brookite TiO₂ with g-C₃N₄: a visible-light-driven photocatalyst for As³⁺ oxidation, MO degradation and water splitting for hydrogen evolution, *J. Mater. Chem. A* 2 (2014) 15774-15780.
- [40] J.Q. Yan, H. Wu, H. Chen, Y.X. Zhang, F.X. Zhang, S.Z.F. Liu, Fabrication of TiO₂/C₃N₄ heterostructure for enhanced photocatalytic Z-scheme overall water splitting, *Appl. Catal. B* 191 (2016) 130-137.
- [41] Z.F. Jiang, C.Z. Zhu, W.M. Wan, K. Qian, J.M. Xie, Constructing graphite-like carbon nitride modified hierarchical yolk-shell TiO₂ spheres for water pollution treatment and hydrogen production, *J. Mater. Chem. A* 4 (2016) 1806-1818.
- [42] H. Tang, S.F. Chang, L.Y. Jiang, G.G. Tang, W. Liang, Novel spindle-shaped nanoporous TiO₂ coupled graphitic g-C₃N₄ nanosheets with enhanced visible-light photocatalytic activity, *Ceram. Int.* 42 (2016) 18443-18452.
- [43] D. Lu, G.K. Zhang, Z. Wan, Visible-light-driven g-C₃N₄/Ti³⁺-TiO₂ photocatalyst co-exposed {001} and {101} facets and its enhanced photocatalytic activities for organic pollutant degradation and Cr (VI) reduction, *Appl. Surf. Sci.* 358 (2015) 223-230.
- [44] H.H. Li, X.Y. Wu, S. Yin, K. Katsumata, Y.H. Wang, Effect of rutile TiO₂ on the

- photocatalytic performance of g-C₃N₄/brookite-TiO_{2-x}N_y photocatalyst for NO decomposition, *Appl. Surf. Sci.* 392 (2017) 531-539.
- [45] Z.W. Li, G.D. Jiang, Z.H. Zhang, Y. Wu, Y.H. Han, Phosphorus-doped g-C₃N₄ nanosheets coated with square flake-like TiO₂: Synthesis, characterization and photocatalytic performance in visible light, *J. Mol. Catal. A-Chem.* 425 (2016) 340-348.
- [46] X.F. Chen, J. Wei, R.J. Hou, Y. Liang, Z.L. Xie, Y.G. Zhu, X.W. Zhang, H.T. Wang, Growth of g-C₃N₄ on mesoporous TiO₂ spheres with high photocatalytic activity under visible light irradiation, *Appl. Catal. B* 188 (2016) 342-350.
- [47] J.W. Shi, X. Zong, X. Wu, H.J. Cui, B. Xu, L.Z. Wang, Carbon-doped titania hollow spheres with tunable hierarchical macroporous channels and enhanced visible light-induced photocatalytic activity, *ChemCatChem* 4 (2012) 488-491.
- [48] J. Zhang, M. Zhang, R.Q. Sun, X. Wang, A facile band alignment of polymeric carbon nitride semiconductors to construct isotype heterojunctions, *Angew. Chem.* 124 (2012) 10292-10296.
- [49] Z.Y. Zhang, J.D. Huang, M.Y. Zhang, Q. Yuan, B. Dong, Ultrathin hexagonal SnS₂ nanosheets coupled with g-C₃N₄ nanosheets as 2D/2D heterojunction photocatalysts toward high photocatalytic activity, *Appl. Catal. B* 163 (2015) 298-305.
- [50] P. Zhang, C.L. Shao, Z.Y. Zhang, M.Y. Zhang, J.B. Mu, Z.C. Guo, Y.C. Liu, In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol, *Nanoscale* 3 (2011) 3357-3368.
- [51] J.H. Park, S. Kim, A.J. Bard, Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting, *Nano Lett.* 6 (2006) 24-28.

- [52] F. Dong, H.Q. Wang, Z.B. Wu, One-step “green” synthetic approach for mesoporous C-doped titanium dioxide with efficient visible light photocatalytic activity, *J. Phys. Chem. C* 113 (2009) 16717-16723.
- [53] S.W. Cao, X.F. Liu, Y.P. Yuan, Z.Y. Zhang, Y.S. Liao, J. Fang, S.C.J. Loo, T.C. Sum, C. Xue, Solar-to-fuels conversion over $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ hybrid photocatalysts, *Appl. Catal. B* 147 (2014) 940-946.
- [54] L. Lin, P. Ye, C. Cao, Q. Jin, G.S. Xu, Y.H. Shen, J. Yuan, Rapid microwave-assisted green production of a crystalline polyimide for enhanced visible-light-induced photocatalytic hydrogen production, *Mater. Chem. A* 3 (2015) 10205-10208.
- [55] Z.F. Jiang, D. Liu, D.L. Jiang, W. Wei, K. Qian, M. Chen, J.M. Xie, Bamboo leaf-assisted formation of carbon/nitrogen co-doped anatase TiO_2 modified with silver and graphitic carbon nitride: novel and green synthesis and cooperative photocatalytic activity, *Dalton Trans.* 43 (2014) 13792-13802.
- [56] M. Fu, J.Z. Liao, F. Dong, H.M. Li, H.Y. Liu, Growth of $\text{g-C}_3\text{N}_4$ Layer on Commercial TiO_2 for Enhanced Visible Light Photocatalytic Activity, *J. Nanomater.* 2014 (2014).
- [57] B. Chai, T.Y. Peng, P. Zeng, J. Mao, Synthesis of fluorinated In_2S_3 decorated with TiO_2 nanoparticles for efficient photocatalytic hydrogen production under visible light, *J. Mater. Chem.* 21 (2011) 14587-14593.
- [58] Y.H. Li, K.L. Lv, W.K. Ho, F. Dong, X.F. Wu, Y. Xia, Hybridization of rutile TiO_2 (rTiO_2) with $\text{g-C}_3\text{N}_4$ quantum dots (CN QDs): An efficient visible-light-driven Z-scheme hybridized photocatalyst, *Appl. Catal. B* 202 (2017) 611-619.
- [59] L. Liu, Y.H. Qi, J.S. Hu, Y.H. Liang, W.Q. Cui, Efficient visible-light photocatalytic hydrogen

- evolution and enhanced photostability of core@shell $\text{Cu}_2\text{O@g-C}_3\text{N}_4$ octahedra, *Appl. Surf. Sci.* 351 (2015) 1146-1154.
- [60] J. Wang, W.D. Zhang, Modification of TiO_2 nanorod arrays by graphite-like C_3N_4 with high visible light photoelectrochemical activity, *Electrochim. Acta* 71 (2012) 10-16.
- [61] J.G. Yu, T.T. Ma, S.W. Liu, Enhanced photocatalytic activity of mesoporous TiO_2 aggregates by embedding carbon nanotubes as electron-transfer channel, *Phys. Chem. Chem. Phys.* 13 (2011) 3491-3501.
- [62] Z.F. Hu, G. Liu, X.Q. Chen, Z.R. Shen, J.C. Yu, Enhancing Charge Separation in Metallic Photocatalysts: A Case Study of the Conducting Molybdenum Dioxide, *Adv. Funct. Mater.* 26 (2016) 4445-4455.
- [63] Y.H. Jiang, F. Li, Y. Liu, Y.Z. Hong, P.P. Liu, L. Ni, Construction of TiO_2 hollow nanosphere/ $\text{g-C}_3\text{N}_4$ composites with superior visible-light photocatalytic activity and mechanism insight, *J. Ind. Eng. Chem.* 41 (2016) 130-140.
- [64] Y.J. Wang, Q.S. Wang, X.Y. Zhan, F.M. Wang, M. Safdar, J. He, Visible light driven type II heterostructures and their enhanced photocatalysis properties: a review, *Nanoscale* 5 (2013) 8326-8339.

TABLES

Table 1 Structural parameters of the samples.

Samples	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore size (nm)	V_{pore} ($\text{cm}^3 \cdot \text{g}^{-1}$)
C-TiO ₂	80.7	10.06	0.92
TCN-1	67.0	8.14	0.64
TCN-2	53.4	9.01	0.63
TCN-3	121.1	9.00	1.52
g-C ₃ N ₄	275.8	3.72	3.03

FIGURES

Fig. 1. Schematic illustration of the preparation of C-TiO₂@g-C₃N₄.

Fig. 2. TEM images of C-TiO₂ (a) and TCN-2 (b) and HRTEM images of C-TiO₂ (c) and TCN-2(d).

Fig. 3. HAADF-STEM image of a single TCN-2 nanosphere (a) and the elemental mapping for elements C, N, Ti, O (b-f).

Fig. 4. XRD patterns of C-TiO₂, g-C₃N₄ and TCN.

Fig. 5. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of C-TiO₂, g-C₃N₄ and TCN.

Fig. 6. XPS spectra of TCN-2, (a) C 1s, (b) N 1s, (c) Ti 2p, (d) O 1s.

Fig. 7. UV-vis diffuse reflectance absorption spectra of $g\text{-C}_3\text{N}_4$, C-TiO_2 and TCN.

Fig. 8. The average H_2 production rates of $\text{C-TiO}_2\text{-R}$, C-TiO_2 , $g\text{-C}_3\text{N}_4$, and TCN samples (a) and cyclic runs for the photocatalytic H_2 production over TCN-2 sample (b).

Fig. 9. Photoluminescence spectra of C-TiO₂, g-C₃N₄ and TCN.

Fig. 10. Photocurrent response (a) and electrochemical impedance spectroscopy (EIS) (b) of

C-TiO₂, g-C₃N₄ and TCN-2.

Fig. 11. Proposed mechanism of the photo-excited electron-hole separation and transport processes at the C-TiO₂@g-C₃N₄ interface under visible light irradiation (a) and the multiply reflection of light within the inner cavity of C-TiO₂@g-C₃N₄ (b).