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Solar-to-Fuels Conversion over $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ Hybrid Photocatalysts

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Abstract

We have achieved in-situ growth of In_2O_3 nanocrystals onto the sheet-like $\text{g-C}_3\text{N}_4$ surface. The resulting In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrid structures exhibit considerable improvement on the photocatalytic activities for H_2 generation and CO_2 reduction. The enhanced activities are attributed to the interfacial transfer of photogenerated electrons and holes between $\text{g-C}_3\text{N}_4$ and In_2O_3 , leading to effective charge separation on both parts. Further studies by transient PL spectroscopy confirm that the In_2O_3 - $\text{g-C}_3\text{N}_4$ heterojunctions remarkably promote the charge transfer efficiency, thereby increase the charge carrier lifetime for the photocatalytic reactions.

Keywords: Photocatalysis; hydrogen production; CO_2 reduction; graphitic carbon nitride; Charge transfer.

1. Introduction

The fuels production through solar-driven water splitting or CO₂ reduction has been considered as a promising way to solve the worldwide energy shortage [1-3]. In the past decade, great efforts have been made to explore solar-to-fuel conversion by using various semiconductor photocatalysts including TiO₂ [4,5], Cu₂O [6,7], SrTiO₃ [8,9], ZnFe₂O₄ [10], CdS [11,12], InVO₄ [13] etc. Among them, In₂O₃ is known as a semiconductor with an indirect bandgap of ~2.8 eV, and has been proved as a visible-light-active photocatalyst [14,15], and has also been used as the efficient sensitizer to extend the absorption spectra of oxide semiconductor photocatalysts from the UV region into visible region [16-18]. More recently, a new type of polymeric nanosheet structure, graphitic carbon nitride (g-C₃N₄), has been introduced as a visible-light photocatalyst for water splitting due to its unique electronic band structure with high thermal and chemical stability [19-21].

In the development of semiconductor-based photocatalysts for solar-to-fuel conversion, one disconcerting drawback is the high recombination rate of photogenerated electron-hole pairs in the individual semiconductor structure [22]. Thus it is very critical to modulate the charge carrier dynamics in semiconductor structures. One effective way is coupling two semiconductor units with appropriate band alignment between the two units to allow interfacial charge transfer upon excitation and promote the separation efficiency of photogenerated electrons and holes [23-29]. Thus the charge carrier lifetime can be significantly improved to enable desired surface reactions and thereby enhance the photocatalytic efficiency for

solar-to-fuels conversion.

Recently researchers have found that two-dimensional (2-D) semiconductor nanostructures offer higher charge mobility and lower recombination rates of charge carriers as compared to 0-D spherical nanoparticles [30,31]. Herein, we present a prototype of 0D-2D semiconductor heterojunction system by in-situ growth of In_2O_3 nanocrystals on g- C_3N_4 nanosheets through a simple solvothermal method. The well-dispersed In_2O_3 nanocrystals on sheet-like g- C_3N_4 surfaces form intimate contact, which allows for effective interfacial charge transfer across the $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ heterojunction since the conduction band (CB) and valance band (VB) positions of In_2O_3 (~ -0.6 eV and $\sim +2.2$ eV, respectively, vs. NHE) [28,29] are both lower than those of g- C_3N_4 (~ -1.1 eV and $\sim +1.6$ eV, respectively, vs. NHE) [19,32]. In particular, the conduction band edge (~ -0.6 eV) of In_2O_3 is high enough for reduction of proton and CO_2 . As such, we found that the $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ hybrid structures are capable for efficient photocatalytic H_2 generation and CO_2 reduction with much higher activities than the pure In_2O_3 and g- C_3N_4 . This is attributed to the highly effective charge separation on $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ hybrids as confirmed by the transient photoluminescence (PL) spectroscopy.

2. Experiments

2.1 Preparation of In_2O_3 -g- C_3N_4 hybrids

g- C_3N_4 powder was synthesized by heating 6 g melamine in an alumina crucible with a cover at 500 °C in a muffle furnace for 2 h at a heating rate of 20 °C /min, and

further heated to 520 °C for another 2 h at a heating rate of 5 °C/min [33]. In-situ growth of In₂O₃ nanocrystals (10 wt%) on g-C₃N₄ nanosheets was carried out as following steps. While stirring, 0.5 mmol of In(Ac)₃ and 600 mg of the as-prepared g-C₃N₄ were added into 50 mL dimethyl sulfoxide (DMSO). The resultant suspension was sealed in a 100 mL teflon-lined stainless-steel autoclave. The autoclave was heated to 180 °C and maintained for 12 h, and then allowed to cool to room temperature. The product was collected after centrifugation, washed with water and ethanol repeatedly, and then dried in a vacuum oven. Pure In₂O₃ and other In₂O₃-g-C₃N₄ hybrids with different ratio were synthesized using the similar route by tuning the dosage of g-C₃N₄.

2.2 Characterization

A Shimadzu XRD-6000 X-ray diffractometer (Cu K α source) was used to record X-ray powder diffraction (XRD) patterns with the 2 θ range from 5 to 80° at a scan rate of 1 °/min. Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were taken with a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). X-ray Photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Theta Probe XPS with monochromatized Al K α ($h\nu=1486.6$ eV) source. The steady-state photoluminescence (PL) spectra were obtained by a Shimadzu RF-5310PC fluorometer at an excitation wavelength of 325 nm.

2.3 Transient optical spectroscopy

For time-resolved PL measurements, the excitation pulse (325 nm) was generated from an optical parametric amplifier (TOPASTM, Light Conversion Ltd). The time-resolved PL spectra were obtained using a streak camera (Optronics GmbH) with a time resolution of 10 ps. The PL decay profile is fitted by using multiexponential function [34,35].

$$I_t = \sum_{i=1}^n A_i \exp\left(-\frac{t}{\tau_i}\right)$$

where I_t is intensity, A_i is the relative magnitude of the i th decay and τ_i is the i th decay time.

2.4 Photocatalytic hydrogen evolution

Typically, 5 mg of the prepared photocatalysts were suspended in 10 mL aqueous solution of 0.1 M L-ascorbic acid (pH=4.0). Pt cocatalyst (0.5 wt%) was in-situ loaded by adding 61 μ L of H_2PtCl_6 (0.08 wt%) aqueous solution into the suspension followed by the irradiation of a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). The suspension was then purged with argon to drive away the residual air before sealed in a quartz flask. The photocatalytic hydrogen evolution was carried out by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). The output light intensity is 200 mW/cm². The gas product composition was analyzed periodically by an Agilent 7890A gas chromatograph (GC) with TCD detector.

2.5 Photocatalytic CO₂ reduction

In the photocatalytic reduction of CO₂, 20 mg of the sample was uniformly

dispersed on a glass substrate with a base area of $2.5 \times 2.5 \text{ cm}^2$, which was then put into a quartz reactor (90 mL). Prior to irradiation, the reactor was purged with high-purity CO_2 gas and 0.1 mL ultrapure water was injected into the reactor. A 500-W Xenon lamp (Newport, USA) with output light intensity of 1200 mW/cm^2 was used as the light source for the photocatalytic reaction. During the irradiation, the gas product was taken from the reaction cell at given intervals to quantitatively analyze gas product composition by an Agilent 7890A gas chromatograph (GC) with TCD detector.

2.6 Photoelectrochemical measurements

Photocurrent measurements were performed on an electrochemical workstation (CHI852c, CH Instruments) with a three-electrode configuration. Our sample, Ag/AgCl electrode, and Pt-wire electrode were employed as the working, reference, and counter electrode, respectively. Irradiation was carried out by using a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420 \text{ nm}$) and an output intensity of 200 mW/cm^2 . The Na_2SO_4 solution (0.1 M) was used as the electrolyte. The working electrodes were prepared by spreading aqueous slurries of various samples on FTO glass substrate, using adhesive tapes as spaces to obtain a $1 \text{ cm} \times 1 \text{ cm}$ electrode. The applied bias was set as 0.4 V.

3. Results and discussion

The XRD patterns of the as-prepared $\text{g-C}_3\text{N}_4$, In_2O_3 , and $\text{In}_2\text{O}_3\text{-C}_3\text{N}_4$ hybrids (10 wt% In_2O_3) are shown in Fig. 1. Two pronounced diffraction peaks locate at 27.4°

and 13.1° for $\text{g-C}_3\text{N}_4$, which could be ascribed to the characteristic interlayer stacking peak of aromatic systems as the (002) peak for graphitic materials, and the interplanar separation as the (100) peak, respectively [33,36]. The XRD pattern of In_2O_3 gives rise to six distinct diffraction peaks at 21.5° , 30.6° , 35.6° , 45.4° , 50.9° , and 60.8° , which can be attributed to the (211), (222), (400), (431), (440), and (622) crystal planes of cubic In_2O_3 (JCPDS No. 71-2194), respectively. The In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrids exhibit characteristic XRD peaks of both In_2O_3 and $\text{g-C}_3\text{N}_4$.

TEM and SEM images (Fig. 2) are taken to directly analyze the structures of the samples. Fig. 2a indicates that the polymeric $\text{g-C}_3\text{N}_4$ has a sheet-like structure. The pure In_2O_3 sample prepared without $\text{g-C}_3\text{N}_4$ is shown as nanoparticle aggregation (Fig. 2b). However, in the presence of $\text{g-C}_3\text{N}_4$, the solvothermal process generated small In_2O_3 nanocrystals well spreading on the $\text{g-C}_3\text{N}_4$ surface, as shown by Fig. 2c. The HRTEM image (Fig. 2d) confirms the existence of small In_2O_3 nanocrystals, and the lattice fringes with d spacing of 0.293 nm can be assigned to the (222) crystal plane of cubic In_2O_3 .

Fig. 3 shows the absorption spectra of the prepared $\text{g-C}_3\text{N}_4$, In_2O_3 , and In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrid (10 wt% In_2O_3). The pure $\text{g-C}_3\text{N}_4$ and In_2O_3 samples presented a similar absorption edge at ~ 450 nm with wide overlap between their absorption spectra, thereby the absorption feature of the In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrids showed very little difference with that of pure $\text{g-C}_3\text{N}_4$. We further examine the In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrid (10 wt% In_2O_3) through XPS. As shown in Fig. 4a, the peak of C 1s binding energies at 284.6 eV and 288.2 eV can be ascribed to sp^2 C-C bonds and

sp²-bonded carbon in N-containing aromatic rings (N–C=N), respectively, which are the major carbon species in the g-C₃N₄ [37,38]. The weak shoulder that can be deconvoluted into a peak at 285.8 eV could be assigned to sp³-coordinated carbon bonds from the defects on g-C₃N₄ surface [21,36]. The N 1s spectrum showed two clear peaks (Fig. 4b) at 398.7 eV and 401.1 eV, corresponding to sp²-bonded N involved in the triazine rings (C–N=C) and amino groups (C–N–H). And the tiny shoulder between these two peaks can be deconvoluted into a peak at 399.8 eV caused by the tertiary nitrogen N–(C)₃ groups [39,40]. The binding energies of In 3d locate at 444.4 and 451.9 eV (Fig. 4c), which can be assigned to the In³⁺ in In₂O₃ nanocrystals [29,41]. The O 1s peaks at 529.7 and 531.5 eV (Fig. 4d) can be assigned to the oxygen in In₂O₃ nanocrystals.

Photocatalytic activities of the prepared samples for hydrogen evolution under visible light ($\lambda > 420$ nm) irradiation were evaluated by using L-ascorbic acid as the sacrificial reagent to consume photoinduced holes, and 0.5 wt% Pt was in-situ deposited as cocatalyst onto the samples to reduce the overpotential of H₂ evolution. L-ascorbic acid has been proved as an effective water soluble electron donor since its ascorbate anion can function as reductive quencher and also allows for the incorporation of a large amount of L-ascorbic acid in the aqueous reaction system [42-44]. Fig. 5a shows the H₂ evolution plots by g-C₃N₄, In₂O₃, and In₂O₃-g-C₃N₄ hybrids (10 wt% In₂O₃) as a function of irradiation time. The pure In₂O₃ sample did not show noticeable H₂ evolution, and the pure g-C₃N₄ showed a H₂ generation rate of 0.19 μ mol/h. Remarkably, when 10 wt% In₂O₃ nanocrystals are decorated on

g-C₃N₄ surfaces, the hybrid structure exhibited 5 times higher H₂ generation rate (0.99 umol/h) than the pure g-C₃N₄.

However, the decoration content of In₂O₃ showed considerable influence on the photocatalytic activity of the In₂O₃-g-C₃N₄ hybrids. Even with small amount of In₂O₃ (2.5 wt%) nanocrystals on g-C₃N₄ surfaces, the H₂ evolution amount can be 2.4 times higher than that of pure g-C₃N₄. As shown in Fig. 5b, the photocatalytic activity of the In₂O₃-g-C₃N₄ hybrids increases with more H₂ generation as the In₂O₃ content rise to 10 wt%. However, excessive In₂O₃ nanocrystals (>10 wt%) grown on g-C₃N₄ surfaces led to decreased photocatalytic activity in H₂ generation, which might be due to the aggregation of In₂O₃ nanocrystals. As shown in Fig. 6a, in the hybrid sample with 20 wt% In₂O₃, excess In₂O₃ nanocrystals are aggregating on the g-C₃N₄ surface, which reduces the interface area between In₂O₃ and g-C₃N₄ and thereby lower the charge separation efficiency relying on interfacial electron transfer. In addition, over-coverage of In₂O₃ may reduce reactive sites on g-C₃N₄ surfaces that are needed to quench the holes. This would also cause decreased photocatalytic activity. In short, our observation indicates that the optimal decoration amount of In₂O₃ nanocrystals is 10 wt% to obtain the highest photocatalytic activity for H₂ generation. We further explore the stability of the optimal In₂O₃-g-C₃N₄ hybrids (10 wt% In₂O₃) by a four-run cycling test of photocatalytic hydrogen evolution. Fig. 6b reveals that no obvious decrease of H₂ evolution was observed after the four cycles under 16-h visible light irradiation, suggesting the excellent stability of the In₂O₃-g-C₃N₄ hybrids in the reactions.

In order to further demonstrate the improved photocatalytic activity by the in-situ grown In_2O_3 nanocrystals on $\text{g-C}_3\text{N}_4$, the prepared samples were evaluated by using reaction of photocatalytic CO_2 reduction into hydrocarbon fuels that is known as a challenging but promising application for sustainable energy resources [45-47]. As shown in Fig. 7a, after 4-h irradiation, the optimal In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrids with 10 wt% In_2O_3 exhibited a CH_4 production yield of 76.7 ppm (over 20 mg samples) without any cocatalyst, which is more than 3 times higher than that of pure $\text{g-C}_3\text{N}_4$ and more than 4 times higher than that of pure In_2O_3 . The influence of In_2O_3 loading content on the CH_4 production yield showed a similar trend with that on photocatalytic H_2 generation. Note that these tests of photocatalytic CO_2 reduction were carried out without loading any cocatalyst. Indeed, if we photo-deposited 0.5 wt% Pt-cocatalyst onto the In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrids (10 wt% In_2O_3), the CH_4 production yield could be further promoted to 159.2 ppm upon 4-h irradiation. This indicates that in the photocatalytic CO_2 reduction, the Pt cocatalyst still can act as electron sinks to effectively improve the charge separation of the In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrid structure.

We also carried out the photoelectrochemical measurements to obtain the transient photocurrent responses for the samples of $\text{g-C}_3\text{N}_4$, In_2O_3 , and 10 wt% In_2O_3 - $\text{g-C}_3\text{N}_4$ under several on-off cycles of irradiation. As shown in Fig. 8, The In_2O_3 - $\text{g-C}_3\text{N}_4$ hybrid sample shows the highest photocurrent intensity among the three samples. This observation indicates that the formed In_2O_3 - $\text{g-C}_3\text{N}_4$ heterojunctions allow for the more efficient separation of photogenerated

electron-hole pairs as compared to the individual g-C₃N₄ and In₂O₃.

On the basis of the above experimental results, we believe that the enhanced photocatalytic activities by the in-situ grown In₂O₃ nanocrystals are attributed to the interfacial transfer of photogenerated electrons and holes between g-C₃N₄ and In₂O₃, which leads to effective charge separation on both parts. To further prove this assumption, we performed measurements by using both steady-state and transient photoluminescence (PL) spectroscopy. Fig. 9a shows that at an excitation wavelength of 325 nm, the pure g-C₃N₄ sample exhibits a strong emission peak centered at ~450 nm. In comparison, when 10 wt% In₂O₃ nanocrystals were present on the g-C₃N₄ surface, the intensity of this emission band dropped significantly, indicating efficient transfer of photoexcited electrons from g-C₃N₄ to In₂O₃ nanocrystals. The lifetime of charge carriers in the In₂O₃-g-C₃N₄ hybrids (10 wt% In₂O₃) were examined by using time-resolved transient PL spectroscopy, as shown in Fig. 9b. The fitted lifetimes of the PL decay profile are listed in Table 1. The pure g-C₃N₄ sample exhibits only one radiative lifetime of 3 ns, which is associated with the photoexcited electron-hole pairs in g-C₃N₄ that eventually undergo recombination [48]. While for the In₂O₃-g-C₃N₄ hybrids, a shorter PL lifetime component ($\tau_1=0.71$ ns with a weighing factor $A_1 = 54.7\%$) appears, suggesting that some excited electrons undergo rapid transfer from g-C₃N₄ to In₂O₃. This evidence of fast electron-injection confirms that the formation of In₂O₃-g-C₃N₄ heterostructures remarkably promotes charge transfer efficiency, thereby favoring the photocatalytic reactions for H₂ evolution and CO₂ reduction.

Fig. 10 shows the schematic illustration of the possible photocatalytic mechanism. The enhanced photocatalytic activity could be attributed to the effective interfacial charge transfer between In_2O_3 and $\text{g-C}_3\text{N}_4$ across the heterojunction. Since the CB of $\text{g-C}_3\text{N}_4$ (~ -1.1 eV vs. NHE) is more negative than that of In_2O_3 (~ -0.6 eV vs. NHE), the photoexcited electrons on the CB of $\text{g-C}_3\text{N}_4$ can rapidly transfer to the CB of In_2O_3 . These accumulated electrons, together with the electrons excited from the VB of In_2O_3 , are capable of reducing H^+ and/or CO_2 into valuable fuels. While the corresponding VB position of In_2O_3 ($\sim +2.2$ eV vs. NHE) is more positive than that of $\text{g-C}_3\text{N}_4$ ($\sim +1.6$ eV vs. NHE), the photogenerated holes on the VB of In_2O_3 can migrate to the VB of $\text{g-C}_3\text{N}_4$, subsequently to oxidize the electron donor (ascorbic acid for H_2 production and OH^- for CO_2 reduction, respectively). As such, effective charge separation can be achieved, resulting in longer lifetime of the photogenerated charge carriers and thereby enhanced photocatalytic activities.

4. Conclusions

In summary, we have successfully prepared $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ hybrid structures through a simple solvothermal method. A small amount of In_2O_3 nanocrystals grown onto $\text{g-C}_3\text{N}_4$ surfaces leads to considerable improvement on the photocatalytic activities for H_2 evolution and CO_2 reduction. The enhanced activities are attributed to the effective interfacial charge transfer across the $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ heterojunction, as evidenced by steady-state and transient PL studies. This work provides a new insight on developing 0D-2D semiconductor hetero-structured systems with effective charge

separation for highly efficient solar-to-fuels conversion.

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Figure captions

Fig. 1 XRD patterns of g-C₃N₄, In₂O₃, and 10 wt% In₂O₃-g-C₃N₄.

Fig. 2 TEM image of (a) g-C₃N₄; (b) In₂O₃; and (c) 10 wt% In₂O₃-g-C₃N₄; (d) HRTEM image of 10 wt% In₂O₃-g-C₃N₄. Inset of Fig. 2a is the SEM image of g-C₃N₄.

Fig. 3 UV-vis absorption spectra of g-C₃N₄, In₂O₃, and 10 wt% In₂O₃-g-C₃N₄.

Fig. 4 XPS spectra of 10 wt% In₂O₃-g-C₃N₄: (a) C 1s; (b) N 1s; (c) In 3d; (d) O 1s.

Fig. 5 (a) Plots of photocatalytic H₂ evolution amount versus irradiation ($\lambda > 420$ nm) time for different samples (5mg); (b) Comparison of H₂ evolution amount over different samples (5 mg) after visible light irradiation for 4 hours.

Fig. 6 (a) TEM image of 20 wt% In₂O₃-g-C₃N₄; (b) Cycling test of photocatalytic H₂ evolution for 10 wt% In₂O₃-g-C₃N₄.

Fig. 7 Comparison of CH₄ production amount from photocatalytic CO₂ reduction after 4-h UV-vis irradiation (a) over different samples (20 mg) without any cocatalyst; (b) over 10 wt% In₂O₃-g-C₃N₄ (20 mg) with and without Pt loading.

Fig. 8 Transient photocurrent responses for the g-C₃N₄, In₂O₃, and 10 wt% In₂O₃-g-C₃N₄ samples.

Fig. 9 (a) Steady-state PL spectra and (b) Time-resolved transient PL decay for pure g-C₃N₄ and the 10 wt% In₂O₃-g-C₃N₄.

Fig. 10 Schematic illustration of the photocatalytic process for H₂ evolution and CO₂ reduction on the In₂O₃-g-C₃N₄ nanohybrids.

Fig. 2

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Fig. 8

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Fig. 10