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Abstract

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Keywords

electrostatically, assembled, construction, ternary, tio₂-cu@c, hybrid, electronic, enhanced, mediator, solar-to-hydrogen, evolution, employing, amorphous, carbon, dots

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Zhu, J., Zhang, M., Xiong, J., Yan, Y., Li, W. & Cheng, G. (2019). Electrostatically assembled construction of ternary TiO₂-Cu@C hybrid with enhanced solar-to-hydrogen evolution employing amorphous carbon dots as electronic mediator. *Chemical Engineering Journal*, 375 121902-1-121902-7.

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**Electrostatically assembled construction of ternary TiO₂-Cu@C
hybrid with enhanced solar-to-hydrogen evolution employing
amorphous carbon dots as electronic mediator[#]**

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[#]The details of experiments are provided in the Supporting Information.

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Abstract

The huge demand for renewable hydrogen produced by water splitting has prompted people to conduct in-depth research on the hydrogen evolution reaction for the development of earth-abundant, non-precious, and multi-functional metal catalysts. Herein, a noble-metal-free ternary composite of TiO₂-Cu@C was prepared by electrostatic self-assembly loaded copper nanoparticles and amorphous carbon dots (CDs) on porous TiO₂ microrods. The good conductivity of the CDs was beneficial to promoting the charge transfer and separation, generating an enhanced solar-to-hydrogen performance on TiO₂-Cu@C. The optimized TiO₂-Cu@C reveals a stable and notable hydrogen evolution rate of 3911 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which is 1.6 times that of TiO₂-Cu and many times higher than that of TiO₂. Instead of providing active sites for hydrogen production, the CDs act as an electronic mediator and provide another electron pathway to further enhance the activity of TiO₂-Cu, where the photogenerated electrons on TiO₂ could pass through the CDs to the copper cocatalyst and reduce water to hydrogen.

Keywords

TiO₂-Cu@C hybrids; photocatalytic water splitting; electrostatical assemble; carbon dots

Introduction

Hydrogen (H₂) is a clean energy source, which does not produce other exhaust gases in combustion except for water. It can play an important role in replacing fossil fuels, further solving environmental problems and the energy crisis. At present, using semiconductor-based photocatalysis technology to covert solar energy into hydrogen is being considered as a potential approach to dealing with these issues. In the most recent progress on photocatalytic systems, the construction of heterojunctions has become a research hotspot because of its feasibility and effectiveness for space separation of

photogenerated electron-hole pairs. The research on TiO₂ used alone has made some progress, but its activity towards water-splitting is still limited. [1-4] Because of its own characteristics, photogenerated electron-hole pairs recombine rapidly, and it has a wide band gap and fewer active sites just like ZnO [5, 6]. Yet the TiO₂-based photocatalytic system for water splitting is also progressing. [7-12] For example, conventional type II heterojunctions of TiO₂, TiO₂ *p-n* heterojunctions, TiO₂/metal heterojunctions, and TiO₂-based Z-scheme heterojunctions have been constructed to greatly enhance its photocatalytic activity towards hydrogen production, although there are few studies on further improvement of the activity of binary complexes through rational surface/interface engineering.

Cost-effective metallic Cu has recently been recognized as a good substitute for precious metals in hydrogen production. [13-18] It was found that metallic Cu has moderate catalytic activity towards hydrogen evolution compared with noble metals according to theoretical studies. [19] When metallic Cu acts as a cocatalyst can optimize the free energy of hydrogen adsorption and improve the catalytic activity of hydrogen production, just like some non-precious electrocatalysts [20, 21]. Moreover, metallic Cu with a specific size and morphology exhibits surface plasmon resonance (SPR) effects similar to those of noble metals. [22-24] Metallic Cu as a cocatalyst, however, has only a single electron transfer path with the semiconductor, and it is likely to be oxidized in the course of a long-term catalytic process because of its direct contact with the semiconductor surface. This limits the photocatalytic activity of binary Cu-based photocatalysts, which needs further improvement.

Carbon dots, as a novel class of nanocarbons, have been widely used in the field of photocatalysis due to their excellent photoelectric properties. [25-29] Zhang et al. applied the electron reservoir characteristic of CDs to capture the electrons generated by metallic Cu nanoparticles, thus hindering electron-hole recombination to improve photocatalytic activity. [26] According to Zhang et al., CDs play

a dual role in improving photocatalytic activity, as photosensitizer and as electron reservoir. [27] In Bian's group, coupling CDs with TiO_2 , in which CDs acted as electron collectors and active sites, makes the activity towards reducing Cr(VI) to Cr(III) about 5.4 times higher than that of pure TiO_2 . [28] Owing to the high conductivity of CDs [30], they could capture photogenerated electrons from the conduction band of semiconductors, so decorating CDs on the binary materials would provide other multi-step electron transfer pathways and possibly inhibit the photocorrosion of the photocatalyst.

In this work, we present a reasonably designed method that operates through a hierarchical electrostatic assembly method to fabricate ternary $\text{TiO}_2\text{-Cu@C}$ composites. The amorphous carbon dots were dispersed on the $\text{TiO}_2\text{-Cu}$ to synthesize $\text{TiO}_2\text{-Cu@C}$ nanocomposites without noble metals, resulting in efficient photocatalytic water splitting. The H_2 evolution rate on $\text{TiO}_2\text{-Cu@C}$ was further enhanced by about 1.6 times over that of the $\text{TiO}_2\text{-Cu}$ binary compound. The improved charge separation was possibly due to the formation of carbon-Cu and carbon- TiO_2 interfaces, which creates another type of electron transfer pathway: electrons pass through the CDs on TiO_2 to metallic Cu to reduce water, beyond the direct electrons transfer from TiO_2 to metallic Cu. This may be the origin of the enhancement of photocatalytic activity of $\text{TiO}_2\text{-Cu@C}$.

Results and discussion

To better understand the electrostatic assemble method for the synthesis of ternary $\text{TiO}_2\text{-Cu@C}$ composites, the surface charges of the related materials estimated by zeta-potential measure were depicted in Figure 1. It can be observed that the materials of TiO_2 , Cu, Carbon dots, and $\text{TiO}_2\text{-Cu}$ had different zeta potential.

Figure 1 Zeta potentials of mesoporous TiO₂ microrods (m-TiO₂), TiO₂-Cu²⁺ precursor, metallic Cu, TiO₂-Cu, and carbon dots (average results of three tests)

The synthesis strategy and formation process of TiO₂-Cu@C are shown in **Figure 2**, in which surface charges play an important role in such a preparation approach. Firstly, negatively charged porous TiO₂ ($\zeta = 28.5$ mV) adsorbed positively charged Cu²⁺-precursor to form the TiO₂-Cu²⁺-precursor ($\zeta = -31.4$ mV). Afterwards, the TiO₂-Cu²⁺-precursor was reduced to a TiO₂-Cu ($\zeta = 5.15$ mV) hybrid that was positively charged on its surface. When the carbon dots solution was added to the TiO₂-Cu, the negatively charged carbon dots ($\zeta = -42.8$ mV) would be electrostatically attracted and loaded on TiO₂-Cu to form the TiO₂-Cu@C ternary composite. Due to the effect of electrostatic attraction, the strong connection existing among the TiO₂, metallic Cu, and carbon dots could make the modified nanoparticles disperse uniformly.

Figure 2. Schematic illustration of the multi-step positive-negative-negative electrostatic assembly synthesis of $\text{TiO}_2\text{-Cu@C}$. (a) mesoporous TiO_2 microrods (m-TiO_2) with positively charged surface in aqueous solution; (b) formation of an electron-bi-layer after absorption of $[\text{CuL}_2(\text{OH})]^{3-}$ precursor onto m-TiO_2 ; (c) formation of $\text{TiO}_2\text{-Cu}$ composite with negatively charged surface in aqueous solution; (d) prepared ternary $\text{TiO}_2\text{-Cu@C}$ hybrid through mixing $\text{TiO}_2\text{-Cu}$ composite with carbon dot solution under stirring at room temperature.

The crystal structure and morphology of the $\text{TiO}_2\text{-Cu@C}$ hybrid were characterized by X-ray diffraction (XRD) (**Figure 3a-b**), X-ray photoelectron spectroscopy (XPS) (**Figure S1**), scanning electron microscopy (SEM) (**Figure 3d**, **Figure S2**), transmission electron microscopy (TEM) (**Figure 3e**), and high resolution TEM (HRTEM) (**Figure 3f**). As shown in **Figure 3a**, most of the X-ray diffraction peaks of the products correspond to anatase TiO_2 (JCPDS card No. 73-1764). The characteristic diffraction peak at $2\theta = 43.3^\circ$ that is indexed to the (111) planes of metallic copper (JCPDS card No. 70-3039) was clearly observed

(Figure 3b). In addition, Fourier transform infrared spectroscopy (FT-IR) characterization was performed to further confirm that CDs were attached on the TiO₂-Cu composite (Figure 3c). The characteristic absorption peaks of the CDs could be detected at 2980, 1568, and 1402 cm⁻¹, which are attributed to the skeleton vibrations of *sp*² C-H, C=O, and C-OH, [27] implying the existence of CDs in the TiO₂-Cu@C composite.

The chemical states of TiO₂, metallic Cu, and CDs were determined by XPS analysis. As shown in Figure S1, the XPS spectra of C 1s, Ti 2p, O 1s, and Cu 2p were compared between pure TiO₂ and TiO₂-Cu@C. After curve fitting, the C 1s spectrum exhibited three typical peaks at 284.6, 286.3, and 288.3 eV, which are attributed to C-C, C-O and O=C-O bonds, respectively. [27, 31, 32] It can be seen that the relative intensity of the characteristic peaks of C 1s increases with the decoration of CDs. Obviously, the relative intensities of the characteristic peaks of Ti 2p (binding energy = 458.6, 464.4 eV) and O 1s (binding energy = 529.8 eV) are lower than that of pure TiO₂, which suggests successful modification by the carbon dots. Moreover, the XPS spectrum of Cu 2p (Figure S1d) displays two peaks at 932.2 and 951.8 eV, which are associated with Cu 2p_{3/2} and Cu 2p_{1/2} of copper metal, [33-35] which can only be observed on ternary TiO₂-Cu@C hybrid. The results are consistent with the XRD images, demonstrating the presence of metallic Cu that is loaded on TiO₂.

Figure 3. (a) XRD patterns of TiO₂, TiO₂-Cu, and TiO₂-Cu@C hybrid; (b) magnified images that corresponds to the XRD; (c) FTIR spectra of TiO₂, carbon dots, and TiO₂-Cu@C; (d) SEM, (e) TEM, and (f) HRTEM images of TiO₂-Cu@C hybrid (insets: inverse fast Fourier transform (IFFT) images).

As shown in **Figure S2**, porous TiO₂ has rod-like structure, where the microrods are about 3-5 μm in length and 0.8-1.1 μm in diameter. It can be seen from the TEM image (**Figure S2**) that the porous rod structure is composed of nanocrystalline TiO₂. Moreover, the high-resolution TEM (HRTEM) images give an understanding of the atomic arrangement on the surfaces of prepared nanoparticles. The lattice fringes with distances of 0.354 nm are well assigned to TiO₂ in the HRTEM image (**Figure S2**). The XRD pattern of amorphous carbon dots is consistent with those reported in the literature [36], as shown in **Figure S3a**. The images (**Figure 3d-e**) of TiO₂-Cu@C displayed a similar rod-like porous structure, and it was composed of aggregated nanoparticles. The CDs could not be distinguished because of their small nanosize (**Figure S3b**) and closeness to the nanoparticles of TiO₂. In the HRTEM image of TiO₂-Cu@C in **Figure 3f**, the lattice fringes with spacing of 0.352 nm are in accordance with the anatase TiO₂ (101) interplanar spacing, while the 0.203 nm fringes agree with the (111) planes of metallic Cu. The results indicate that ternary TiO₂-Cu@C hybrid can be formed via the electrostatic assembly method.

Element mapping was performed to further confirm the composition of the $\text{TiO}_2\text{-Cu@C0.5}$ hybrid.

Figure S4 displays the area where the elemental mapping performed and the distribution of elements in the $\text{TiO}_2\text{-Cu@C0.5}$ hybrid with energy-dispersive X-ray (EDX) elemental mapping. The four different colors represent the distribution of O, Cu, C and Ti. The existence of the four elements in the sample is in agreement with the proposed $\text{TiO}_2\text{-Cu@C0.5}$ hybrid. As shown in **Figure S4**, it was clearly observed that Ti, O, Cu and C elements were evenly distributed on TiO_2 , which indicated the $\text{TiO}_2\text{-Cu@C}$ hybrid was successfully synthesized by this method. Moreover, the weight percentage of the elements in the $\text{TiO}_2\text{-Cu@C0.5}$ was roughly estimated through selecting two different microrods in the SEM image depicted in **Figure S5**. The corresponding data were listed in Table S1 and Table S2, and it was found that the weight percentage of carbon dot in the $\text{TiO}_2\text{-Cu@C0.5}$ is about 17%. A comparison of ultraviolet-visible diffuse reflectance spectra of TiO_2 , $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-C}$, and $\text{TiO}_2\text{-Cu@C}$ is presented in **Figure S6**. Compared with pure TiO_2 , the absorption edge of $\text{TiO}_2\text{-Cu}$ has a red shift, which means that the loading with metallic Cu will enhance light absorption. After further modification by the CDs, a certain enhancement in the absorption is observed in the range of 550-750 nm on $\text{TiO}_2\text{-Cu@C}$. This could explain the successful preparation of $\text{TiO}_2\text{-Cu@C}$ composite through modification by the metallic Cu particles and CDs decorated on the TiO_2 mesoporous microrods.

Water splitting technology driven by solar energy is a promising clean hydrogen production technology. Consequently, the photocatalytic properties of $\text{TiO}_2\text{-Cu@C}$ nanocomposites were studied under UV-vis light irradiation with methanol (20 vol%) aqueous solution as the hole sacrificial agent.

Figure 4a shows the photocatalytic activity of $\text{TiO}_2\text{-Cu@C}$ hybrids and the control samples for hydrogen production. There is no obvious H_2 generation on TiO_2 and binary $\text{TiO}_2\text{-C}$. This is probably due to the fact that the carbon dots only serve as electronic mediators rather than active sites. When

photocatalytic reaction was carried out on binary TiO₂-Cu, the evolution rate of H₂ was enhanced sharply to 2462 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which means that metallic Cu acts as a cocatalyst with benefits for the photocatalytic activity. Furthermore, the activity of TiO₂-Cu increased by 1.6 times to 3911 $\mu\text{mol g}^{-1} \text{h}^{-1}$ when the optimum amount of CDs was used to form TiO₂-Cu@C0.5 ternary composite. Compared with other reported catalysts, TiO₂-Cu@C0.5 hybrid has better hydrogen evolution activity as shown in **Table 1**. The high photoactivity is attributed to the synergistic effects of the metallic Cu and carbon dots in TiO₂-Cu@C, which greatly improves the separation of photogenerated electrons and holes. At the same time, it was found that the hydrogen evolution activity of ternary TiO₂-Cu@C was lower than that of binary TiO₂-Cu composite when the CDs content was lower or higher than the optimum loading amount. We speculate that when the loading of CDS is lower than the optimum amount, because the good conductivity of CDs and metallic Cu, CDs near metallic Cu but not in contact will divert part of the photogenerated electrons from TiO₂, which makes the catalytic activity of TiO₂-Cu slightly higher than that of TiO₂-Cu@C_x; When the loading of CDs is higher than the optimum amount, excessive CDs will cover the active sites of metallic Cu cocatalyst, thus reducing the catalytic activity. The apparent quantum efficiency (AQE) of ternary TiO₂-Cu@C0.5 was measured using a 365 nm (± 2 nm) band-pass filter (12.8 mW/cm²), and the AQE value was calculated to be 4.64% according to the previously reported work [37-39]. More importantly, TiO₂-Cu@C exhibits high photocatalytic stability. As depicted in **Figure 4b**, the photocatalytic hydrogen evolution rate did not decrease detectably after four cycles, which indicates that TiO₂-Cu@C photocatalyst has good stability and reusability.

Figure 4. (a) Hydrogen production activity of different photocatalysts; (b) photostability for the H₂ production

of TiO₂-Cu@C0.5 under UV-vis light.

Table 1. Photocatalytic performance comparison for H₂ evolution with other reports

Materials	Amount of catalyst (g)	H ₂ evolution rate (μmol g ⁻¹ h ⁻¹)	Ref.
TiO ₂ -CQDs	0.05	196	[40]
g-C ₃ N ₄ -CQDs-Pt	0.05	3538	[41]
TiO ₂ -CQDs	0.02	395	[42]
g-C ₃ N ₄ -CQDs-MoS ₂	0.05	212.4	[43]
TiO ₂ -Cu@C	0.025	3911	This work

To better understand the photocatalytic activity of TiO₂-Cu@C, the specific surface and pore size distribution were studied (**Figure S7**). **Table S3** shows there are no obvious differences among the samples in their BET surface areas and pore-sizes, which means that the specific surface area has no effect towards the improvement of photocatalytic activity. Photoelectrochemical tests were carried out to study the performance of the composite catalyst, as shown in **Figure 5a**. As expected, TiO₂-Cu@C

exhibits the highest photocurrent intensity compared with TiO_2 , $\text{TiO}_2@\text{C}$, and $\text{TiO}_2\text{-Cu}$ due to the dual-electron transfer path in the ternary system. Interestingly, sole metallic Cu or carbon dots can greatly improve the charge separation efficiency, which is ascribed to their excellent conductivity. Moreover, electrochemical impedance spectroscopy (EIS) was used to investigate the separation and transfer of photogenerated electron and holes of samples. [44] EIS Nyquist plots of **Figure 5b** depicted that ternary $\text{TiO}_2\text{-Cu}@0.5$ hybrid shows the fastest interfacial charge transfer characteristics compared with pure TiO_2 , $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-C}$. Furthermore, binary $\text{TiO}_2\text{-Cu}$ and $\text{TiO}_2\text{-C}$ composites exhibited smaller arc compared with pure TiO_2 , which indicates that metallic Cu and carbon dots are helpful to inhibit photogenerated electron-hole recombination, which is also consistent with the corresponding photocurrent results.

Figure 5 (a) Photocurrent response and (b) Electrochemical impedance spectra (EIS) of TiO_2 , $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-C}$, and $\text{TiO}_2\text{-Cu}@0.5$.

In addition, the electron transfer of TiO_2 in both the binary and ternary composites was investigated by using photoluminescence (PL), as shown in **Figure S8**. The PL intensity of TiO_2 in both binary and ternary systems is decreased. The marked decline of the PL signals indicates a significant separation of photogenerated carriers, resulting from the efficient electron transfer from the TiO_2 to carbon dots and metallic Cu. In order to further understand the charge carrier dynamics, time-resolved

photoluminescence decay transient spectroscopy was applied to evaluate the charge transfer paths of $\text{TiO}_2\text{-Cu@C}$, and the normalized decay plots are shown in **Figure 6a**. The peak attenuation of photoluminescence was fitted to calculate the amplitude and lifetime, as depicted in **Figure 6b** and **Figure S9** (for detailed calculations see Section S1). The estimated average lifetime of the $\text{TiO}_2\text{-C}$ ($\tau_{\text{Ave}} = 2.95$ ns) is shorter than that of pure TiO_2 ($\tau_{\text{Ave}} = 4.03$ ns), implying the emergence of a non-radiative pathway from the electronic interactions between TiO_2 and the carbon dots. [45, 46] In addition, the emission lifetime of $\text{TiO}_2\text{-Cu}$ ($\tau_{\text{Ave}} = 5.24$ ns) is obviously increased when compared with pure TiO_2 . The results show that metallic Cu deposition on TiO_2 can effectively inhibit charge recombination and prolong carrier lifetime. [47] The results for the ternary $\text{TiO}_2\text{-Cu@C}$ hybrid indicate a longer fluorescence lifetime ($\tau_{\text{Ave}} = 5.27$ ns). It was speculated that there may be two electron transfer pathways that contribute to the hydrogen production in the photocatalytic process for ternary $\text{TiO}_2\text{-Cu@C}$.

Figure 6. (a) time-resolved photoluminescence decay transients and (b) the lifetimes calculated by the exponential decay function of TiO_2 , $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-C}$, and $\text{TiO}_2\text{-Cu@C0.5}$.

Based on the above results and analysis, the details of the photocatalytic process of ternary $\text{TiO}_2\text{-Cu@C}$ heterostructure could be determined. As shown in **Figure 7**, when the photocatalytic reaction occurs, the photogenerated electrons from the valence band (VB) of TiO_2 move to its conduction band

(CB), leaving the holes in the VB. Subsequently, photogenerated electrons are transferred at the TiO_2 -Cu, TiO_2 -C, and carbon-Cu interfaces due to the matching of work functions and intimate contact through two electron transfer paths: (1) direct transfer of the photogenerated electrons from TiO_2 to the metallic Cu or carbon dots; and (2) injection of the photogenerated electrons from TiO_2 to the carbon dots to the metallic Cu. Based on the comprehensive photocatalytic and photoelectric tests, it is proposed that carbon dots can only be used as a medium for electrons, but not as an active site to reduce water to hydrogen. Thus, it was concluded that the further increase in the activity of ternary TiO_2 -Cu@C should be attributed to the transfer of electrons excited on TiO_2 to carbon dots first and then to metallic Cu.

Figure 7. Schematic illustration of the transport and separation of photogenerated electrons in (a) TiO_2 @C, (b) TiO_2 -Cu, and (c) TiO_2 -Cu@C composites.

Conclusions

In conclusion, we have developed a simple and feasible electrostatic self-assembly method to control the synthesis of ternary $\text{TiO}_2\text{-Cu@C}$ composites without noble metal catalysts. The composites exhibited highly efficient photocatalytic activity towards water decomposition into hydrogen. The optimum $\text{TiO}_2\text{-Cu@C0.5}$ hybrid achieved a high hydrogen evolution rate of $3911 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is many times higher than that of pure TiO_2 and 1.6 times higher than that of $\text{TiO}_2\text{-Cu}$. We found that the CDs could not be used as catalysis active sites, but could be used as an electronic mediator, so the enhancement of activity was attributed to effective charge transfer. The formation of the interface between C-Cu and C- TiO_2 provides another route for electron transfer, which enables photogenerated electrons on TiO_2 to be transferred to metallic Cu through CDs, not just by direct transfer to metallic Cu. This rational design could further broaden the preparation of ternary nanocomposites for photocatalysis.

Contributions

GC and JX designed the project, organized the entire research, and revised the manuscript. JZ prepared the materials, did the photocatalysis, photocurrent, and EIS measurements. MZ, YY and WL were involved in interpretation of the result and commented on the manuscript. All authors reviewed the manuscript.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21501137) and Hubei Provincial Natural Science Foundation (2018CFB680). Dr. W. J. Li thanks the Australian Research Council for funding through Discovery Early Career Researcher Award (DECRA, No. DE180101478). The authors also thank Dr. Tania Silver for critical reading of the manuscript.

Conflict of Interest

The authors report no conflict of interest.

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