

View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. Wang, D. Xu, B. Cheng, J. Yu and C. jiang, *J. Mater. Chem. A*, 2017, DOI: 10.1039/C6TA11121A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Hybrid carbon@TiO₂ hollow spheres with enhanced photocatalytic CO₂ reduction activity

Weikang Wang,^a Difa Xu,^{ab} Bei Cheng,^a Jiaguo Yu*^{ac} and Chuanjia Jiang*^a

Photocatalytic conversion of carbon dioxide (CO₂) into solar fuels is an attractive strategy for solving the increasing energy crisis and greenhouse effect. This work reports the synthesis of hybrid carbon@TiO₂ hollow spheres by a facile and green method using carbon nanosphere template. The carbon content of the carbon@TiO₂ composites was adjusted by changing the duration of the final calcination step, and was shown to significantly affect the physicochemical properties and photocatalytic activity of the composites. The optimized carbon@TiO₂ composites exhibited enhanced photocatalytic activity for CO₂ reduction compared with commercial TiO₂ (P25): the photocatalytic CH₄ production rate (4.2 μ mol g⁻¹ h⁻¹) was twice that of TiO₂; moreover, a large amount of CH₃OH was produced (at a rate of 9.1 μ mol g⁻¹ h⁻¹). The significantly improved photocatalytic activity was not only due to increased specific surface area (110 m² g⁻¹) and CO₂ uptake (0.64 mmol g⁻¹), but also to a local photothermal effect around the photocatalyst caused by the carbon. More importantly, UV–vis diffuse reflectance spectra (DRS) showed remarkable enhancement of light absorption owing to the incorporation of visible-light-active carbon core with UV light-responsive TiO₂ shell for increased solar energy utilization. Furthermore, electrochemical impedance spectra (EIS) revealed that the carbon content can influence the charge transfer efficiency of the carbon@TiO₂ composites. This study can bring new insights in designing seminconductor@carbon nanostructures for applications such as solar energy utilization and storage.

Introduction

Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06.

Solar energy conversion toward chemical energy by photocatalysis is an attractive candidate solution for global environmental and energy problems because solar energy is the most abundant and sustainable natural energy source.¹⁻³ Although significant accomplishments in semiconductor photocatalytic materials have been achieved in the past years, the efficiency of photocatalytic carbon dioxide (CO2) conversion toward solar fuels is still rather low and far from commercial applications.⁴⁻⁹ As an abundant, nontoxic, photostable and highly efficient photocatalyst, titania (TiO₂) and Ti-based composites with anatase, rutile, and brookite crystalline structures were exploited and investigated by various methods to enhance photocatalytic activity.10-15 However, there are two disadvantages of TiO₂ in part limiting its applications in photocatalysis: one is the low quantum efficiency due to the high recombination rate of electron-hole pairs generated in photocatalytic reactions. Moreover, TiO2 with a large band gap energy of approximately 3.2 eV can only

utilize ultraviolet (UV) light. Therefore, tremendous efforts have been devoted to solving these problems. For example, photocatalysts with hierarchical, hollow, yolk-shell and other novel structures have been fabricated in recent years.16-19 Hollow structure can increase light-harvesting efficiency due to multi-scattering of light. More exposed TiO2 nanoparticles in hollow structure lead to higher specific surface area. Thus, Ao et al. reported the synthesis of TiO₂ hollow microspheres based on carbon-sphere templates for degradation of methylene blue (MB).¹⁷ Afterward, Chen *et al.* used carbonaceous materials to improve transfer efficiency of charge carriers and enhance light absorption.¹⁹ Integration of semiconductors with carbon materials to form hybrid nanostructure has recently attracted much attention.^{10,18,20,21} In summary, carbon-based materials can act as photo-sensitizer, which greatly improve visible-light absorption. More importantly, both the high electron mobility and increased separation efficiency of electron-hole pairs endow carbon materials with superior electron acceptor and transport channel.22,23

Herein, the carbon@TiO₂ composite hollow spheres were systematically synthesized based on colloidal carbon spheres. TiO₂ hollow spheres with different carbon contents were fabricated by changing the duration of calcination. The carbonaceous materials inside hollow structure not only increased specific surface area and CO₂ uptake capacities of the composite samples, but also created a local photothermal effect around the photocatalyst. As expected, the carbon@TiO₂ composite nanostructure exhibited excellent photocatalytic CO₂

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Luoshi Road 122, Wuhan 430070, P. R. China. *E-mail: jiaguoyu@yahoo.com (J. Yu); jiangcj2016@yahoo.com (C. Jiang)

Jiang) ^b Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha, 410022, P. R. China

^c Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE

Page 2 of 11

reduction performance and selectivity under simulated solar light compared with P25 TiO₂. Moreover, the fabrication process of the hollow structure and photocatalytic CO₂ reduction mechanism of carbon@TiO₂ composite products were investigated. The results of this study provide a new idea to finely control novel nanostructures in photocatalysis.

Experimental

Sample preparation

All reagents were A.R. grade from Shanghai Chemical Reagent Factory of China and used as received. Deionized (DI) water was used in all experiments.

For the synthesis of carbon nanosphere (CNS) mold,²⁴ 12 g of glucose was dissolved in DI water (80 mL) to form a clear solution, which was sealed in a 100 mL Teflon-lined autoclave and maintained at 180 °C for 4 h. The obtained brown products were isolated by centrifugation and ultrasonication, washed with water and ethanol five times, and then dried at 55 °C for 8 h under vacuum.

In a typical synthesis of hollow TiO₂ spheres with CNS cores, the initial suspension was prepared by mixing 0.3 g of as-prepared CNS and 60 mL of ethanol. Then, 3 mL of tetrabutyl titanate (TBOT) was added into the ethanolic suspension, ultrasonically redispersed and then stirred vigorously for 2 h in a sealed beaker. The products were centrifuged, washed and ultrasonically redispersed in ethanol for five cycles. After being aged in air at room temperature for 12 h and oven-dried at 55 °C under vacuum for 4 h, carbon spheres with TiO₂ precursor shell (CSTS) were formed.²⁴ In order to fabricate carbon@TiO₂ hollow structure, the CSTS were put into a crucible with a cover and then heated in static air inside a furnace at 450 °C for 60, 90, 120 and 180 min, and labeled as T60, T90, T120 and T180, respectively.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-RB X-ray diffractometer (Japan) with Cu K_{α} radiation source. Raman analysis was carried out on a Renishaw inVia micro-Raman spectrometer in the back-scattering geometry of 633 nm Ar⁺ laser as an excitation source. The morphology observation of the as-prepared products was conducted on a field emission scanning electron microscope (FESEM) (JSM 7500F). Transmission electron microscopy (TEM) images were observed by a JEM-2100F electron microscope (JEOL, Japan). The elemental mapping images were performed on Tecnai G2 F30 scanning transmission electron microscopy (STEM). The nitrogen adsorption and desorption isotherms were obtained by an ASAP 2020 (Micromeritics Instruments, USA) nitrogen adsorption apparatus. The CO₂ adsorption measurement was carried out at ambient temperature by an ASAP 3020 carbon dioxide adsorption apparatus (Micromeritics, USA). The UVvis diffuse reflectance spectra (DRS) of the composites were measured on a Shimadzu UV-vis spectrophotometer (UV2550, Japan). Fourier transform infrared (FTIR) spectra of all the samples were recorded via a Shimadzu IR Affinity-1 FTIR

spectrometer (Japan). X-ray photoelectron spectroscopy, (XPS) was performed by using ultrahigh vacuum $\mathbb{VG}^{1}\mathbb{E}\mathbb{X}^{C}\mathbb{A}\mathbb{E}\mathbb{A}\mathbb{B}^{1}\mathbb{P}\mathbb{H}^{0}$ electron spectrometer using Al K_a radiation as X-ray source. Thermal gravimetric analysis (TGA) was accomplished by a Shimadzu DTG-60H analyzer (Japan) in air. Electrochemical analysis was performed on a CHI660C workstation (Shanghai Chenhua Instruments, China) using a three-electrode electrochemical cell with a working electrode, a platinum counter electrode and a Ag/AgCl reference electrode in electrolyte of 0.5 M Na₂SO₄ aqueous solution. The working electrode was prepared by coating samples onto the fluorine-tin oxide (FTO) glass.

Photocatalytic CO₂ reduction test

The photocatalytic CO₂ reduction tests were carried out in a 200 mL custom-made Pyrex glass reactor at atmospheric pressure and ambient temperature, similar to our previously reported procedures.²⁵ The gaseous products were determined by the retention time and quantified by calibration with a standard gas mixture. Photocatalytic CO₂ reduction studies of each composite sample were repeated three times.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

The in situ DRIFTS experiments were performed on a Nicolet iS50 FTIR spectrometer (Thermo Fisher, US), similar to our previously reported literature.²⁵ A representative sample T120 was degassed at 100 °C prior to measurement. The specimen chamber loaded with the sample was purged with flowing nitrogen for 1 h to remove air, and then a mixed gas of CO₂ and water vapour was flowed into the chamber and irradiated with monochromatic light (365 nm) for 2 h, during which the infrared absorbance within the wavenumber range of 1900–1200 cm⁻¹ was recorded at certain time points.

Results and Discussion

Phase structures and morphology

The phase structure and relative crystallinity of as-synthesized products were confirmed by XRD analysis. The XRD patterns of the carbon@TiO₂ composites (Fig. 1) show that anatase phase titania formed after calcination at 450 °C for 60–180 min. The characteristic diffraction peaks appeared at $2\theta = 25.3^{\circ}$ (101), 36.9° (103), 37.9° (004), 38.6° (112), 48.0° (200), 53.9° (105), 55.1° (211), 62.1° (213), which are easily assigned to anatase TiO₂ (JCPDS No. 71–1166). Notably, with increasing calcination time, the intensity of the XRD diffraction peaks increased, which arose from reduced shielding effect of carbonaceous species in TiO₂ hollow structure as well as grain growth of TiO₂. This indicates that the change of calcination duration has evident positive effect on the crystallinity of TiO₂.

Furthermore, FESEM and TEM images were used to investigate the morphology and nanostructure of the samples. Fig. 2a shows the FESEM images of the carbon nanospheres (CNS) with an average diameter of approximately 350 nm. After TBOT was added into the ethanolic suspension of CNS and aged for 24 h, the average diameter of the spheres increased



visibly to 420 nm (Fig. 2b). This change in diameter illustrates that a TiO₂ shell was coated on CNS uniformly by hydrolysis and condensation with the surface functional groups of CNS. Besides, from Fig. 2c, e and g, the carbon@TiO₂ composite samples exhibited regular spherical shape with coarse and rough surface, which is beneficial for light-harvesting. The surface morphology arises from the shrink of TiO₂ spherical shell with the CNS mold inside collapsed during calcination treatment. Therefore, the diameter of carbon@TiO₂ composite spheres decreased obviously from 300 nm (T60) to 100 nm (T180). The broken spheres (inset of Fig. 2c) imply a hollow

spherical structure with carbon core inside for the sample T60. Moreover, the corresponding TEM image (Fig. 2d) further confirms the hollow structure with carbon core inside, which can be defined as yolk-shell spheres.

It can be seen in Fig. 2g and 2h that carbon cores disappeared completely when the calcination duration increased to 180 min. Furthermore, Fig. 2e and 2f reveal a stable and uniform hollow spherical structure for sample T120, with a certain content of carbon remaining inside. The carbon@TiO₂ structure of T120 can not only enhance the visible-light absorption by the carbon core, but also leave some space for multi-scattering of light by the TiO₂ shell. In addition, elemental mapping images of an individual spherical yolk-shell particle of T60 are shown in Fig. 2i. The colorful images reveal that the C, O, and Ti elements are uniformly distributed over the whole nanostructure with C inside the sphere and O and Ti in the shell, demonstrating that uniform carbon@TiO₂ hybrid nanoarchitecture was formed successfully.

Raman analysis

The broad peak in the 2θ region of 19° to 28° indexed to carbon materials were too weak to find in the XRD spectra of the composites, so Raman spectroscopy was used to verify the existence of carbon in the carbon@TiO₂ composites. As shown in Fig. 3, there was no obvious difference in the four main Raman vibrational peaks (A_{1g} + B_{1g} + two E_g) of carbon@TiO₂ composite samples (T60, T120, T180), which are characteristic of the standard anatase spectrum.²⁶ More importantly, the Raman pattern of CNS and composite samples T60 and T120



Fig. 2 FESEM images of typical samples CNS (a), CSTS (b), T60 (c), T120 (e) and T180 (g); TEM images of T60 (d), T120 (f) and T180 (h). (i) STEM image of T60 and corresponding elemental mapping images of C, O and Ti.



Fig. 3 Fourier Transform Raman spectra of typical samples (using 633 nm Ar⁺ laser excitation source).

ARTICLE

showed two characteristic Raman bands corresponding to carbon species: the one at 1363 cm⁻¹ corresponds to the carbon defect-induced Raman band (D band), and the other at 1582 cm⁻¹ corresponds to the ordered graphitic structure (G band).^{27,28} The relative intensity of the D and G bands changed very little in different samples, indicating that the form of carbon in the carbon@TiO₂ composite samples was similar to that in CNS template. Moreover, the Raman spectra of sample T180 exhibited no D or G band, suggesting the absence of carbon in this sample, which is consistent with the TEM observations in Fig. 2h. Consequently, the carbon content remaining in the TiO₂ hollow spheres can be adjusted by varying the duration of the calcination treatment.

Thermal gravimetric analysis (TGA)

In order to investigate the content of carbon in the carbon@TiO2 composites, we studied the TG curves of composite samples prepared with different calcination durations (Fig. 4). All of the composite products show initial weight loss from approximately 60 to 300 °C due to the evaporation of surface adsorbed water, gases and disintegration of amorphous carbon impurities. Between 400 and 580 °C, the T180 sample exhibited no weight loss, while significant weight loss occurred for the carbon@TiO2 samples T60, T90 and T120, which corresponded to the decomposition of remaining carbon core. The weight loss listed in Table 1 was used to estimate the weight percentage of the carbon core in the carbon@TiO2 composites: 60.3% for sample T60 to 0% for sample T180. These results further confirm that carbon@TiO₂ composite samples with different carbon contents can be obtained as designed by controlling the calcination duration.

FTIR spectra and formation mechanism

FTIR spectroscopy study was used to analyze the formation mechanism of TiO₂ hollow spheres with different contents of CNS cores. The FTIR spectra (Fig. 5) show the typical vibrations associated with Ti–O–Ti bonding (500–800 cm⁻¹) and surface adsorbed water molecules (1630 cm⁻¹, 3000–3700 cm⁻¹) by anatase TiO₂ in T60, T120 and T180 samples. The adsorbed water is beneficial for photocatalytic CO₂ reduction. More importantly, there is a moderate intensity band near 1050 cm⁻¹ observed for the carbon@TiO₂ composite nanospheres, which is characteristic of Ti–O–C bonds.²⁹ However, with decreasing carbon content, the band was absent in T120 and T180. The Ti–O–C bond derived from carbonaceous species formed between TiO₂ and CNS core in the as-prepared carbon@TiO₂ nanocomposites.

The characteristic absorption bands of CNS at 1709 and 1622 cm⁻¹ are attributed to C=O and C=C vibrations, respectively. The two characteristic vibrations support the concept of aromatization glucose during hydrothermal treatment. Moreover, the bands in the range of 1000–1300 cm⁻¹ involve the C–OH stretching and O–H bending vibrations, which imply the existence of hydroxyl groups. After TBOT was added in the ethanolic CNS suspension, the amount of surface reducing organic functional groups decreased, which was

Herein, the fabrication mechanism of the carbon@TiO2 composite hollow structure is illustrated in Scheme 1. Glucose undergoes a series of reactions under hydrothermal conditions, which results in a complex mixture of organic compounds. The growth of CNS conforms to the LaMer model in the sealed vessel.³¹ Some aromatic compounds and oligosaccharides are formed initially, which can be called the "polymerization" process. Then cross-linking occurs in the carbonization process, induced by intermolecular dehydration of linear or branched oligosaccharides, or other macromolecules. The resulting nuclei grow uniformly and isotropically by diffusion of solutes toward the particle surfaces until the final size is attained eventually.²⁴ Blue wavy lines on sphere surface in Scheme 1 represent hydrophilic CNS surface and a distribution of oxygenous functional groups (-OH and C=O). The functional groups on CNS can combine with TBOT during stirring in the ethanolic CNS suspension. Thus, large amounts of TiO₂ are formed on the CNS surface by hydrolysis and condensation with functional groups, as shown in Scheme 1.32 After calcination for different time, hybrid carbon@TiO2 hollow nanospheres with various carbon contents are formed.



Fig. 4 TG curves of thermal decomposition of carbon@TiO₂ composite samples. (Preheated at 50 °C for 1 h and heated at a constant rate of 5 °C min⁻¹ in air.)

Table 1 Weight loss of carbon@TiO2 composite san	nples
--	-------

Sample	T60	T90	T120	T180
Weight loss (%)	60.7	35.3	7	~0

Journal Name



Fig. 5 FTIR spectra of typical samples.



Scheme 1 Illustration of formation mechanism for the carbon @ TiO₂ composite hollow structure.

XPS analysis

Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06.

XPS measurements were carried out to further analyze the interaction between TiO_2 and carbon, and identify the chemical status of Ti and O on the surface of the typical sample T120. Fig. 6a demonstrates that Ti, O, and C elements existed in the carbon@TiO₂ composite sample. Fig. 6b shows two bands locating at binding energies of 464.3 and 458.6 eV, which were assigned to the Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons in Ti⁴⁺ chemical state. The splitting between these bands is 5.7 eV and the binding energy of O 1s is 529.8 eV, demonstrating the normal state Ti⁴⁺ in the prepared carbon@TiO₂ nanocomposites. In Fig. 6c, the C 1s spectrum of T120 can be fitted as three peaks at binding energies of 284.8, 286.1 and 288.7 eV. Notably, no carbonaceous species with binding energy around 282 eV was observed, which can rule out the lattice doping of carbon element for C–Ti.³³ The peak at 284.8 eV



Fig. 6 XPS survey spectrum (a) and corresponding high-resolution XPS spectra of Ti 2p (b), C 1s (c) and O 1s (d) of the T120 sample.

can be attributed to the sp² hybridized carbon (C-C bonds) and carbon contaminants from ambience. The C 1s peaks at 286.1 and 288.7 eV can be assigned to the hydroxyl carbon (C-OH) and carboxyl carbon (C=O) functional groups, respectively. These groups are ascribed to the surface functional groups of exposed carbon in some broken spheres. More importantly, the peak at 288.7 eV also corresponds to carbonaceous species that form Ti-O-C structure between TiO₂ and carbon in the composites as also shown in the FTIR spectra (Fig. 5).34 This structure results from the condensation reaction between the CNS surface groups and the Ti-OH groups during TBOT adsorption on CNS surface. With respect to the XPS spectra of O 1s in Fig. 6d, two peaks of 529.8 and 531.3 eV were fitted, which can be assigned to lattice oxygen (Ti-O-Ti) and surface hydroxyls (Ti-OH), respectively.^{35,36} The O 1s binding energy for Ti-OH was slightly lower than that for pure TiO₂ (531.5 eV),³⁵ indicating the presence of C-O-Ti bonds through which the carbonaceous materials was grafted onto the TiO2 shell. The structure is favorable for the desired charge transfer upon light excitation.37,38

Pore structures

The BET specific surface area (S_{BET}) and pore structure are two important factors of the carbon@TiO2 nanocomposites for photocatalytic CO₂ reduction, which were investigated via nitrogen adsorption-desorption measurements. Fig. 7 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distribution (inset) of the typical samples T60, T120 and T180. According to Brunauer-Deming-Deming-Teller (BDDT) classification, the isotherms for the three samples are type IV, revealing the presence of mesopores.³⁹ Meanwhile, the nonlimiting adsorption at a high P/P_0 is characteristic of type H3 hysteresis loop, which is often associated with slit-shape pores due to the aggregation of platelike particles. The pore size distribution (inset of Fig. 7) of T60 exhibits bimodal distribution including small mesopores (3-4

urnal of Materials Chemistry A Accepted Manusc

Journal Name

ARTICLE

nm) and macropores; in addition, micropores (<2 nm) also existed in T60, as indicated by the sharp increase in N2 adsorption amount at extremely low relative pressure ($P/P_0 <$ Table 2 Textural properties and CO2 adsorption capacities of the as-prepared samples.

Sample	$S_{\rm BET}$ (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	APS (nm)	CA (mmol g ⁻¹)
T60	275	0.16	2.4	1.19
T120	110	0.17	6.2	0.64
T180	74	0.21	11.9	0.24
P25	45	0.16	13.4	0.11

Notes: PV: pore volume; APS: average pore size; CA: CO₂ adsorption quantity corresponding to P/P_0 of 1.0.



Fig. 7 N₂ adsorption-desorption isotherms and pore size distribution curves (inset) of T60, T120 and T180.

0.02) of the adsorption isotherm (Fig. 7). The micropores are attributed to the amorphous carbonaceous materials of the CNS core, while the small mesopores and macropores were primarily derived from the aggregation of primary TiO2 nanoparticles and that of the carbon@TiO2 spheres, respectively. In the inset of Fig. 7, with increasing calcination duration, the amount of mesopores and macropores increased due to the decrease of carbonaceous content. Meanwhile, the SBET decreased from 275 (T60) to 74 m² g⁻¹ (T180), while both pore volume and average pore size increased with longer calcination duration (Table 2). These changes indicate that CNS core released gases during calcination, which can change the pore structure of the composite samples. Moreover, the results can also verify that the primary particles are packed more closely with increasing calcination time, consistent with the TEM results. In summary, the presence of carbon materials resulted in increased specific surface area and improved pore structure of TiO₂ hollow spheres, which can lead to enhancement of photocatalytic performance.

UV-vis diffuse reflectance spectra (DRS)

relevant to their optical absorption properties In Fig9 &, 6the1121A UV-vis DRS of the composite samples demonstrate a significant fundamental optical absorption threshold near 400 nm, which can be assigned to the intrinsic band gap absorption of anatase TiO2 in the composites.40-43 Notably, the curves of all the composite samples show significant enhancement of light absorption in visible light range of 400-800 nm as shown in Fig. 8. Moreover, the visible light absorbance increased for composites with higher carbon contents, i.e., T60 > T120 > T90 > T180. It is obvious that remnant carbon in the core of hollow spheres affects the light absorption characteristics of TiO₂. The enhanced visible light absorption is mainly attributed to carbon inside the spheres which can effectively absorb visible light.44

Photocatalytic activity of semiconductors is vieparticularly

Photocatalytic activity and CO₂ adsorption capacity

Photocatalytic CO₂ reduction activity was evaluated using the prepared samples under simulated solar light ($\lambda > 200$ nm). Control experiments show that no reduction products were detected in the absence of photocatalyst, gaseous CO2 or light irradiation. This suggests that CO2 reduction indeed proceeded via photocatalytic reaction on the prepared samples, and possibilities of contamination from other carbon sources can be excluded.45,46

Fig. 9 shows the photocatalytic methane (CH4) and methanol (CH3OH) production rates of the carbon@TiO2 composite samples. It is obvious that carbon inside the hollow spheres has significant influences on photocatalytic activity of the composites. P25 without carbon exhibited a relative low photocatalytic CH₄-production rate (2.02 μ mol h⁻¹ g⁻¹) due to low specific surface area and high recombination rate of photogenerated electrons and holes in TiO2. By contrast, all the carbon@TiO2 composite samples can yield two kinds of products (i.e., CH₄ and CH₃OH) in the photocatalytic reaction. Sample T60 exhibited a relative low performance compared with other carbon@TiO2 samples. This can be ascribed to the fact that CNS of large size inside the T60 sample absorbed most of incident light due to the black body effect. Meanwhile, the large volume of carbon in



Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06.



Fig. 9 Comparison of the photocatalytic CH_4 or CH_3OH evolution rate of carbon@TiO₂ composite samples and P25 (under simulated solar light).



Fig. 10 CO_2 adsorption isotherms of tested samples. (All the samples were degassed at 100 °C prior to measurement.)

TiO₂ hollow spheres shielded the active sites on the inner surface of TiO₂ hollow spheres, which is called the "shielding effect". In addition, due to the high carbon content (Table 1), per unit mass of T60 contains much less TiO2 than the other samples, which can negatively affect electron photoexcitation. On the other hand, highest CH₃OH evolution rate was observed for sample T120, which was about 3 times that observed for T60. Moreover, high CH₄-production rate of 4.22 μ mol h⁻¹ g⁻¹ was also obtained using T120. It can be observed that CNS in the composite samples calcined longer than 60 min were dispersed more evenly in the hollow spheres (Fig. 2). Thus, a suitable content of carbon is crucial for optimizing photocatalytic activity of the carbon@TiO2 composites. Similar conclusions were made in previous studies on graphene-based photocatalytic hydrogen production, reduction of organics and metal ions.47-49 In addition, the optimized carbon@TiO2 composite photocatalyst exhibited a higher activity for photocatalytic CO₂ reduction than that of the previously reported TiO2-graphene and TiO2-multiwalled carbon nanotube nanocomposites.50

Since the adsorption of CO_2 onto the photocatalyst surface is the first step essential for photocatalytic reduction of CO_2 , we further investigated the CO₂ adsorption capacity of the typical composite samples, P25 and CNS. As DShown 39/CfHe11@02 adsorption isotherms (Fig. 10), T60, T120 and CNS showed a rapid rise of CO₂ adsorption with increasing CO₂ partial pressure in the low pressure region ($P/P_0 < 0.2$), which is attributed to adsorption by the small mesopores of carbon. The enhanced CO₂ adsorption capacity of the composite samples cannot be explained by the increased specific surface area alone (Table 2), but is also associated with carbon content. Thus, it is reasonable to assume that the delocalized π -conjugated binding π_6^6 in the core of carbon nanospheres (as shown in Scheme 1) conduces to the adsorption of CO2. CO2 molecules also contain delocalized π -conjugated binding π_3^4 . Therefore, the unique π - π conjugation interaction between CO₂ and CNS can significantly enhance the adsorption of CO2 molecules onto the carbon@TiO2 nanocomposite samples.51 As a consequence, T60 and T120 with certain content of carbon and high specific surface area exhibited much higher CO2 uptake capability compared with T180 and P25. Moreover, CO2 adsorption of CNS was not as much as those of T60 and T120, which results from TiO₂ hollow structure and pore structure of carbon changed during calcination treatment. More CO₂ can be adsorbed due to the plentiful porous structure (inset of Fig. 7) and high specific surface area (Table 2). The results show that carbon inside TiO₂ hollow spheres plays a very important role in enhancing the CO₂ adsorption capability besides the specific surface area. Such enhanced CO₂ concentration bv carbonaceous materials inside hollow spheres is beneficial for improving photocatalytic CO2 reduction performance.

Electrochemical impedance analysis

Carbon-based materials play a very important role in acting as an electron storage and transfer channel, which can hinder the recombination of photogenerated electron-hole pairs,^{52,53} thus EIS of the carbon@TiO2 composites were measured to investigate their charge transfer ability. As shown in the Nyquist plots (Fig. 11), the diameter of the semicircles for carbon@TiO2 samples T120 and T180 (inset of Fig. 11) are much smaller than those of T60 and T90, indicating that the composite samples with lower carbon content had superior charge transfer capacity. The result can be attributed to the fact that carbon inside dispersed more evenly and contacted more closely to the inner surface of TiO2 hollow spheres when calcined for 120 min or longer. On the other hand, too much amorphous carbon in the composites leads to relative low conductivity of the samples, such as T60 and T90. However, the conductivity of the samples did not increase monotonically with lower carbon content, and sample T120 had the smallest semicircle diameter (and thus the lowest charge transfer resistance) among the composite samples. When the calcination time was 180 min, the carbon content was close to 0% (Table 1), and interface states between carbon and TiO₂ greatly decreased, which resulted in the higher charge transfer resistance of T180 than that of T120. Therefore, optimized

ARTICLE



Fig. 11 Electrochemical impedance spectra of carbon@ TiO_2 composite samples and magnified spectra of T120 and T180 (inset).

carbon content was obtained by calcination for 120 min, which led to the best charge transfer efficiency for sample T120. The improved conductivity of nanocomposites has significant positive impacts on the photocatalytic reaction, which is consistent with the trend of photocatalytic CO_2 reduction activity (Fig. 9).

In situ DRIFTS

Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06.

In situ DRIFTS of typical sample T120 was conducted to identify adsorbed intermediates and understand the photocatalytic conversion process. When T120 was irradiated with monochromatic light (365 nm) in a flow of CO2/H2O vapour mixture, multiple peaks were observed in the DRIFTS spectra (Fig. 12), which could be assigned to carbonate, adsorbed formate (HCOO), methoxyl group (CH₃O), and molecularly adsorbed formaldehyde (HCHO). The peaks at 1681, 1618, 1520, 1507, 1437 and 1312 cm⁻¹ are attributed to carbonate species, those at 1868, 1844, 1825, 1700, 1649, 1592, 1558, 1540, 1455, 1395, 1372 and 1340 cm⁻¹ are ascribed to adsorbed HCOO, and those at 1770, 1749, 1715, 1418 and 1249 cm⁻¹ can be assigned to adsorbed HCHO.54,55 More importantly, the peaks at 1732 and 1472 cm⁻¹ result from the vibration of CH₃O groups.⁵⁵ However, CH₄ cannot be detected because of its nonpolar property and low affinity onto sample surface. In addition, the peak intensity of formate, formaldehyde and methoxyl group was gradually increased, while those of carbonate species did not change significantly. These results indicate that HCOOH, HCHO and CH3OH are the products in a multi-step photocatalytic conversion process of CO2 to CH4. 25,56



Fig. 12 In situ DRIFTS spectra of T120 in a flow of CO₂/H₂O vapour mixture as a function of irradiation time.



Scheme 2 Photoexcitation process of the carbon@TiO₂ composite hollow structure.

Photocatalytic CO₂ reduction mechanism

As discuss above, photocatalytic reduction of CO₂ into solar fuels demands energy input to break C=O bonds and form C–H/C–C bonds, involving the participation of multiple electrons and a corresponding number of protons.⁴⁵ Photocatalytic CO₂ reduction with H₂O into CH₄ and CH₃OH is an upward reaction with a highly positive change in Gibbs free energy, and a multistep reduction process is presented for the conversion of CO₂ to CH₄: CO₂ \rightarrow HCOOH \rightarrow HCHO \rightarrow CH₃OH \rightarrow CH₄.^{56,57}

During the photocatalytic activity measurement, the temperature of the whole custom-made Pyrex glass reactor, especially the bottom of the flask with catalyst powder on it, increased significantly after irradiation for 1 h. This observation indicates that carbon materials like graphene absorb almost the whole spectrum of solar light due to its black color and zero band gap, which results in increasing temperature around the photocatalyst to create a local photothermal effect.^{51,53,58} The Near Infrared Ray (NIR) light absorption into carbon of composite samples particularly allows photogenerated electrons to obtain more energy and move faster in carbon@TiO2

Journal Name

hemistry A Accepted Manusc

urnal of Materials

Journal Name

composite samples with rising temperature.⁵⁹ Therefore, local photothermal effect of carbon also has positive effects on the activity of photocatalytic CO_2 reduction over the nanocomposites.

Based on the above results, a probable reaction mechanism for photocatalytic over carbon@TiO₂ composites is proposed and illustrated in Scheme 2. Firstly, CO₂ is adsorbed on the surface of TiO₂ hollow spheres. Meanwhile, the CO₂ adsorption on CNS core also plays a very important role via π - π conjugation interaction. During light irradiation, charge separation occurs in TiO₂ generating a large amount of electron-hole pairs. The electron-hole pairs were separated and the electrons transferred through carbon materials. Then electrons initiated photocatalytic reduction reaction by reacting with CO₂ and water. Water was oxidized by holes, generating oxygen and H⁺ ions. And CO₂ was reduced into methane and methanol by reaction with H⁺ ions and electrons.^{60,61}

In this process, difference in the quasi Fermi energies created nonequilibrium charging state between TiO_2 and carbon. Thus, these photoexcited electrons transfer from conduction band (CB) of TiO_2 to neighboring carbon. The process improves electron transfer efficiency, which leads to charge equilibrium between these two components in the composite materials. Moreover, the electron transfer to CNS reduces the amount of electrons in the lattice of TiO_2 , which can hinder electron-hole recombination efficiently and allow more holes to be generated on the TiO_2 surface for the oxidation of water. Therefore, overall photocatalytic activity of the carbon@TiO_ nanocomposites can be enhanced during the process.

Conclusions

Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06

In summary, a hybrid carbon@TiO₂ hollow spherical structure was fabricated by a facile and green method. The as-designed hybrid semiconductor@carbon products not only enhanced the visible-light absorption and CO₂ adsorption, but also improve the photogenerated charge transfer efficiency. As a result, the hybrid carbon@TiO₂ photocatalyst exhibited a much higher activity for photocatalytic CO₂ reduction and produced more variety of solar fuels compared with P25. The approach for fabricating the hybrid nanostructure may also bring new insights for a variety of semiconductor-based applications such as supercapacitor, catalysis, sensors and energy conversion.

Acknowledgements

This study was partially supported by the 973 program (2013CB632402), NSFC (51572209, 51320105001, 51372190, 21433007 and 21573170). Also, this work was financially supported by the Natural Science Foundation of Hubei Province of China (2015CFA001), the Fundamental Research Funds for the Central Universities (WUT: 2015-III-034) and Innovative Research Funds of SKLWUT (2015-ZD-1)

References

- P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo Energy Environ. Sci., 2012, 5, 5902.
 DOI: 10.1039/C6TA11121A
- 2 S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, Angew. Chem., Int. Ed., 2013, 52, 7372.
- 3 S. Yan, S. Ouyang, H. Xu, M. Zhao, X. Zhang and J. Ye, J. Mater. Chem. A, 2016, 4, 15126.
- 4 M. Marszewski, S. W. Cao, J. G. Yu and M. Jaroniec, *Mater. Horiz.*, 2015, **2**, 261.
- 5 J. G. Yu, K. Wang, W. Xiao and B. Cheng, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11492
- 6 W. L. Yu, D. F. Xu and T. Y. Peng. J. Mater. Chem. A, 2015, 3,19936.
- 7 (a) L. Yuan, Y. J. Xu, *Appl. Surf. Sci.*, 2015, **342**, 154; (b) S. Ye, R. Wang, M. Z. Wu, Y. P. Yuan, *Appl. Surf. Sci.*, 2015, **358**, 15; (c) B. S. Kwak, M. Kang, *Appl. Surf. Sci.*, 2015, **337**, 138.
- 8 J. X. Low, B. Cheng and J. G. Yu, Appl. Surf. Sci., 2017, 392, 658.
- 9 B. Kwak and M. Kang, Appl. Surf. Sci., 2015, 337, 138.
- 10 J. Ming, Y. Q. Wu, S. Nagarajan, D. J. Lee, Y. K. Sun and F. Y. Zhao, J. Mater. Chem., 2012, 22, 22135.
- 11 (a) M. S. Akple, J. X. Low, Z. Qin, S. Wageh, A. A. Al-Ghamdi, J. G. Yu and S. W. Liu. *Chin. J. Catal.*, 2015, 36, 2127; (b) J. Wen, X. Li, W. Liu, Y. Fang, J. Xie, Y. Xu, *Chin. J. Catal.*, 2015, 36, 2049; (b) Y. Li, W. Zhang, X. Shen, P. Peng, L. Xiong, Y. Yu, *Chin. J. Catal.*, 2015, 36, 2229.
- 12 H. Xu, S. Ouyang, L. Liu, P. Reunchan, N. Umezawa, J. Ye, J. Mater. Chem. A, 2014, 2, 12642.
- 13 Z. Jiang, C. Zhu, W. Wan, K. Qian and J. Xie, *J. Mater. Chem. A*, 2016, **4**, 1806.
- 14 Z. He, J. Tang, J. Shen, J. Chen and S. Song, *Appl. Surf. Sci.*, 2016, **364**, 416.
- 15 C. P. Sajan, S. Wageh, A. A. Al-Ghamdi, J. G. Yu and S. W Cao, *Nano Res.*, 2016, 9, 3.
- 16 X. Li, J. G. Yu and M. Jaroniec, Chem. Soc. Rev., 2016, 45, 2603.
- 17 Y. Ao, J. Xu, D. Fu and C. Yuan, *Catal. Commun.*, 2008, 9, 2574.
- 18 L. Zhang, J. Zhang, H. Jiu, C. Ni, X. Zhang and M. Xu, J. Phys. Chem. Solids, 2015, 86, 82.
- 19 J. S. Chen, H. Liu, S. Z. Qiao and X. W. Lou, J. Mater. Chem., 2011, 21, 5687.
- 20 Y. Zhang, Y. Yang, H. Hou, X. Yang, J. Chen, M. Jing, X. Jia and X. Ji, *J. Mater. Chem. A*, 2015, **3**, 18944.
- 21 P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, *Energy Environ. Sci.*, 2012, 5, 5902.
- 22 S. W. Cao, J. G. Yu, J. Photochem. Photobio. C, 2016, 27, 72.
- 23 J. X. Low, B. Cheng, J. G. Yu and M. Jaroniec, *Energy Storage Mater.*, 2016, **3**, 24.
- 24 (a) X. M. Sun and Y. D. Li, Angew. Chem., Int. Ed., 2004, 43, 597; (b) M. Titirici, M. Antonietti and A. Thomas, Chem. Mater. 2006, 18, 3808.
- (a) Q. L. Xu, J. G Yu, J. Zhang, J. F. Zhang, G. Liu, Chem. Commun., 2015, 51, 7950; (b) P. F. Xia, B. C. Zhu, J. G. Yu, S. W. Cao and M. Jaroniec, J. Mater. Chem. A, 2017 (in press) DOI: 10.1039/c6ta08310b.
- 26 T. Ohsaka, J. Phys. Soc. Jpn., 1980, 48, 1661.
- 27 G. Williams and P. V. Kamat, *Langmuir*, 2009, **25**, 13869. 28 L. X. Yang, S. L. Luo, S. H. Liu and Q. Y. Cai, *J. Phys.*
- *Chem. C*, 2008, **112**, 8939. 29 J. X. Chen, R. Franking, R. E. Ruther, Y. Z. Tan, X. Y. He, S.
- R. Hogendoorn and R. J. Hamers, *Langmuir*, 2011, 27, 6879.
 W. Tian, L. M. Yang, Y. Z. Xu, S. F. Weng and J. G. Wu, *Carbohydr. Res.*, 2000, 324, 45.
- 31 V. K. LaMer, *Ind. Eng. Chem.*, 1952, **44**, 1270.
- 32 W. Li, J. P. Yang, Z. X. Wu, J. X. Wang, B. Li, S. S. Feng, Y. H. Deng, F. Zhang and D. Y. Zhao, *J. Am. Chem. Soc.*, 2012, 134, 11864.

This journal is © The Royal Society of Chemistry 20xx

- Chem., 2011, 21, 1049.
- 34 L. Chen, F. Chen, Y. Shi and J. Zhang, J. Phys. Chem. C, 2012, 116, 8579.
- Y. B. Li, C. B. Zhang, H. He, J. H. Zhang and M. Chen, 35 Catal. Sci. Technol., 2016, 6, 2289.
- 36 P. Zhang, C. L. Shao, Z. Y. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo, Y. Y. Sun and Y. C. Liu, J. Mater. Chem., 2011, 21, 17746.
- 37 B. Li, Z. Zhao, F. Gao, X. Wang and J. Qiu, Appl. Catal., B, 2014, 147, 958.
- 38 L. Zhao, X. F. Chen, X. C. Wang, Y. J. Zhang, W. Wei, Y. H. Sun, M. Antonietti and M. M. Titirici, Adv. Mater., 2010, 22, 3317.
- 39 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouqerol and T. Siemieniewska, Pure Appl. Chem., 1985, 57, 603.
- 40 K. L. Lv, B. Cheng, J. G. Yu and G. Liu, Phys. Chem. Chem. Phys., 2012, 14, 5349.
- 41 C. Tan, W. H. Fan and W. X. Wang, Environ. Sci. Technol., 2012, 46, 469.
- 42 W. H. Fan, M. M. Cui, H. Liu, C. A. Wang, Z. W. Shi, C. Tan and X. P. Yang, Environ. Pollut., 2011, 159, 729.
- 43 X. H. Zhang, H. Liu, W. Z. Li, G. F. Cui, H. Y. Xu, K. Han and Q. P. Long, Catal. Lett., 2008, 125, 371.
- C. Lettmann, K. Hildenbrand, H. Kisch, W. Macyk and W. F. 44 Maier, Appl. Catal., B, 2001, 32, 215.
- A. Dhakshinamoorthy, S. Navalon, A. Corma and H. Garcia, Energy Environ. Sci., 2012, 5, 9217.
- 46 J. Jin, J. G. Yu, D. P. Guo, C. Cui and W. K. Ho, Small, 2015, 11. 5262.
- 47 L. Jia, D. H. Wang, Y. X. Huang, A. W. Xu and H. Q. Yu, J. Phys. Chem. C, 2011, 115, 11466.
- 48 Q. Li, X. Li, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, Adv. Energy Mater., 2015, 5, 1500010.
- 49 Q. J. Xiang, B. Cheng and J. G. Yu, Angew. Chem., Int. Ed., 2015, 54, 11350.
- 50 (a) W. Ong, L. Tan, S. Chai, S. Yong, and A. R. Mohamed, Nano Res., 2014, 7, 1528; (b) M. Gui, S. Chai, B. Xu, A. R. Mohamed, Sol. Energy Mater. Sol. Cell, 2014, 122, 183.
- 51 J. X. Low, J. G. Yu and W. K. Ho, J. Phys. Chem. Lett., 2015, 6, 4244.
- 52 J. G. Yu, J. X. Low, W. Xiao, P. Zhou and M. Jaroniec, J. Am. Chem. Soc., 2014, 136, 8839.
- 53 W. J. Wang, J. C. Yu, D. H. Xia, P. K. Wong and Y. C. Li, Environ. Sci. Technol., 2013, 47, 8724.
- 54 (a) J. L. Wang, P. Y. Zhang, J. G. Li, C. J. Jiang, R. Yunus, J. Kim, Environ. Sci. Technol., 2015, 49, 12372; (b) J. L. Wang, D. D. Li, P. L. Li, P. Zhang, Q. L. Xu, J. G. Yu, RSC Adv., 2015, 5, 100434; (c) S. Sun, J. J. Ding, J. Bao, C. Gao, Z. M. Qi, C.X. Li, Catal. Lett., 2010, 137, 239.
- 55 (a) J. W. Ye, X. F. Zhu, B. Cheng, J. G. Yu and C. J. Jiang, Environ. Sci. Technol. Lett., 2017 (in press) DOI: 10.1021/acs.estlett.6b00426; (b) M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagic and H. Yoshida, J. Mater. Chem. A, 2015, 3, 16810.
- 56 (a) D. G. Nocera, Acc. Chem. Res., 2012, 45, 767; (b) J. G. Yu, J. Jin, B. Cheng, M. Jaroniec, J. Mater. Chem. A, 2014, 2, 3407; (c) X. Li, J. Wen, J. Low, Y. Fang, J. Yu, Science China Mater., 2014, 57, 70.
- 57 G. H. Liu, N. Hoivik, K. Y. Wang and H. Jakobsen, Sol. Energy Mater. Sol. Cells, 2012, 105, 53.
- 58 L. C. Sim, K. H. Leong, P. Saravanan and S. Ibrahim, Appl. Surf. Sci., 2015, 358, 122.
- 59 Z. X. Gan, X. L. Wu, M. Meng, X. B. Zhu, L. Yang and P. K. Chu, Acs Nano, 2014, 8, 9304.
- 60 Y. Li, W. N. Wang, Z. L. Zhan, M. H. Woo, C. Y. Wu and P. Biswas, Appl. Catal., B, 2010, 100, 386.

ARTICLE

Published on 07 February 2017. Downloaded by Freie Universitaet Berlin on 08/02/2017 02:54:06

33 J. G. Yu, G. P. Dai, Q. J. Xiang and M. Jaroniec, J. Mater. 61 A. Kongkanand and P. V. Kamat, Acs Nano, 2007, 1, 13. DOI: 10.1039/C6TA11121A

Graphic abstract



Photocatalytic CO_2 conversion toward solar fuels via hybrid carbon@TiO₂ hollow spheres.