Simple Preparation of Hierarchically Porous Ce/TiO₂/Graphitic Carbon Microspheres for the Reduction of CO₂ with H₂O under Simulated Solar Irradiation

Chengli Zhang,*†‡, Weiping Zhang,† Jing Qian,† Hongdan Cheng,† Shaoyun Ren,† Chaosheng Zhang,§ Jianhua Ma,†‡ and Zhiyong Guo*†*

†College of Environment and Planning and ‡Institute of Natural Resources and Environment, Henan University, Kaifeng 475001, China
§School of Geography and Archaeology, National University of Ireland, Galway H91 TK33, Ireland

ABSTRACT: Hierarchically porous Ce/TiO₂/graphitic carbon microsphere composites (xCe/TiO₂/GCM, where x = 0.2, 1.0, 2.0, 5.0 mmol·L⁻¹) were prepared for the first time by using a simple colloidal crystal template and characterized by X-ray diffraction, nitrogen adsorption and desorption, scanning electron microscopy, and ultraviolet–visible diffuse reflectance spectra. In addition, the photocatalytic activity of CO₂ reduction by H₂O under simulated solar irradiation was studied. The results showed that the Ce/TiO₂/GCM composite material was characterized by large porosity, high concentration of metal compounds and graphitized carbon matrix, and the content of acetone solvent having a great impact on its form. In terms of the photocatalytic CO₂ reaction, the CH₄ and CO productions were 4.587 and 1.367·mol·g⁻¹, respectively. The 2Ce/TiO₂/GCM photocatalyst gave the highest production rate for three products. Under simulated solar irradiation, the Ce/TiO₂/GCM has excellent photocatalytic activity in the photoreduction of CO₂ from H₂O, which was related to the special composition and the Ce/TiO₂/GCM structure.

INTRODUCTION

The problem of climate change and global warming caused by excessive CO₂ discharges is becoming increasingly serious but, unfortunately, the future exhaustion of fossil fuel resources is also worrying. An ideal solution to global warming and the carbon cycle in nature is to reap solar energy to convert photocatalytic CO₂ into renewable hydrocarbon fuels using H₂O. For this purpose, researchers have attempted to develop efficient technologies such as high-performance photocatalysts.

The preparation methods of composite photocatalysts include chemical reduction, light-induced reduction, photodeposition, thermal decomposition, liquid impregnation, sol–gel, and hydrothermal method. Photocatalysts synthesized by various methods have effective photocatalytic properties, which provide broad prospects for applications in the fields of optical computation, solar cells, photocatalysis, and communication. For instance, the photocatalysts of Ce⁴⁺ and TiO₂ were synthesized by chemical coprecipitation peptization and hydrothermal methods, respectively, in Xie and effectively improved the photocatalytic performances through Ce⁴⁺–TiO₂ sol and nanocrystallites. The photocatalytic solar fuel of TiO₂ photocatalyst prepared by anodizing and calcining without a template has the characteristics of slow photon and local surface photothermal effect as well as improvement in the catalytic reaction rate and light utilization, respectively. Using ionic liquid as a template, mesoporous palladium-doped TiO₂ with an anatase phase and a high specific surface area was synthesized by the green sol–gel method. At the same residence time, the photodegradation performance of NOx (88%) and CO (74%) was significantly better than that of IL-TiO₂ (59 and 56%) without doping. Despite some achievements in catalyst preparations, preparation methods still have the disadvantages of cumbersomeness and high cost.

Herein, we proposed a method for the convenient synthesis of layered porous Ce/TiO₂/graphitic carbon microspheres (xCe/TiO₂/GCM, where x = 0.2, 1.0, 2.0, and 5.0 mmol·L⁻¹) via colloidal crystal templating. The structural characteristics of the composites were analyzed by X-ray diffraction (XRD), nitrogen adsorption–desorption, scanning electron microscopy (SEM), and ultraviolet–visible light diffuse reflectance spectra. Their photocatalytic activity for reducing CO₂ from H₂O under simulated solar irradiation was studied. The results showed that the induced Ce significantly improved the photocactivity of the hierarchically porous TiO₂/GCM.

Received: June 10, 2019
Accepted: September 19, 2019
Published: October 1, 2019
RESULTS AND DISCUSSION

Preparation of the Ce/TiO₂/GCM Composites. As shown in Figure 1, the colloidal crystal templating method for the synthesis of hierarchically porous Ce/TiO₂/GCM is actually much simpler than the traditional multistep synthesis method.

The preparation flow chart is shown in Figure 1. Acetone, soybean oil, TiCl₄, and Ce(NO₃)₃·6H₂O were mixed under stirring to form a stable microemulsion, which was then mixed with monodisperse SiO₂ microspheres under stirring to form a suspension. After 3 days, acetone evaporated from the microemulsion droplets, and the interaction between monodisperse SiO₂ microspheres was intensified to form colloidal superparticles of SiO₂ microspheres. Furthermore, the microemulsion with colloidal superparticles of SiO₂ microspheres was placed in the tube furnace for carbonaceous polymerization/graphitization heat treatment. With the gradual increase of temperature, during the heat treatment process at
900 °C under an Ar atmosphere, metallic crystals grew in situ and were embedded into the graphitic carbon matrix. The hierarchically porous Ce/TiO₂/GCM, which can be classified as colloidal superparticles,²⁵,²⁶ was formed after the removal of the SiO₂ colloidal crystal sphere template by the silica colloidal crystal ball template and was incubated in sodium hydroxide solution at room temperature. Finally, Ce/TiO₂/GCM was synthesized as expected.

XRD of Ce/TiO₂/GCM Composites. The formation of Ce/TiO₂/GCM composites with different compositions was first proved by XRD (Figure 2). The anatase phase of TiO₂ is observed for all photocatalysts. The diffraction peaks at 2θ of 25, 48, 53, 55, and 63° correspond to the (101), (200), (105), (211), and (204) crystal planes of the pure anatase phase of TiO₂, respectively. The peak of graphite carbon at 25° (002) was overlapped by that of anatase at 25° (101) in each composite.²¹,²⁷ The XRD signal of 0.2Ce/TiO₂/GCM is even noisier than the results. Since there were almost no peaks in the background spectrum, none of the crystal information extracted from the above complexes can be considered reliable. However, owing to the small size of the nanoparticles it is difficult to track the evolution as Ce concentration increases. Fortunately, the peaks of the anatase Ce are strengthened with the increasing Ce content in the composites, indicating that the increase of the crystal particle size, which is well consistent with the EDS results in Figure 2 (inset: 0.2Ce/TiO₂/GCM EDS spectrum). For instance, the contents of Ce, C, O, and Ti in 0.2Ce/TiO₂/GCM are 1.11, 5.08, 37.90, and 55.92 wt %, respectively.

N₂ Adsorption–Desorption of the Ce/TiO₂/GCM. The N₂ adsorption–desorption isotherms and corresponding pore size distribution curves of the porous carbons are shown in Figure 3. All isotherms in Figure 3a show strong absorption of N₂ due to capillary condensation within the wide relative pressure (P/P₀) range of 0.6–0.9, which suggests the existence of multiform pore distributions.²⁸,²⁹ It is associated with the interparticle voids to the small absorption at P/P₀ of 0.9–0.99.³⁰,³¹ Additionally, as shown in Figure 3b, most of the pores are located at 3.8–12 and 21–175.1 nm, which proves the graded porosity of the composite materials. The structural properties of all composites are shown in Table 1. The average diameter of graded porous composites is 13.37 nm, and much larger Brunauer–Emmett–Teller (BET) surface areas than the largest surface area of graphitic carbon composites are reported by Cai³² (132–204 vs 52.3 m²·g⁻¹). Among all composite materials, the specific surface area of 2Ce/TiO₂/GCM was the

| samples          | S_{BET} a (m²·g⁻¹) | D_p b (nm) |
|------------------|--------------------|------------|
| 0.2Ce/TiO₂/GCM   | 132.0              | 17.1       |
| 1Ce/TiO₂/GCM     | 143.3              | 12.8       |
| 2Ce/TiO₂/GCM     | 204.0              | 12.4       |
| 5Ce/TiO₂/GCM     | 176.7              | 11.2       |

²⁵S_{BET}: the specific surface area is calculated by the BET method. bD_p: the pore diameter is calculated by the Barrett–Joyner–Halenda (BJH) method.

Figure 4. SEM micrographs of (a) 0.2Ce/TiO₂/GCM, (b) 1Ce/TiO₂/GCM, (c) 2Ce/TiO₂/GCM, and (d) 5Ce/TiO₂/GCM with 45 mL acetone.
The highest, which is 204 m²·g⁻¹. Thus, the Ce/TiO₂/GCM composites have large specific surface areas and advanced pore structures.

**SEM Analysis of Ce/TiO₂/GCM Composites.** With acetone (45 mL) as the solvent, some representative SEM images are shown in Figure 4. Clearly, the microsphere morphology of the monodisperse SiO₂ template was copied into the porous materials. Finally, the long period structure of the colloidal crystal with the most valuable properties was left after the original colloidal SiO₂ particles were removed. The long-term arrangement of layered porosity has led to potential applications in emerging nanotechnologies, advanced coatings, and optical information processing and storage, and other areas.35,36 This valuable feature was further verified by the N₂ adsorption test (Figure 3). The diameters of Ce/TiO₂/GCM composites are about 2 µm.

**Photoreduction of CO₂ under Simulated Solar Irradiation.** We measured the photocatalytic activity of xCe/TiO₂/GCM on the photoreduction of gas-phase CO₂ under simulated solar irradiation. Figure 5 shows the change rule of CH₄ and CO products with the irradiation time for all samples. The results showed that the yields of all composites increased with the increase in the reaction times. The synergistic effect of GCM and Ce significantly enhanced the photocatalytic activity of the composite because the introduction of Ce improves the electrical conductivity and light absorption of TiO₂/GCM.

The solar fuel production rates increase with the Ce content increasing from 0.2 to 2 mmol and then decrease (Figure 5a), which is similar but not identical to the trend of the CO₂ adsorption capacity.35−37 However, the activity decreases with a further increase of the Ce content to 5 mmol, indicating that an appropriate Ce content is very important to achieve the best photocatalytic activity. The yield is lower compared with the Ce-free samples under the same conditions. The yield maximizes to 4.59 µmol·g⁻¹ at the Ce content of 2 mmol.

Figure 5b shows the CO production rates of solar fuels. With prolonging the irradiation time, 2Ce/TiO₂/GCM showed a strong catalytic performance. The CO yield maximizes to 359.85 µmol·g⁻¹ in 2Ce/TiO₂/GCM after 6 h of simulated sun exposure. The optimum 2Ce/TiO₂/GCM exhibited several times higher CO evolution rate than pure TiO₂ in this study and NH-Uio−66 synthesized by Crake et al.38 The results show that the Ce content is the most important factor to determine the optimal photocatalytic activity and a further increase of the Ce content will slow down the photoreduction conversion of CO₂.

**Mechanism of Photocatalytic Reduction of CO₂ with H₂O.** Solar energy is used to realize the recycling reaction of CO₂ and H₂O, and its working principle is as follows:39−42

![Proposed mechanism for the photocatalytic reduction of CO₂ with H₂O.](image-url)
semiconductor materials with a certain band gap width generate electron-photogenic holes (h⁺) and photogenic electrons (e⁻) during the excitation by sunlight, which migrate to the semiconductor catalyst as active sites with reduction and oxidation potential, respectively, and then react with CO₂ and H₂O adsorbed on the surface. Holes capture electrons in H₂O and decompose them to form strongly oxidizing hydroxide (HO*) and hydrogen ion (H⁺). Meanwhile, CO₂, as an electron acceptor, is reduced to strongly oxidized carbon dioxide anion radical (·CO₂⁻), and the specific process is shown in eqs 1, 2, 3, and 4. Then, ·CO₂⁻ is further combined with hydrogen ions and photogenic electrons to obtain hydrocarbons such as formaldehyde, formic acid, methanol, or methane. The specific reaction process is shown in Figure 6

$$\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{HO}^+ + \text{H}^+ \quad (1)$$

$$\text{CO}_2 + \text{e}^- \rightarrow \cdot\text{CO}_2^- \quad (2)$$

$$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E = -0.52 \text{ V} \quad (3)$$

$$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E = -0.24 \text{ V} \quad (4)$$

## CONCLUSIONS
Hierarchically porous Ce/TiO₂-graphitic microsphere carbon (GCM) composites were prepared by simple colloidal crystal template using SiO₂ colloidal crystals as the template and titanium tetrachloride as the precursor of Ti. According to the XRD analysis, the Ce/TiO₂/GCM composite material has hierarchical porosity, high pore volume, large specific surface area and graphitic framework, and N₂ sorption. The CH₄ and CO yields were 4.587 and 357.851 μmol·g⁻¹, respectively. In addition, among the four samples, the specific surface area of 2Ce/TiO₂/GCM was the highest, so they give the highest production rate for two products. The excellent photocatalytic activity of Ce/TiO₂/GCM in CO₂ photoreduction with H₂O under simulated solar irradiation is attributed to the special composition and structure.

## EXPERIMENTAL SECTION
**Chemicals.** Absolute alcohol, acetone, ammonia, tetraethoxysilane, Ce(NO₃)ₓ·6H₂O, NaOH, and soybean oil were used as raw materials.

**Catalyst Preparation.** Colloidal SiO₂ microspheres were prepared with 0.31 mol·L⁻¹ ammonia by Stöber’s method, except that the volume was increased by 10 times.

The hierarchically porous Ce/TiO₂/GCM was synthesized via colloidal crystal templating. Typically, x mmol of Ce(NO₃)ₓ·6H₂O (x = 0.2, 1.0, 2.0 or 5.0), 5.0 g of soybean oil, and 10 mmol of TiCl₄ were dissolved into 45 mL acetone, respectively. Then, 2.5 g of SiO₂ microspheres was added to the above mixed solution and stirred for about half an hour to form a suspension. After aging at room temperature for 3 days, the suspension carbonizes the precursor for 4 h at 900 °C under an Ar flow rate in a tubular furnace. The silica gel template was removed after multiple treatments with a 2 mol·L⁻¹ NaOH solution.

**Catalyst Characterization.** The XRD patterns were collected in the 1–2 θ mode on a Rigaku D/Max2B-II diffractometer (Cu K₁ radiation, λ = 1.5406 Å) at 100 mA and 40 kV. SEM was performed on a Philips XL-30 SEM device, and the acceleration voltage was 25 kV. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Pore size distributions were obtained from desorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. The total pore volumes were estimated at a relative pressure of 0.99.

**Photocatalytic Performance Tests.** The photocatalytic activity of CO₂ reduction with H₂O was tested in a self-made device, as shown in Figure 7. The photocatalytic reaction was carried out in a quartz glass reactor with a volume of 1500 mL. The catalyst powder (0.10 g) was evenly dispersed on a stainless steel omentum and placed in the middle of the photocatalytic reactor. A glass filament soaked with 5.0 g of deionized water was placed at the bottom of the reactor to keep the reactor saturated with water vapor, and an Xe arc lamp (300 W) with a solar radiation spectrum was placed 8 cm above the quartz window to illuminate the whole catalyst. To control the reaction temperature at 30 °C, we placed the Xe lamp in a cold trap to keep the whole reactor system in a state of air circulation. Prior to ignition, the reactor was first cleaned with a CO₂ + H₂O mixture at 100 mL·min⁻¹ for 2 h, then at 20 mL·min⁻¹ for another hour to reach an adsorption–desorption equilibrium; the volume concentrations of CO₂ and the H₂O gas phase were controlled at about 95.5 and 4.5%, respectively. The reactor was then sealed and the pressure of CO₂ was maintained at 110 kPa. After that, the light source...
300 W xenon lamp was turned on. GC 8000 Top gas chromatography—mass spectrometry system was used to collect and analyze the gas-phase products at different time points during the irradiation. Each sample was injected 5 μm into the loop, and 25 m × 0.32 mm CP-PorapLOT QHT column (Chrompack) was injected via 0.5 m × 0.32 mm deactivated precolumn, which was maintained at 23 °C. Helium at 2.0 mL·min⁻¹ was used as the carrier gas. The mass spectrometer operates in a single-ion monitoring mode with electron ionization (70 eV). The retention times of CH₄ and CO were 1.6 and 2.3 min, respectively. The total detection time of one sample was 3.3 min, which was enough for sample collection, injection, chromatography, and data collection for 2.5 min.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhangcl@henu.edu.cn (C.Z.).
*E-mail: guory9888@163.com (Z.G.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China under Grant (41601522, 21776061 and 21576071), China Postdoctoral Science Foundation under Grant (2017M612387), and Henan Postdoctoral Science Foundation under Grant (001701033). We sincerely appreciate the laboratory and diving assistance by the Science & Technology Innovation Team in Universities of Henan Province (19IRTSTHN029).

■ REFERENCES

(1) Zhu, X. B.; Liu, J. H.; Li, X. S.; Liu, J. L.; Q, X.; Zhu, A. M. Enhanced effect of plasma on catalytic reduction of CO₂ to CO with hydrogen over Au/CeO₂ at low temperature. *J. Energy. Chem.* 2017, 26, 488–493.
(2) Rao, H.; Bonin, J.; Robert, M. Non-sensitized selective photochemical reduction of CO₂ to CO under visible light with an iron molecular catalyst. *Chem. Commun.* 2017, 53, 2830–2833.
(3) Mei, D. H.; Zhu, X. B.; Wu, C. F.; Ashford, B.; Williams, P. T.; Tu, X. Plasma-photo catalytic conversion of CO₂ at low temperatures: Understanding the synergistic effect of plasma-catalysis. *Appl. Catal., B* 2016, 182, 525–532.
(4) Gao, S.; Lin, Y.; J. X. C.; Sun, Y. F.; Luo, Q. Q.; Zhang, W. H.; Li, D. Q.; Yang, J. L.; Xie, Y. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Fuel* 2016, 529, 68–71.
(5) Wei, Y. C.; Jiao, L. G.; Zhao, Z.; Liu, L.; Li, J. M.; Jiang, G.; Wang, Y.; Duan, A. J. Fabrication of inverse opal TiO₂-supported Au@CdS core–shell nanoparticles for efficient photocatalytic CO₂ conversion. *Appl. Catal., B* 2015, 179, 422–432.
(6) Kuriki, R.; Sekizawa, K.; Ishitani, O.; Maeda, K. Visible-Light-Driven CO₂ reduction with carbon nitride, Enhancing the activity of ruthenium catalysts. *Angew. Chem., Int. Ed.* 2015, 54, 2406–2409.
(7) Fu, Y.; Sun, D.; Chen, Y.; Huang, R.; Ding, Z.; Fu, X.; Li, Z. An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-induced activity for CO₂ reduction. *Angew. Chem., Int. Ed.* 2012, 51, 3364–3367.
(8) Hud, L.; Sampson, M. D.; Deria, P.; Kubiak, C. P.; Farha, O. K.; Hupp, J. Fe-porphyrin based MOF films as high-surface-concentration, heterogeneous catalysts for electrochemical reduction of CO₂. *ACS Catal.* 2015, 5, 6302–6308.
(9) Fei, H.; Sampson, M. D.; Lee, Y.; Kubiak, C. P.; Cohen, S. M. Photocatalytic CO₂ reduction to formate using a Mn(II) molecular catalyst in a robust metal–organic framework. *Inorg. Chem.* 2015, 54, 6821–6825.
(10) Lin, L. Y.; Yao, N.; Kavadiya, S.; Soundappan, T.; Biswas, P. N. doped reduced graphene oxide promoted nano TiO₂ as a bifunctional adsorbent/photocatalyst for CO₂ photoreduction: Effect of N species. *Chem. Eng. J.* 2017, 316, 449–460.
(11) Cao, C.; Yan, Y. B.; Yu, Y. L.; Yang, X. D.; Liu, W. S.; Cao, Y. A. Modification of Pd and Mn on the Surface of TiO₂ with enhanced photocatalytic activity for photoreduction of CO₂ into CH₄. *J. Phys. Chem. A* 2017, 121, 270–277.
(12) Zhao, J.; Wang, Y.; Li, Y. X.; Yue, X.; Wang, C. Y. Phase-dependent enhancement for CO₂ photocatalytic reduction over CeO₂/TiO₂ catalysts. *Catal. Sci. Technol.* 2016, 6, 7967–7975.
(13) Soleimani, F.; Hosseini, H. R. M.; Ordikhani, F.; Mokhtar-Dizaji, M. M. Enhancing sonocatalytic properties of TiO₂ nanocatalysts by controlling the surface conditions: effect of particle size and PVA modification. *Desalin. Water Treat.* 2016, 57, 28378–28385.
(14) Hu, B. B.; Guo, Q.; Wang, K.; Wang, X. T. Enhanced photocatalytic activity of porous In₃O₅ for reduction of CO₂ with H₂O. *J. Mater. Sci.*: *Mater. Electron.* 2019, 30, 7950–7962.
(15) Yanipour, F.; Shariatinia, Z.; Sahedellar, S.; Iranoudini, A. The effects of synthesis operation conditions on the properties of modified α-alumina nanocatalysts in methanol dehydration to dimethyl ether using factorial experimental design. *Fuel* 2015, 139, 40–50.
(16) Długęckę, M.; Łuczak, J.; Polkowska, Z.; Zaleska-Medynska, A. Z. The effect of microemulsion composition on the morphology of Pd nanoparticles deposited at the surface of TiO₂ and photoactivity of Pd-TiO₂. *Appl. Surf. Sci.* 2017, 405, 220–230.
(17) Mortazavi-Derazkola, S. M.; Salavati-Niasari, M. S.; Mazhari, M. P.; Khojasteh, H.; Hamadanian, M.; Bagheri, S. Magnetically separable FeO₃ @SiO₂ @TiO₂ nanostructures supported by neodymium(III): fabrication and enhanced photocatalytic activity for degradation of organic pollution. *J. Mater. Sci.: Mater. Electron.* 2017, 28, 14271–14281.
(18) Mirabedini, A.; Mirabedini, S. M.; Babalou, A. A.; Pazañikárd, S. Synthesis, characterization and enhanced photocatalytic activity of TiO₂/SiO₂ nanocomposite in an aqueous solution and acrylic-based coatings. *Prog. Org. Coat.* 2011, 72, 453–460.
(19) Bouna, L.; Rhouta, B.; Maury, F. Physicochemical study of photocatalytic Activity of TiO₂ supported polygorskite clay mineral. *Int. J. Photoenergy* 2013, 1–6.
(20) Xie, Y.; Yuan, C. Visible-light-responsive cerium ion modified titania sol and nanocrystallites for X-3B dye photodegradation. *Appl. Catal., B* 2004, 46, 251–259.
(21) Zhang, C. L.; Zhang, Q. Y.; Kang, S. F.; Li, X.; Wang, Y. G. Facile Synthesis of hierarchically porous metal-TiO₂/graphitic carbon microspheres by colloidal crystal pemplating method. *Int. J. Electrochem. Sci.* 2013, 8, 8299–8310.
(22) Van Helden, A. K.; Jansen, J. W.; Vrij, A. Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents. *J. Colloid Interface Sci.* 1981, 81, 354–368.
(23) Wang, J. Q.; Wu, Y. Y.; Yuan, S. S.; Zhang, M.; Chen, X. B. Preparation and optical properties of tin dioxide inverse opal film. *Rare Met.* 2015, 7, 1–5.
(24) Yang, S. K.; Zeng, H. B.; Zhao, H. P.; Zhang, H. W.; Cai, W. P. Luminescent hollow carbon shells and fullerene-like carbon spheres produced by laser ablation with toluene. *J. Mater. Chem.* 2011, 21, 4432–4436.
(25) Zhang, C. L.; Zhang, Q. Y.; Kang, S. F.; Li, X. A novel route for the facile synthesis of hierarchically porous TiO₂/graphitic carbon microspheres for lithium ion battery. *J. Mater. Chem. A* 2014, 2, 2801–2806.
(26) Liu, Y.; Goebl, J.; Yin, Y. Templated synthesis of nanostructured materials. *Chem. Soc. Rev.* 2013, 44, 1–3.
(27) Wang, J. J.; Jing, Y. H.; Yang, T. O.; Zhang, Q.; Chang, C. T. Photocatalytic reduction of CO₂ to energy products using Cu–TiO₂/ ZSM-5 and Co–TiO₂/ZSM-5 under low energy irradiation. *Catal. Commun.* 2015, 59, 69–72.
(28) Wang, Y. G.; Li, B.; Zhang, C. L.; Song, X. F.; Tao, H.; Kang, S. F.; Li, X. A simple solid–liquid grinding/templating route for the synthesis of magnetic iron/graphitic mesoporous carbon composites. *Carbon* 2013, 51, 397–403.

(29) Cui, L. Preparation of magnetic iron/graphitic mesoporous carbon composites as efficient recyclable adsorbents for methyl orange removal. *Int. J. Electrochem. Sci.* 2016, 11, 8346–8353.

(30) Pellicer, E.; Menéndez, E.; Fornell, J.; Nogués, J.; Vantomme, A.; Temst, K.; Sort, J. Mesoporous oxide-diluted magnetic semiconductor supports prepared by Co-implantation in nanocast 3D-ordered In$_2$O$_3$–y materials. *J. Phys. Chem. C* 2013, 117, 17084–17091.

(31) Ji, P. F.; Zhang, J. L.; Chen, F.; Anpo, M. Ordered mesoporous CeO$_2$ synthesized by nanocasting from cubic Ia3d mesoporous MCM-48 silica: Formation, characterization and photocatalytic activity. *J. Phys. Chem. C* 2008, 112, 17809–17813.

(32) Cai, Q.; Liu, C. L.; Yin, C. C.; Huang, W.; Cui, L. F.; Shi, H. C.; Fang, X. Y.; Zhang, L.; Kang, S. F.; Wang, Y. G. Bio-templating synthesis of graphitic carbon coated TiO$_2$ and its application as efficient visible-light-driven photocatalyst for Cr$^{6+}$ remove. *ACS Sustainable Chem. Eng.* 2017, 5, 3938–3944.

(33) Fu, M.; Zhou, J.; Xiao, Q.; Li, B.; Zong, R.; Chen, W.; Zhang, J. ZnO nanosheets with ordered pore periodicity via colloidal crystal template assisted electrochemical deposition. *Adv. Mater.* 2006, 18, 1001–1004.

(34) Chen, A. B.; Yu, Y. F.; Li, Y. T.; Wang, Y. Y.; Li, Y. Q.; Li, S. H.; Xia, K. C. Synthesis of macro-mesoporous carbon materials and hollow core/mesoporous shell carbon spheres as supercapacitors. *J. Mater. Sci.* 2016, 51, 4601–4608.

(35) Kityakarn, S.; Worayingsong, A.; Suramit, A.; Smith, M. F. Ce-doped nanoparticles of TiO$_2$. Rutile-to-brookite phase transition and evolution of Ce local-structure studied with XRD and XANES. *Mater. Chem. Phys.* 2013, 139, 543–549.

(36) Wang, Y.; Bai, X.; Qin, H.; Wang, F.; Li, Y.; Li, X.; Kang, S.; Zuo, Y.; Cui, L. Facile one-step synthesis of hybrid graphitic carbon nitride and carbon composites as high-performance catalysts for CO$_2$ photocatalytic conversion. *ACS Appl. Mater. Interfaces* 2016, 8, 17212–17217.

(37) Li, H. L.; Gao, Y.; Wu, X. Y.; Lee, P. H.; Shih, K. M. Fabrication of heterostructured g-C$_3$N$_4$/Ag-TiO$_2$ hybrid photocatalyst with enhanced performance in photocatalytic conversion of CO$_2$ under simulated sunlight irradiation. *Appl. Surf. Sci.* 2017, 402, 198–207.

(38) Crake, A.; Christoforidis, K. C.; Kafizas, A.; Zafeiratos, S.; Petit, Y. C. CO$_2$ capture and photocatalytic reduction using bifunctional TiO$_2$/MOF nanocomposites under UV–vis irradiation. *Appl. Catal., B* 2017, 210, 131–140.

(39) Kang, S. F.; Li, S. S.; Pu, T. T.; Fang, X. Y.; Yin, C. C.; Dong, M. D.; Cui, L. F. Mesoporous black TiO$_2$ array employing sputtered Au cocatalyst exhibiting efficient charge separation and high H$_2$ evolution activity. *Int. J. Hydrogen Energy* 2018, 43, 22265–22272.

(40) Wu, T.; Ma, Y.; Qu, Z. B.; Fan, J. C.; Li, Q. X.; Shi, P. H.; Xu, Q. J.; Min, Y. L. Black Phosphorus–Graphene Heterostructure-Supported Pd Nanoparticles with Superior Activity and Stability for Ethanol Electro-oxidation. *ACS Appl. Mater. Interfaces* 2019, 11, 5136–5145.

(41) Cai, Q.; Liu, C. L.; Yin, C. C.; Huang, W.; Cui, L. F.; Shi, H. C.; Fang, X. Y.; Zhang, L.; Kang, S. F.; Wang, Y. G. Biotemplating Synthesis of Graphitic Carbon-Coated TiO$_2$ and Its Application as Efficient Visible-Light-Driven Photocatalyst for Cr$^{6+}$ Remove. *ACS Sustainable Chem. Eng.* 2017, 5, 3938–3944.

(42) He, W.; Guo, X.; Zheng, J.; Xu, J.; Hayat, T.; Alharbi, N. S.; Zhang, M. Structural Evolution and Compositional Modulation of ZIF-8-Derived Hybrids Comprised of Metallic Ni Nanoparticles and Silica as Interlayer. *Inorg. Chem.* 2019, 58, 7255–7266.

(43) Gong, S. Q.; Jiang, Z. J.; Shi, P. H.; Fan, J. C.; Xu, Q. J.; Min, Y. L. Noble-metal-free heterostructure for efficient hydrogen evolution in visible region: Molybdenum nitride/ultrathin graphitic carbon nitride. *Appl. Catal., B* 2018, 238, 318–327.

(44) Zhang, C. L.; Ren, S. Y.; Cheng, H. D.; Zhang, W. P.; Ma, J. H.; Zhang, C. S.; Guo, Z. Y. Thallium pollution and potential ecological risk in the vicinity of coal mines in Henan Province, China. *Chem. Speciation Bioavailability* 2018, 30, 107–111.

(45) Wei, Y. C.; Jiao, J. Q.; Zhao, Z.; Liu, J.; Li, J. M.; Jiang, G. Y.; Wang, Y. J.; Duan, A. J. Fabrication of inverse opal TiO$_2$-supported Au@CdS core–shell nanoparticles for efficient photocatalytic CO$_2$ conversion. *Appl. Catal., B* 2015, 179, 422–432.

(46) Zhao, Y. L.; Wei, Y. C.; Wu, X. X.; Zheng, H. L.; Zhao, Z.; Liu, J.; Li, J. M. Graphene-wrapped Pt/TiO$_2$ photocatalysts with enhanced photocogenerated charges separation and reactant adsorption for high selective photoreduction of CO$_2$ to CH$_4$. *Appl. Catal., B* 2018, 226, 360–372.

(47) Zhang, W. P.; Qian, J.; Xu, G. J.; Zhang, D. M.; Kang, C.; Feng, D. X.; Shi, L.; Zhang, C. L.; Guo, Z. Y.; Ma, J. H.; Zhang, C. S. Characterization and evaluation of heavy metal pollution in soil-wheat system around coal mines in Pingdingshan, China. *Appl. Ecol. Environ. Res.* 2019, 17, 5435–5447.

(48) Jiao, J. Q.; Wei, Y. C.; Zhao, Z.; Liu, J.; Li, J. M.; Duan, A. J.; Jiang, G. Y. Photocatalysts of 3D Ordered Macroporous TiO$_2$ Supported CeO$_2$ Nanolayers: Design, Preparation, and Their Catalytic Performances for the Reduction of CO$_2$ with H$_2$O under Simulated Solar Irradiation. *Ind. Eng. Chem. Res.* 2014, 53, 17345–17354.

(49) Wang, T.; LaMontagne, D.; Lynch, J.; Zhuang, J.; Cao, Y. C. Colloidal superparticles from nanoparticle assembly. *Chem. Soc. Rev.* 2013, 42, 2804–2806.