Design and synthesis of core-shell Au(Pt)@CdS nanoparticles supported on 3D ordered macroporous TiO_2 with enhanced catalytic activity for the photocatalytic reduction of CO_2 into hydrocarbons

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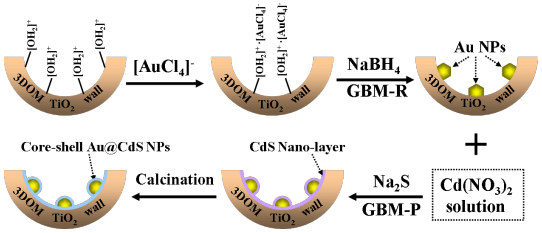
Introduction

The photocatalytic conversion of CO_2 into hydrocarbons using solar energy has attracted much attention under the current background of the depletion of fossil resources and the increase of CO_2 emissions. TiO_2 is by far the most common semiconductor in photocatalysis[1-3]. It is generally accepted that the noble metal co-catalyst may facilitate the separation of photogenerated electrons and holes by trapping electrons, and CdS has the lower energy band. Moreover, three-dimensionally ordered macroporous (3DOM) materials with big pore size (>50 nm) have a diffuse light effect. Therefore, we designed and synthesized the novel catalyst of 3D ordered macroporous TiO_2-supported Au(Pt)@CdS nanoparticles via the one-pot of gas bubbling-assisted membrane reduction-precipitation (GBMR/P) method[4-5].

Materials and Methods

The monodispersed polymethyl methacrylate (PMMA) microsphere was synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphase double initiators. And 3DOM TiO_2 support was prepared by the colloidal crystal template (CCT) method using tetrabutyl titanate as precursor solution [4]. 3DOM Au@CdS/TiO_2 catalysts were synthsized by one-pot process of the gas bubbling-assisted membrane reduction-precipitation (GBMR/P) method. The synthesis mechanism of the preparation method is presented in Scheme 1.



Scheme 1. Schematic representation for the one-pot synthesis of 3DOM Au@CdS/TiO2 catalysts by the GBMR/P method.

Results and Discussion

As shown in Figure 1A, the UV-Vis diffuse reflectance spectrum of 3DOM Au/TiO_2 catalyst displays distinct and well-defined surface plasmon absorption band centered at about 550 nm, which is the plasmon absorption peak of supported Au nanoparticles. With increasing of CdS shell content in 3DOM Au@CdS/TiO_2 catalysts, the intensity of the absorption band at visible region is remarkably increased and the plasmon absorption peak disappeared, but the position of the plasmon absorption peak is almost unchanged. And in XRD patterns (Figure 1B), the diffraction peaks (2θ) at 25.3, 37.8, 48.0, 53.9, 55.1, 62.7 and 75.0 ° can be indexed to the (101), (004), (200), (105), (211), (204) and (215) crystal faces of 3DOM TiO_2 with a tetragonal anatase structure (PDF# 21-1272), respectively. And the weak diffraction peaks (2θ) at 27.4 ° can be indexed to the (110) crystal faces of 3DOM TiO_2 with a tetragonal rutile structure (PDF# 65-0191). It indicates the coexistence of the two crystal phase structures for 3DOM TiO_2 support. As shown in Figure 1C and 1D, TEM and HRTEM images show 3DOM structure with overlapped pores can be clearly observed. One Au nanoparticle on the surface of 3DOM TiO_2 was covered by the CdS nanoparticles and formed the core-shell structural Au@CdS nanoparticles (Figure 1D). 3DOM Au@CdS/TiO_2 catalysts exhibit high photocatalytic activity for conversion of CO_2 into CH_4, i.e., the formation rate of CH_4 over the catalysts are more than 5 $\mu mol \cdot g^{-1} \cdot h^{-1}$.

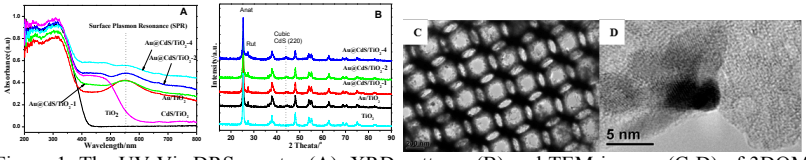


Figure 1. The UV-Vis DRS spectra (A), XRD patterns (B) and TEM images (C-D) of 3DOM Au@CdS/TiO2 catalysts

Significance

We successfully fabricated 3DOM Au@CdS/TiO_2 catalysts by one-pot process of GBMR/P method. The structure of catalysts is well-defined and uniformed. 3DOM Au@CdS/TiO_2 catalysts exhibit super catalytic performance for the CO_2 photoreduction into CH_4. The method can potentially be extended to other nanoparticle cores with different compositions, sizes and shapes and to other shell compositions on the surface of 3DOM support. The fabrication of metal@oxides core-shell nanostructure on 3DOM oxides surface could be widely applied in various heterogeneous oxides-metals photocatalytic systems.

Acknowledgements

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