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# Photocatalytic reduction of $CO_2$ with $H_2O$: significant enhancement of the activity of Pt–$TiO_2$ in $CH_4$ formation by addition of MgO†

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Shunji Xie, Yu Wang, Qinghong Zhang,* Wenqing Fan, Weiping Deng and Ye Wang*

**Photocatalytic activity in the reduction of $CO_2$ with $H_2O$ to $CH_4$ was significantly enhanced by simply adding MgO to $TiO_2$ loaded with Pt. A positive correlation between $CH_4$ formation activity and basicity was observed. The interface between $TiO_2$, Pt and MgO in the trinary nanocomposite played a crucial role in $CO_2$ photocatalytic reduction.**

The diminishing fossil resources and the growing concerns over the emissions of $CO_2$ have stimulated research activities on the utilization of $CO_2$.[1] The activation of $CO_2$ is one of the most challenging themes in chemistry since $CO_2$ is a highly stable molecule. Typically, a large energy input or co-feeding of a high-energy reactant such as $H_2$ is required for the activation and conversion of $CO_2$. The photocatalytic conversion of $CO_2$ using solar energy, *i.e.*, the artificial photosynthesis, is one of the most attractive routes for the utilization of $CO_2$. Inoue *et al.* reported a pioneering study on the reduction of $CO_2$ in aqueous suspensions containing semiconductor powders.[2] Semiconductor-based photocatalytic reduction of $CO_2$ with $H_2O$ has attracted much attention in recent years.[3–6] Various semiconductors such as $TiO_2$,[3–6] $Ga_2O_3$,[7] $ZnGe_2O_4$,[8] $ZnGa_2O_4$[9] have been reported for the photocatalytic conversion of $CO_2$. Several strategies that are usually used for promoting the photocatalytic $H_2$ evolution,[6] *e.g.*, the addition of noble or coinage metals or metal oxides onto the semiconductor,[10] the preparation of semiconductors with different crystalline structures or morphologies,[11] and the preparation of semiconductor–semiconductor nanocomposites,[12] have also been exploited for $CO_2$ reduction. The photocatalytic activity is, however, still low. Undoubtedly, new strategies are required to further promote the photocatalytic reduction of $CO_2$ with $H_2O$.

Enhanced adsorption of $CO_2$ on basic sites may promote its subsequent photocatalytic reduction. Photocatalytic conversion of $CO_2$ to CO was reported over solid bases such as MgO, an insulator, in the presence of $H_2$ or $CH_4$.[13] Very recently, layered double hydroxides, typical solid bases, were reported to promote the photodecomposition of $CO_2$ to CO and $O_2$ or the photoreduction of $CO_2$ to $CH_4$ with $H_2O$ with deep ultraviolet (UV) radiation ($\lambda < 200$ nm).[14,15] These reactions, however, do not involve the semiconductor catalyst and have been proposed to proceed *via* different mechanisms. To the best of our knowledge, there is no study on the effect of basic additives on the performance of a semiconductor-based photocatalyst in the reduction of $CO_2$ with $H_2O$ under UV or visible light irradiation. Herein, we report a significant enhancement of photocatalytic activity of $TiO_2$-based catalysts by simply adding a basic metal oxide. Our work provides a novel strategy for the design of efficient semiconductor-based nanocomposite photocatalysts for the reduction of $CO_2$ with $H_2O$.

Fig. 1 displays the photocatalytic performances of several $TiO_2$-based photocatalysts in the reduction of $CO_2$ in the presence of $H_2O$ (see the ESI† and Fig. S1 for experimental details). CO and $CH_4$ were the two main products. $TiO_2$ (Degussa P25) alone provided CO and $CH_4$ with amounts of 0.24 and 0.07 μmol, respectively. The loading

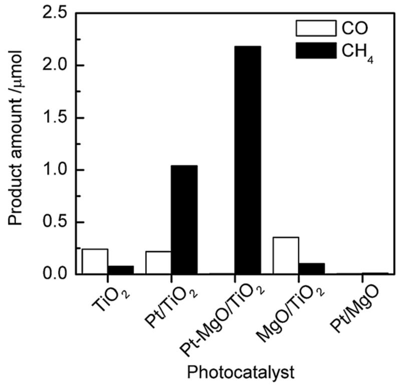

**Fig. 1** Amounts of CO and $CH_4$ formed in the photocatalytic reduction of $CO_2$ in the presence of $H_2O$. Reaction conditions: catalyst, 0.020 g; $CO_2$ pressure, 2 MPa; $H_2O$, 1.0 mL; irradiation time, 10 h.

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*State Key Laboratory of Physical Chemistry of Solid Surfaces, Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*
*E-mail: wangye@xmu.edu.cn, zhangqh@xmu.edu.cn; Fax: +86-592-2183047;*
*Tel: +86-592-2186156*

† Electronic supplementary information (ESI) available: Experimental details, comparison of $CH_4$ formation in the presence and absence of $CO_2$, effect of various basic metal oxide modifiers on photocatalytic performances of Pt–$TiO_2$. See DOI: 10.1039/c3cc00107e

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of Pt nanoparticles onto $TiO_2$ with a content of 0.5 wt% using a photodeposition method increased the amount of $CH_4$ to 1.0 μmol. The increase in $CH_4$ formation because of a noble metal co-catalyst was also reported by other groups.[10,16] This is attributable to the efficient electron–hole separation caused by the Pt nanoparticles.[10b] The addition of 1.0 wt% MgO onto $TiO_2$, followed by loading of Pt nanoparticles, further significantly increased the amount of $CH_4$ to 2.2 μmol. The amount of $CH_4$ increased almost linearly with reaction time, whereas almost no $CH_4$ was observed in the absence of $CO_2$ (Fig. S2, ESI†), confirming that $CH_4$ was formed by the photocatalytic conversion of $CO_2$. The formation of $O_2$ over the Pt–MgO/$TiO_2$ was confirmed, and the molar ratio of $O_2$/$CH_4$ was approximately 2.5/1, slightly higher than the stoichiometric ratio (2/1) expected from the photocatalytic conversion of $CO_2$ with $H_2O$ to $CH_4$ and $O_2$ (see the ESI†). On the other hand, the addition of 1.0 wt% MgO onto $TiO_2$ without loading Pt only slightly increased the amounts of CO and $CH_4$. The 0.5 wt% Pt–MgO was almost inactive in photocatalytic reduction of $CO_2$, confirming that the reduction of $CO_2$ arises from the photogenerated electrons from $TiO_2$. These observations indicate the significant role of MgO in photocatalytic formation of $CH_4$ and the importance of co-existence of Pt nanoparticles.

The modifying effect of other metal oxides on the photocatalytic activity of the 0.5 wt% Pt–$TiO_2$ catalyst was further investigated. We found that the modification of the Pt–$TiO_2$ using basic oxides such as SrO, CaO, BaO, $La_2O_3$ and $Lu_2O_3$ could also increase the amount of $CH_4$ (Table S1, ESI†). Over these modified catalysts, the formation of CO was inhibited. The mean sizes of Pt nanoparticles over these modified catalysts were 3.8–4.1 nm, close to that (4.2 nm) over the Pt–$TiO_2$ catalyst without modification. The Brunauer–Emmett–Teller (BET) surface areas of the modified catalysts measured using $N_2$ physisorption were 43–51 $m^2\ g^{-1}$, slightly lower than that (55 $m^2\ g^{-1}$) of the Pt–$TiO_2$ catalyst. Thus, the increase in the photocatalytic activity as a result of modification with basic oxides should not be due to the changes in the size of Pt nanoparticles or the surface area of photocatalysts. We evaluated the catalyst basicity by measuring the amount of $CO_2$ chemisorption.[17] We found a linear correlation between the amount of $CH_4$ formed and the amount of chemisorbed $CO_2$ over a series of basic oxide-modified Pt–$TiO_2$ photocatalysts (Fig. 2). This allows us to propose that the catalyst basicity contributes to the photocatalytic reduction of $CO_2$ with $H_2O$ to $CH_4$.

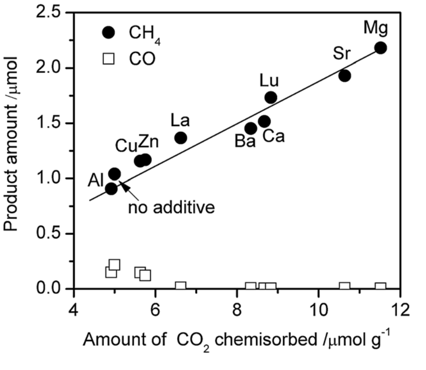

**Fig. 2** Correlation between the amount of $CH_4$ formed and the amount of $CO_2$ chemisorbed on the Pt–$TiO_2$ photocatalysts modified with various basic metal oxides. Reaction conditions: catalyst, 0.020 g; $CO_2$ pressure, 2 MPa; $H_2O$, 1.0 mL; irradiation time, 10 h.

**Table 1** Effect of the content of MgO on photocatalytic performances of the Pt–MgO/$TiO_2$ in the reduction of $CO_2$ in the presence of $H_2O$[a]

| Photocatalyst[b] | $S_{BET}$[c] ($m^2\ g^{-1}$) | Mean size of Pt (nm) | Chemisorbed $CO_2$ (μmol $g^{-1}$) | Product amount (μmol) | |
|---|---|---|---|---|---|
| | | | | CO | $CH_4$ |
| Pt–$TiO_2$ | 55 | 4.2 | 5.0 | 0.22 | 1.0 |
| Pt–0.25% MgO/$TiO_2$ | 41 | 3.8 | 7.4 | 0.058 | 1.3 |
| Pt–0.5% MgO/$TiO_2$ | 43 | 4.1 | 10 | 0.006 | 1.6 |
| Pt–1.0% MgO/$TiO_2$ | 43 | 4.0 | 12 | 0.006 | 2.2 |
| Pt–2.0% MgO/$TiO_2$ | 42 | 4.2 | 15 | 0.006 | 1.8 |
| Pt–3.0% MgO/$TiO_2$ | 44 | 4.1 | 17 | 0.004 | 1.3 |
| Pt–$TiO_2$ + MgO/$TiO_2$[d] | — | 4.2 | — | 0.28 | 0.70 |

[a] Reaction conditions: catalyst, 0.020 g; $CO_2$ pressure, 2 MPa; $H_2O$, 1.0 mL; irradiation time, 10 h. [b] Pt loading in each catalyst was 0.50 wt%. [c] BET surface area. [d] The physical mixture with the same composition as the 0.5 wt% Pt–1.0 wt% MgO/$TiO_2$ photocatalyst.

The Pt–MgO/$TiO_2$ catalyst exhibited the best photocatalytic performance in $CH_4$ formation among the modified Pt–$TiO_2$ catalysts examined in our work. We further investigated the effect of the content of MgO on the photocatalytic performance. Table 1 shows that the amount of chemisorbed $CO_2$ increases monotonically with the content of MgO. However, there is an optimum content of MgO for $CH_4$ formation; the amount of $CH_4$ increases with increasing content of MgO up to 1.0 wt%, and then decreases with a further increase in the content of MgO. The BET surface area and the size of Pt nanoparticles did not undergo significant changes with an increase in the content of MgO from 0.25 wt% to 3.0 wt%. Thus, there may exist other factors controlling the photocatalytic performance in the Pt–MgO/$TiO_2$ trinary nanocomposite.

We performed transmission electron microscopy (TEM) studies of the Pt–MgO/$TiO_2$ catalysts with MgO contents of 1.0 wt% and 3.0 wt%. As displayed in Fig. 3, MgO existed as amorphous thin layers located on the surfaces of $TiO_2$ crystallites in both catalysts. Over the 0.5 wt% Pt–1.0 wt% MgO/$TiO_2$ photocatalyst, the interface between $TiO_2$, Pt and MgO could be clearly observed in the enlarged image (Fig. 3b). Moreover, because the MgO layer is thin, Pt nanoparticles could be easily

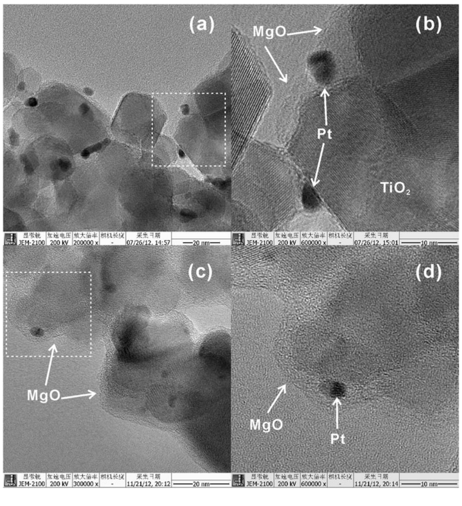

**Fig. 3** TEM micrographs of 0.5 wt% Pt–1.0 wt% MgO/$TiO_2$ (a and b) and 0.5 wt% Pt–3.0 wt% MgO/$TiO_2$ (c and d). (b and d) Enlarged images of (a) and (c).

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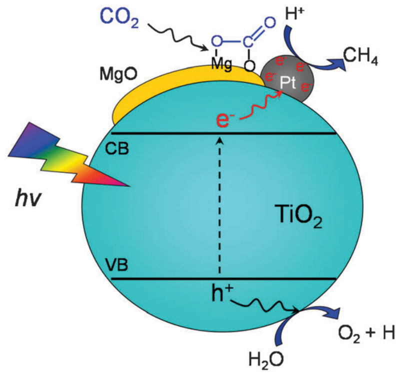

**Fig. 4** Proposed functioning mechanisms of the MgO layer and Pt nanoparticles over $TiO_2$ for photocatalytic reduction of $CO_2$ in the presence of $H_2O$.

accessed by the reactants such as $H_2O$ (or protons) during the reaction. On the other hand, relatively thicker MgO layers were observed over the 0.5 wt% Pt–3 wt% MgO/$TiO_2$ photocatalyst. The thicker MgO layer could cover Pt nanoparticles (Fig. 3d). This may lead to the decrease in the photocatalytic activity. Thus, the proper location of the three components in the photocatalyst should also determine the photocatalytic performance. This has further been confirmed by the experimental fact that the physical mixture of Pt–$TiO_2$ and MgO/$TiO_2$ with the same composition as in the 0.5 wt% Pt–1.0 wt% MgO/$TiO_2$ photocatalyst exhibited much inferior performances (Table 1).

Based on the results described above, we propose functioning mechanisms of MgO and Pt co-catalysts for accelerating the formation of $CH_4$ in Fig. 4. $CO_2$ is first chemisorbed on the MgO layer on $TiO_2$ crystallites. The chemisorbed $CO_2$ molecule becomes destabilized and its reactivity is believed to be higher than that of the linear $CO_2$ molecule.[14,17] On the other hand, photogenerated electrons on $TiO_2$ can be easily trapped by the Pt nanoparticles because of the lower Fermi energy level of the noble metal. It is known that the formations of CO and $CH_4$ require two and eight electrons, respectively. The enriched electron density on Pt nanoparticles would favour the formation of $CH_4$, which is thermodynamically more feasible than the formation of CO.[10b] Our result has demonstrated that Pt enhances the photocatalytic reduction of $CO_2$ to $CH_4$ but not to CO (Fig. 1). The synergistic effect between MgO, which enhances the density of destabilized $CO_2$ molecules on the catalyst surface, and Pt nanoparticles with enriched electron density can further accelerate the reduction of $CO_2$ to $CH_4$. Clearly, such a synergistic effect requires the intimate contact of Pt between both $TiO_2$ and MgO, strengthening the key role of the interface.

Besides the role of basicity, MgO layers on $TiO_2$ surfaces might also capture the holes and facilitate the separation of photogenerated electrons and holes. Actually, such a role of $Al_2O_3$ thin layers coated on $Fe_2O_3$ surfaces was once reported by Formal *et al.*[18] Moreover, the coverage of $TiO_2$ surfaces with MgO might hinder the direct contact of CO or $CH_4$ with $TiO_2$ surfaces, reducing the reoxidation possibilities for CO and $CH_4$.

In conclusion, we have demonstrated for the first time that the photocatalytic reduction of $CO_2$ with $H_2O$ to $CH_4$ can be significantly enhanced by simply adding MgO, a basic oxide, onto $TiO_2$ in the presence of a Pt co-catalyst. A positive correlation between the activity of $CH_4$ formation and the catalyst basicity has been observed in the trinary nanocomposites containing $TiO_2$, Pt and a basic metal oxide. The interface between $TiO_2$, Pt and MgO plays a crucial role in the photocatalytic reaction. The functions of MgO are proposed to be mainly enhancing the density of $CO_2$ on the catalyst surface and destabilizing $CO_2$ molecules, which are subsequently reduced by the photogenerated electrons enriched on the nearby Pt nanoparticles from $TiO_2$.

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