Retraction for Journal of Materials Chemistry A:

Synthesis of Pt@TiO$_2$@MnO$_x$ hollow spheres with high spatial charge separation efficiency for photocatalytic overall water splitting

Lichen Liu, Weixin Zou, Xianrui Gu, Chengyan Ge, Yu Deng, Changjin Tang, Fei Gao, Lin Dong and Avelino Corma


We, the named authors, hereby wholly retract this *Journal of Materials Chemistry A* article due to the subsequent realisation that the O$_2$ evolution rates reported summarised in Fig. 5 cannot be repeated in the Valencia labs. However, the H$_2$ evolution rates can still be reproduced. Because the oxidation products are mainly radicals or H$_2$O$_2$, we do not observe much O$_2$ evolved. In addition, we also find that the O$_2$ evolution rates seem to be related to the activity test equipment (the Hg lamp we used and the additives in H$_2$O).

Signed: Lichen Liu, Weixin Zou, Xianrui Gu, Chengyan Ge, Yu Deng, Changjin Tang, Fei Gao, Lin Dong and Avelino Corma, February 2014.

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Synthesis of Pt@TiO$_2$$@$MnO$_x$ hollow spheres with high spatial charge separation efficiency for photocatalytic overall water splitting

Lichen Liu,$^a$ Weixin Zou,$^a$ Xianrui Gu,$^a$ Chengyan Ge,$^a$ Yu Deng,$^b$ Changjin Tang,$^a$ Fei Gao,$^{ab}$ Lin Dong$^{ab}$ and Avelino Corma$^a$

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The charge separation efficiency is a key problem that restricts the catalytic performances of photocatalytic materials. A composite material is constructed based on TiO$_2$ hollow spheres. MnO$_x$ and Pt nanoparticles are chosen as oxidation and reduction co-catalysts and they are anchored on the inner surface and outer surface of TiO$_2$ hollow spheres, respectively. Under UV light excitation, the photogenerated electrons and holes will move to the co-catalysts located on the two sides of the TiO$_2$ shells, resulting in the efficient spatial separation. With the spatial separation of co-catalysts, the photocatalytic overall water splitting efficiency is significantly improved compared with TiO$_2$ hollow spheres with random distribution of co-catalysts. High H$_2$ and O$_2$ evolution rates can be achieved, indicating that rational design of the distribution of co-catalysts is important to build highly active photocatalysts.

Photocatalytic water splitting for H$_2$ evolution is considered as one of the most promising strategies for clean and renewable energy sources.$^{1-3}$ Although great efforts have been made to develop new photocatalytic materials, the catalytic performances using semiconductors are still low. One of the key issues related to this problem is the low charge separation efficiency of the photogenerated electrons and holes in semiconductors.$^4$ To overcome this problem, various strategies have been used, among them loading co-catalysts is proved to be very effective.$^5$ Co-catalysts (including reduction and oxidation co-catalysts) can serve as the trapping sites of photogenerated charge carriers and the reaction sites for surface photo-reactions.$^6$ With the synergistic effect of Pt and RuO$_2$, Li et al. have demonstrated that overall water splitting can be realized on Pt-RuO$_2$/ZnGeO$_2$ under UV light.$^7$ Moreover, in the work of Domen et al., GaN:ZnO solid solution shows excellent overall water splitting performance under visible light after loading Rh/Cr$_2$O$_3$ and Mn$_3$O$_4$.$^8$

Except for loading co-catalysts, building ordered nanomaterials with anisotropic structures is another effective approach to high-performance photocatalysts for water splitting. Through building well-designed nanoscale heterostructures, the photogenerated electrons and holes can be transported to different reaction zones to achieve the charge separation.$^9$ Recently, Yang and his co-workers have fabricated a fully integrated nanowire system for solar overall water splitting.$^9$ The reduction reaction and oxidation reaction are occurred on Si nanowires and TiO$_2$ nanowires, respectively. IrO$_2$ and Pt nanoparticles are deposited on Si and TiO$_2$ nanowires respectively to serve as the co-catalysts. But the photocatalytic efficiency may need to be further improved due to the low surface areas of these nanowire materials.$^{13}$

However, in most of the previous studies, the dual co-catalysts are randomly loaded on the semiconductors, which is not favoured for the oriented charge separation. In the natural photosynthesis system, the photo-oxidation and photo-reduction reactions are occurred on two sides of thylakoid membrane.$^{14,15}$ Because of this artistic design and the high photoactivities of enzymes, the natural photosynthetic systems show highly efficient energy conversion. Inspired by the nature’s strategy, we intend to synthesize composite TiO$_2$ hollow spheres with co-catalysts located on the inner surface and outer surface. Herein, we choose Pt and MnO$_x$ as the reduction and oxidation co-catalyst, respectively. In this Pt@TiO$_2$$@$MnO$_x$ nanostructure, after light excitation, the photogenerated electrons will move to the Pt nanoparticles (reduction co-catalyst), and holes will move to the MnO$_x$ (oxidation co-catalyst) on the outer surface, leading to an efficient spatial charge separation. The charge separation efficiency will be much higher compared with TiO$_2$ hollow spheres with random distribution of co-catalysts (as shown in Scheme 1a). Because of its advantages in charge separation, the Pt@TiO$_2$$@$MnO$_x$ hollow spheres may show promising applications in photocatalytic overall water splitting.

In this work, the Pt@TiO$_2$$@$MnO$_x$ hollow spheres are synthesized as described in Scheme 1b. Carbon nanospheres...
with diameters of 200–300 nm (Fig. S1) are obtained through the hydrothermal treatment on glucose and used as hard templates. As displayed in Fig. S2, Pt clusters (1–2 nm) can be in-situ loaded on the carbon spheres without additive reductive agents because of reductive organic groups on the surface of carbon spheres. Afterwards, TiO$_2$ shells are coated on the C@Pt nanoparticles through a sol-gel method. After calcination in air at 500 °C, the carbon sphere templates can be fully removed and Pt@TiO$_2$ hollow spheres are obtained. At last, MnO$_2$ are loaded on the outer surface of Pt@TiO$_2$ hollow spheres through a photo-deposited method, resulting in the formation of Pt@TiO$_2$@MnO$_2$ hollow spheres.

As shown in Fig. 1a, the as-prepared Pt@TiO$_2$ hollow spheres have diameters ranging from 250 nm to 350 nm. In Fig. 1b, we can figure out that the thickness of the TiO$_2$ shell is about 25 nm. Pt nanoparticles with average size of 3.5 nm are uniformly dispersed in TiO$_2$ hollow spheres. The sizes of Pt nanoparticles have grown larger due to the calcination at 500 °C. Because of the high temperature calcination, Pt nanoparticles can have a more intimate contact with TiO$_2$, which may favor the charge transfer across the metal-semiconductor interface. Furthermore, from Fig. 1c, we can find that no Pt nanoparticles can be found on the outer surface of TiO$_2$ hollow spheres, suggesting that they are anchored on the inner surface. HRTEM image in Fig. 1d also confirms the existence of Pt nanoparticles with a lattice space of 0.22 nm ([111]) facets. The lattice space of TiO$_2$ nanoparticles is 0.35 nm, which is corresponding to {101} facets of anatase.

$\text{TiO}_2$. The STEM-HAADF mapping is employed to figure out the distribution of Pt nanoparticles. The elemental mapping of a single Pt@TiO$_2$ hollow sphere is displayed in Fig. 1e. Through comparing the mapping results of Ti, O and Pt, it is confirmed that Pt nanoparticles are encapsulated by TiO$_2$ shell.

When Pt@TiO$_2$ is irradiated by UV light in aqueous of Mn(Ac)$_2$, photogenerated electrons will be trapped by Pt nanoparticles and the holes will mainly transfer to the outer surface of TiO$_2$ hollow spheres and react with Mn$^{2+}$. After oxidized by the holes, Mn$^{2+}$ will be deposited on the outer surface in the form of MnO$_2$, leading to the formation of Pt@TiO$_2$@MnO$_2$ composite structure. The morphological information about Pt@TiO$_2$@MnO$_2$ is also investigated by TEM. The morphology of Pt@TiO$_2$@MnO$_2$ hollow spheres is similar with Pt@TiO$_2$ hollow spheres, as displayed in Fig. 2a. On the outer surface of TiO$_2$ shell, sheet-like MnO$_2$ can be observed (Fig. 2b). As for Pt nanoparticles, they are still located on the inner surface of TiO$_2$ shells. HRTEM images in Fig. 2c and Fig. 2d show the lattice information of TiO$_2$ and Pt, which is similar with those in Pt@TiO$_2$ hollow spheres. In Fig. 2d, a HRTEM image of MnO$_2$ nanoparticle is also presented. The lattice spacing is 0.38 nm, which can be ascribed to the (102) facet of MnO$_2$. In addition, the element distributions in the Pt@TiO$_2$@MnO$_2$ composite hollow spheres are studied with STEM-HAADF. Elemental mapping of Pt@TiO$_2$@MnO$_2$ hollow spheres are presented in Fig. 2e. The overlap image can be used to identify the location of these elements. Obviously, mapping signal of Pt is surrounded by Ti and O, which is corresponding with their
These samples show similar phase structures and we can find that both Pt and Mn show low contents. Chemical statuses of Pt and Mn in the as-prepared materials are studied by XPS. As shown in Fig. S3, both of them show the typical XRD patterns of anatase TiO$_2$. Peaks corresponding to Pt or MnO$_x$ cannot be found, which is probably caused by their low contents. Chemical statuses of Pt and Mn in the as-prepared materials are studied by XPS. Since Pt nanoparticles are encapsulated by TiO$_2$ shells, the XPS signal of Pt 4f region is very weak in Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$. According to the binding energy of XPS peak in 4f region (Fig. S4), Pt exists in metallic state. For Mn, both Mn$^{2+}$ and Mn$^{4+}$ can be found (Fig. S5), which is corresponding to MnO$_x$ (1.5<x<2). The surface chemical components of Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$ obtained from XPS are also listed in Table S2. Compared with the results in Table S1, we can find that the amount of Pt in Table S1 is higher than that in Table S2, while amount of Mn in Table S1 is lower than that in Table S2. These differences are consistent with the different spatial distributions of Pt and Mn. We also measure the pore structures of Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$ through N$_2$ adsorption-desorption isotherms. As shown in Fig. S6 and Table S3, they show similar pore size distributions and BET surface areas.

![Fig. 3 Time-resolved PL spectra of TiO$_2$ hollow spheres, TiO$_2$@MnO$_x$ hollow spheres, Pt@TiO$_2$ hollow spheres, Pt-MnO$_x$/TiO$_2$ hollow spheres and Pt@TiO$_2$@MnO$_x$ hollow spheres.](image)

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<th>Sample</th>
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<th>τ$_2$/ns</th>
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<td>Pt-MnO$_x$/TiO$_2$</td>
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<td>5.65</td>
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</table>

**Table 1** Fitting parameters of time-resolved PL spectra of TiO$_2$ hollow spheres, TiO$_2$@MnO$_x$ hollow spheres, Pt@TiO$_2$ hollow spheres, Pt-MnO$_x$/TiO$_2$ hollow spheres and Pt@TiO$_2$@MnO$_x$ hollow spheres.

For comparison, we also prepared pure TiO$_2$ hollow spheres using carbon nanospheres as templates. Using pure TiO$_2$ hollow spheres as basic materials, TiO$_2$@MnO$_x$ hollow spheres and Pt-MnO$_x$/TiO$_2$ hollow spheres are also prepared. The details of the synthesis and structural characterizations are presented in supporting information (Fig. S7-S10). For the Pt-MnO$_x$/TiO$_2$ sample, both MnO$_x$ and Pt nanoparticles are found on both surfaces of TiO$_2$ hollow spheres, suggesting that they are randomly dispersed. The amounts of Mn and Pt in TiO$_2$@MnO$_x$ and Pt-MnO$_x$/TiO$_2$ are almost the same with those in Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$ hollw spheres (Table S1 and Table S2). Besides, these samples show similar phase structures and BET surface areas compared with Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$ hollow spheres (Table S3), which indicates that they are suitable materials for comparison to investigate the effects of the spatial distributions of co-catalysts on the photocatalytic performances.

The chemical status of Mn and Pt in TiO$_2$@MnO$_x$ and Pt-MnO$_x$/TiO$_2$ hollow spheres are almost compared with those in Pt@TiO$_2$ and Pt@TiO$_2$@MnO$_x$ hollow spheres. As we can see in Fig. S11 and Fig. S12, MnO$_x$ in both TiO$_2$@MnO$_x$ and Pt-MnO$_x$/TiO$_2$ hollow spheres show similar chemical status with Pt@TiO$_2$@MnO$_x$. In addition, the signal intensities of TiO$_2$@MnO$_x$ and Pt-MnO$_x$/TiO$_2$ in Mn 2p region are weaker than that of Pt@TiO$_2$@MnO$_x$, which also confirms their different spatial distribution. Pt in those samples are all in the state of Pt(0), although the intensity of Pt 4f signal intensities are different, which is caused by their different nanoscale structures.

To investigate the efficiencies of the above TiO$_2$-based hollow spheres in charge separation, time-resolved photoluminescence (PL) spectra are employed to measure them. As shown in Fig. 3, these samples are excited by a 350 nm-laser pulse, resulting in emission of photoluminescence as a result of recombination of photogenerated electrons and holes. The sample with efficient charge separation will show a slow PL signal decay due to the long lifetime of photogenerated holes and electrons. The half-lives of decay time of these samples are listed in Table 1 according to fitting the data points in Fig. 3. TiO$_2$ hollow spheres without any co-catalysts show a slow PL decay and short half-life. After loading Pt or MnO$_x$, the decay time is prolonged. When Pt and MnO$_x$ are co-loaded on TiO$_2$ hollow spheres in a random way, the decay time is further prolonged compared with the TiO$_2$ hollow spheres with single co-catalyst. For Pt@TiO$_2$@MnO$_x$ composite hollow spheres, the decay time is significantly increased, indicating the lifetimes of photogenerated electrons and holes are greatly improved. With long-lived photogenerated charge carriers, the photocatalytic activities of TiO$_2$ hollow spheres will be promoted.
In order to study the effects of spatial distribution of co-catalysts, the photoelectrochemical properties of pure and modified TiO₂ hollow spheres are measured. The transient photoresponse spectra are presented in Fig. 4. For the photoelectrode made of pure TiO₂ hollow spheres, the photocurrent is quite weak. When MnO₂ or Pt nanoparticles are loaded on TiO₂ hollow spheres, the photocurrent is increased, suggesting that the co-catalysts can enhance the charge separation efficiency. For the Pt-MnO₂/TiO₂ sample, due to the synergistic effects of Pt and MnO₂, the photocurrent is further increased. However, this improvement is not quite obvious. Notably, the photocurrent of Pt@TiO₂/MnO₂ is dramatically enhanced compared with other samples, indicating a more efficient charge separation. The order of the intensities of photocurrents is well consistent with the order of the half-lives of photogenerated charge carriers in Table 1.

Besides, the electrochemical impedance spectra (Fig. S13) also confirm that the charge separation efficiency can be significantly improved through designing nanostructures with spatial separation of co-catalysts. Combining the results obtained from time-resolved PL spectra, we can conclude that the spatial distribution of co-catalysts has a significant influence on the charge separation process. Through anchoring MnO₂ and Pt nanoparticles on the outer surface and inner surface of TiO₂ hollow spheres respectively, efficient spatial separation of photogenerated electrons and holes can be realized.

The photocatalytic overall water splitting to H₂ and O₂ is employed as a probe reaction to test the effects of spatial distribution of co-catalysts on the photocatalytic activities. The activity results of pure TiO₂ and modified-TiO₂ hollow spheres are shown in Fig. 5. For pure TiO₂ hollow spheres, the evolution rates of H₂ and O₂ are quite low (1.5 μmol h⁻¹ for H₂ and 0.74 μmol h⁻¹ for O₂), which is caused by the large over-potentials on TiO₂ surface. When MnO₂ is loaded on TiO₂ hollow spheres, the activity (9.3 μmol h⁻¹ for H₂ and 4.6 μmol h⁻¹ for O₂) is improved because MnO₂ can work as the traps of holes and contribute the water oxidation half reaction. For Pt@TiO₂ hollow spheres, the H₂ and O₂ evolution rates (18.2 μmol h⁻¹ for H₂ and 9.1 μmol h⁻¹ for O₂) are further increased since Pt nanoparticles are efficient co-catalyst for proton reduction half reaction. Interestingly, the activity of Pt@TiO₂ is almost two times of that of TiO₂@MnO₂, which is similar with previous work. The Pt-MnO₂/TiO₂ sample with dual co-catalysts show higher photoactivity (32.5 μmol h⁻¹ for H₂ and 16.1 μmol h⁻¹ for O₂) than Pt@TiO₂, TiO₂@MnO₂ and even the sum of them, indicating that synergistic effect should exist between Pt and MnO₂. Furthermore, the H₂ and O₂ evolution of Pt@TiO₂@MnO₂ hollow spheres (96.5 μmol h⁻¹ for H₂ and 48.1 μmol h⁻¹ for O₂) are much higher than Pt-MnO₂/TiO₂ hollow spheres (about three times), suggesting that the distribution of co-catalysts have a significant influence on the photoactivity. Compared to pure TiO₂ hollow spheres, the H₂ and O₂ evolution rates are almost enhanced for two orders.

According to the previous structural characterizations, Pt@TiO₂@MnO₂ hollow spheres shows similar phase structures, pore structures and chemical components with Pt-MnO₂/TiO₂ hollow spheres. The major difference between these two samples is the spatial distributions of Pt and MnO₂. As a consequence of this difference, the separation efficiency of photogenerated electrons and holes in these two samples are different. From Fig. 3 and Table 1, we have proved that Pt@TiO₂@MnO₂ shows a more efficient charge-separation than Pt-MnO₂/TiO₂. The lifetimes of the active photogenerated electrons and holes are much longer than those in Pt-MnO₂/TiO₂. Based on the photoelectrochemical measurements in Fig. 4, it is further confirmed that the combination of photogenerated electrons and holes are suppressed in Pt@TiO₂@MnO₂, leading to higher photocurrent than Pt-MnO₂/TiO₂. As described in the Scheme 1a, the photogenerated electrons and holes will move towards opposite directions, resulting in spatial charge separation. This type of charge separation is more effective because the possibility of recombination during the charge migration will be decreased. Combining the above analysis and photocatalytic results, we can conclude that the spatial separation of reduction co-catalyst and oxidation co-catalyst is more superior to the random distribution of co-catalysts.

The cyclability test of Pt@TiO₂@MnO₂ is also carried out. As shown in Fig. S14, the H₂ and O₂ evolution rates keep stable after three runs. TEM images (Fig. S15) show that the locations of MnO₂ and Pt nanoparticles in Pt@TiO₂@MnO₂ hollow spheres are also preserved after five tests, suggesting that this type of nanostructure is quite stable. Thus, the as-prepared Pt@TiO₂@MnO₂ hollow spheres are promising photocatalytic materials for water splitting reaction.

Conclusions

In summary, Pt@TiO₂@MnO₂ composite hollow spheres are constructed based on TiO₂ hollow spheres. MnO₂ and Pt nanoparticles are anchored on the inner surface and outer surface of TiO₂ hollow spheres, respectively. Under UV light excitation, the photogenerated electrons and holes will move to the co-catalysts located on the two sides of the TiO₂ shells, resulting in opposite migration of charge carriers and efficient spatial separation. With these composite TiO₂ hollow spheres, the photocatalytic overall water splitting efficiency is significantly improved compared with TiO₂ hollow spheres with random distribution of co-catalysts. This work indicates that rational design of the distribution of co-catalysts is important to build highly active photocatalysts.

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Notes and references
5 * Key Laboratory of Mesoscopic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China. E-mail: donglin@nju.edu.cn
6 † Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China. E-mail: gaofei@nju.edu.cn
7 * Instituto de Tecnología Química UPV-CSIC Avda. Los Naranjos s/n, 46022, Valencia, Spain. Fax: (+34) 963877809. E-mail: acorma@itq.upv.es
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