Phase-selectivity photocatalysis: a new approach in organic pollutants' photodecomposition by nanovoid core(TiO$_2$)/shell(SiO$_2$) nanoparticles†

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Core(TiO$_2$)/shell(SiO$_2$) nanoparticles, with a void layer between the TiO$_2$ core and the silica layer, act as phase-selectivity photocatalysts for the photodecomposition of organic pollutants (gas phase) without any damage to their organic supports (solid phase).

Even though the superior photocatalytic performance of titanium(IV) dioxide (TiO$_2$) has been known for almost 30 years, a limitation quite prohibits its application in investigations. Because of the high photocatalytic activity and photostabilization of TiO$_2$, photocatalytic processes to decompose organic pollutants by oxidation utilizing TiO$_2$, either in the form of unsupported suspended TiO$_2$ powder or in the form of TiO$_2$ immobilized on supports, have been the subject of extensive research.[1–5] Considering that it is difficult to deal with the powder, there is a preference to use immobilized TiO$_2$ as the catalyst in photocatalytic decomposition. However, such immobilized systems suffer from some serious drawbacks that limit their utilization, because organic supports such as textiles, paints, plastic films *etc.*, will be photo etched by the high redox activity of TiO$_2$. The core/shell technique is the most common method that people use to obtain shell-protected TiO$_2$ nanoparticles in order to avoid the instability of the supports.[6,7] However, most works have to confront the problem that the core/shell catalysts always lose their activity because the activity sites of TiO$_2$ will be shielded by the shell. This problem seems difficult to overcome and it is generally accepted that "there was no guaranteed method to obtain both long term mechanical stability of the organic supports and/or photocatalytic activity".[8,9] However, we attempt to challenge this problem and we aim at creating a void layer between the TiO$_2$ core and the silica layer to obtain a phase-selective photocatalyst. The catalyst can keep the inherent photocatalytic activity for photodecomposition of organic pollutants

(gas phase) without any damage to the immobilized organic support (solid phase).

Nanovoid core(TiO$_2$)/shell(SiO$_2$) nanoparticles, in which a void layer is present between the TiO$_2$ core and the silica layer, were prepared in three steps.[10,11] First, a carbon layer was coated on TiO$_2$ (P-25, Degussa Co. Ltd.) by a hydrothermal reaction. To an aqueous solution containing glucose (0.5 M, 40 ml), 250 mg TiO$_2$ was added. The reaction was performed at 453 K for 5 h, and isolated by filtration. After washing by water and ethanol, carbon coated TiO$_2$ (denoted as C@TiO$_2$) was obtained. In the second step, a second silica layer was coated on the C@TiO$_2$ *via* the conventional alkoxide sol-gel method.[12,13] An appropriate amount of carbon-coated TiO$_2$ (C@TiO$_2$) thus-obtained was suspended in a mixed solution of acetone (23 ml) and chloroform (36 ml). Then water (4 ml) was gradually added to the suspension. After stirring the suspension, 60 mM of tetraethyl orthosilicate (TEOS) in ethanol (18 ml) was added and the suspension was further stirred for 3 h at RT. The solid part was collected and dried at 393K for 3h, silica coated C@TiO$_2$ (denoted as SiO$_2$@C@TiO$_2$) was collected. Finally, SiO$_2$@C@TiO$_2$ powder was calcined at 773 K for 3 h to yield nanovoid structure TiO$_2$ nanoparticles (denoted as SiO$_2$@@TiO$_2$). On the other hand, as a reference sample, silica coated TiO$_2$ nanoparticles (silica coating directly without the nanovoid structure, denoted as SiO$_2$/TiO$_2$) were prepared according to the procedures of silica coating mentioned above.

The morphologies of samples were obtained by TEM measurements (JEM-2010 (HR) model). Fig. 1 illustrates the respective photographs of the nanoparticles with diameters of 20 to 40 nm. In contrast to the angular morphologies of TiO$_2$ (P-25), the carbonization of glucose formed a relatively uniform carbon layer of *ca.* 3 to 5 nm in thickness that entirely covered the TiO$_2$ core (C@TiO$_2$, brown colour powder, Fig. 1a). After the silica coating process, a TEM image of the sample showed that no obvious change had occurred, except that some indefinite boundaries existed inside the coating layer (SiO$_2$@C@TiO$_2$, brown colour powder, Fig. 1b). The sample was then calcined at 773 K for 3 h. A bright ring was observed between the TiO$_2$ core and the silica layer with a relatively uniform thickness (SiO$_2$@@TiO$_2$, white colour powder, Fig. 1c) (The image of the ring formation was shown in ESI Fig. S1†). On the other hand, the TEM image of SiO$_2$/TiO$_2$ (as the reference sample for SiO$_2$@@TiO$_2$, Fig. 1d) exhibited no obvious nanovoid structure except some "island" formations on the rough surface.

Energy dispersive X-ray analysis (EDXA, Inca Energy-200) showed that in the case of C@TiO$_2$, the existence of carbon

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† Electronic supplementary information (ESI) available: XRD data; photocatalytic reactor; SEM images of nanoparticles immobilized PET fibers; ICP determination; preparation of SiO$_2$@@TiO$_2$ (or TiO$_2$) immobilized PET fibers; anticipated TEM image of nanovoid structure; photocatalytic decomposition of gaseous formaldehyde by SiO$_2$@@TiO$_2$ immobilized PET fibers. See DOI: 10.1039/b802127a
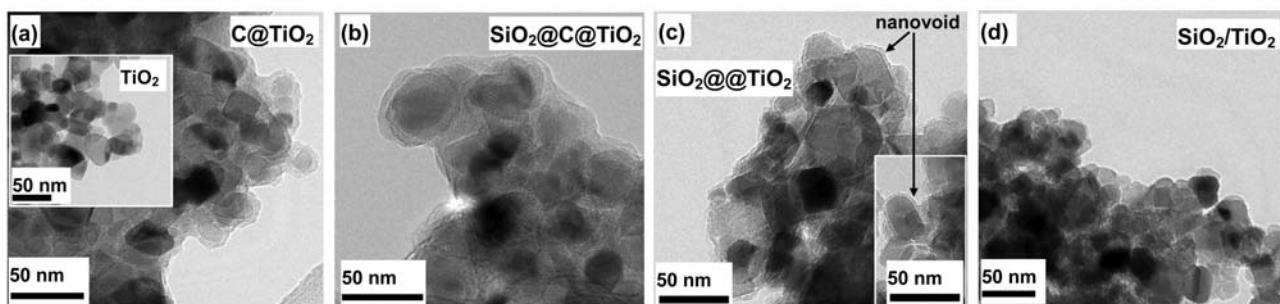
Fig. 1 TEM images of samples: (a) untreated TiO_2 (P-25) and $C@TiO_2$. (b) $SiO_2@C@TiO_2$. (C) $SiO_2@@TiO_2$. (d) SiO_2/TiO_2.

element was found and after silica coating process ($SiO_2@C@TiO_2$), the presence of Si and C were confirmed. After calcination, no carbon peak existed in EDXA spectrum of $SiO_2@@TiO_2$, indicating that the carbon layer was burned by high temperature (Fig. 2). Considering that $SiO_2@@TiO_2$ only consists of Si and Ti, the part of the bright ring that was mentioned in TEM image should indicate the decreasing concentration of Si element. Therefore, it is strongly suggested that the bright ring can be thought of as the residual space after the combustion of the carbon layer. (That is the reason why we call this residual space the "nanovoid"). The formation process for the nanovoid core(TiO_2)/shell(SiO_2) nanoparticles should be the following, shown in Scheme 1.

X-ray diffraction (XRD, Rigaku D/Max-2550pc) patterns of the samples showed that there was no obvious anatase-to-rutile phase transformation in the formation process of $SiO_2@@TiO_2$, suggesting that the TiO_2 core kept as the P-25 phase throughout the reaction steps (ESI Fig. S2†). Chemical analyses of $SiO_2@@TiO_2$ by an inductive coupled plasma emission spectrometer (ICP, IRIS Intrepid) showed that the composition ratio of Si to Ti was 3.5 : 1 (ESI S3†).

The photocatalytic decomposition reaction was performed under UV light irradiation in order to demonstrate the photocatalytic activity of samples (ESI Fig. S4†). All of the samples were ensured to have equimolar amounts of TiO_2. Acetic acid was selected as a model organic acid, and the overall photocatalytic activity was measured by the amount of CO_2 that evolved from the photocatalytic decomposition of acetic acid.[14]

In general, the efficiency of light utilization and the number of active sites are the most important parameters contributing to high photocatalytic activity. In our research, the photocatalytic activity of the core should be influenced by the shell with two factors. First, the material of the shell may influence the light absorption of TiO_2 core. Second, the structure of the shell may influence mass transfer between reactants and the catalyst-active sites. Before calcination (Fig. 3), both the samples (SiO_2/TiO_2 and $SiO_2@C@TiO_2$) were negligibly active for the degradation of acetic acid to give CO_2, even though the silica shell does not
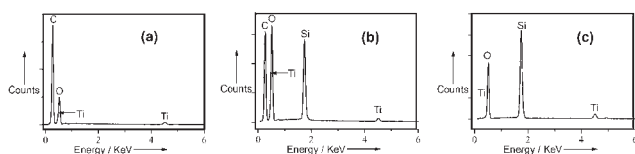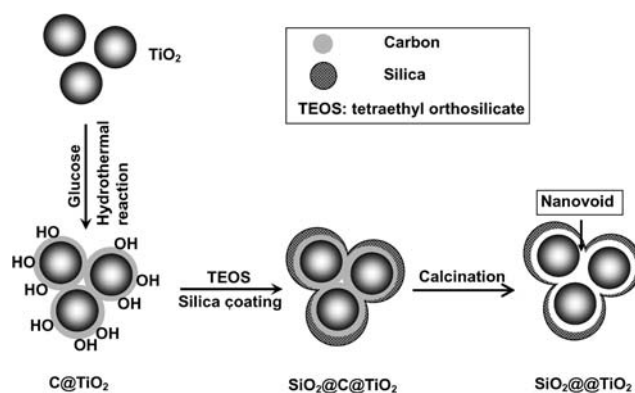

Scheme 1 Formation process of nanovoid $SiO_2@@TiO_2$ nanoparticles.

influence the efficiency of light utilization of TiO_2. In addition, from the TEM observation it should also be noted that the SiO_2 layer covers the TiO_2 core uniformly and successively. It is evident that the layer prevents mass transfer between reactants and the catalyst-active sites, and causes the catalyst to lose its photoactivity. However, after calcination (Fig. 4), both calcined samples (SiO_2/TiO_2, $SiO_2@@TiO_2$) showed appreciable photocatalytic ability. The result can be explained by a porous structure of the silica layer is formed during the heat treatment process,[15,16] which is beneficial to the mass transfer of the reactants. Futhermore, one of the most striking features of nanovoid $SiO_2@@TiO_2$ is that the calcination process of $SiO_2@C@TiO_2$, by removing carbon layer to obtain $SiO_2@@$-TiO_2, led to a significant photocatalytic activity enhancement, which is about 6 times as large as that of SiO_2/TiO_2. To some

Fig. 2 EDXA spectrum of samples: (a) $C@TiO_2$. (b) $SiO_2@C@TiO_2$. (c) $SiO_2@@TiO_2$.
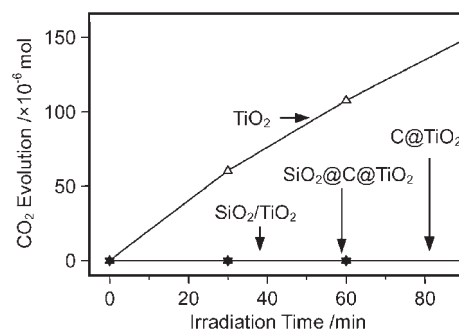

Fig. 3 Relationship between the amount of evolved CO_2 and irradiation time before the calcination.
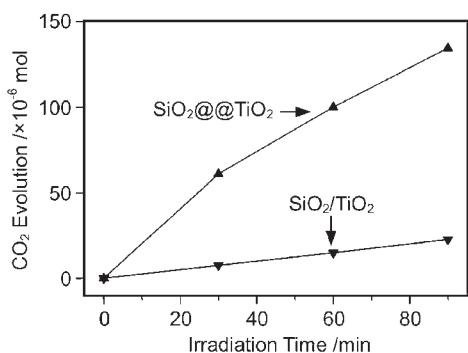
Fig. 4 Relationship between the amount of evolved CO_2 and irradiation time after the calcination. The photocatalytic activity of $SiO_2@@TiO_2$ was significantly restored and is about 6 times as large as that of SiO_2/TiO_2.

degree the increased photocatalytic activity of the $SiO_2@@TiO_2$ particles can be explained partly by the increased porosity of the SiO_2 shell created by removal of the carbon layer. However, in this structure the SiO_2 shell and the TiO_2 core were completely separated by the carbon layer (ESI Fig. S5†). Thus, the nanovoid structure plays an important role after the combustion process, which avoids the active sites of TiO_2 core to being shielded by the silica coating directly, and ensures that the TiO_2 core keeps its inherent active sites for photocatalytic decomposition. We also consider that calcined SiO_2/TiO_2 (the sample that was directly silica coated) has a weak photoactivity owing to the fact that only a few active sites of TiO_2, those just underneath the "pores" of the silica layer, are not shielded by the silica layer and can carry out the photocatalytic decomposition.

Photocatalyst-immobilized PET fibers were prepared (ESI S6†) and some interesting results were shown in Fig. 5 (ESI S7†). In a blank test, under the UV light irradiation, a large amount of CO_2 evolution was detected from a TiO_2 immobilized PET fiber system, which indicates that the organic supports were photo etched by naked TiO_2. However, there was no CO_2 evolution in the $SiO_2@@TiO_2$ immobilized PET fiber system, suggesting that the good structural integrity of the silica layer is helpful to protect the organic support. SEM images of the samples were also in agreement with the experimental conclusions (ESI Fig. S8†).
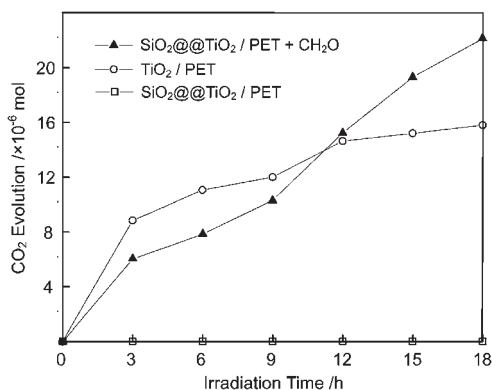

Fig. 5 Relationship between the amount of evolved CO_2 and irradiation time in photocatalyst-immobolized PET systems.

After adding an amount of gaseous formaldehyde into the closed system, the $SiO_2@@TiO_2$ immobilized system showed remarkably high photoactivity. The decomposition of the reactant was efficiently caused by the immobilized photocatalyst under the UV irradiation. Considering that the catalytic reaction is essentially the surface reaction , it could be thought that formaldehyde molecules first go through the porous structure of the silica layer, then reach the nanovoid space and finally react with the active sites of TiO_2 core. Although we could not give much evidence to prove this theory, it is assumed that since this porous structure can admit the passage of CO_2 through the silica shell during the combustion of the carbon layer, the same structure can be utilized for the diffusion of formaldehyde. Further investigation on this is under way.

All of the results mentioned above seem consistent with the mechanism of phase-selectivity photocatalysis; core(TiO_2)/shell(SiO_2) nanoparticles with a nanovoid structure that lies between the SiO_2 shell and TiO_2 core to protect the active sites for photodecomposition of organic pollutants (gas phase) without any damage to their organic supports (solid phase). Thus, we have shown a new concept of phase-selectivity photocatalysis, which could widen the range of the heterogeneous photocatalysis. Furthermore, it should be noted that the nanovoid structure makes surface modification with organic functional groups possible. Further study for the improvement of the photoactivity by organic modification of the surface is now under way.

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