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Heilongjiang University, China

Small Ag clusters confined in channels of ordered mesoporous anatase TiO$_2$ are fabricated via vacuum-induced assistant wet-impregnated method, which exhibit excellent solar-light-driven photocatalytic performance, owing to the synergistic effects of small Ag clusters acting as traps to effectively capture the photogenerated electrons and the surface plasmon resonance.
Small Ag clusters confined in the channels of well-ordered mesoporous anatase TiO₂ and the excellent solar-light-driven photocatalytic performance

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¹ Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, Harbin 150080 P. R. China, Tel.: +86 451 8660 4330, Fax: +86 451 8666 1259, E-mail: fuhg@vip.sina.com

² Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201204 P. R. China

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ABSTRACT
Small Ag clusters confined in the channels of ordered mesoporous anatase TiO₂ have been fabricated via vacuum-induced assistant wet-impregnated method, utilizing well-ordered mesoporous anatase TiO₂ with high thermal stability as hosts. The composites are characterized in detail by X-ray diffraction, X-ray photoelectron spectroscopy, X-ray absorption fine structure spectroscopy (XAFS), N₂ adsorption, UV-visible diffuse reflectance spectroscopy and transmission electron microscopy. The results indicate that small Ag clusters are formed and confined in the channels of mesoporous TiO₂ effectively and uniformly due to the obvious confinement effect. The strong Ag-O interactions between the intimate contact Ag clusters and pore-walls of mesoporous TiO₂ are indeed existed, which are confirmed by XAFS analysis, and favor the separation of photogenerated electron-hole pairs, which are proved by steady-state surface photovoltage spectroscopy and transient-state surface photovoltage. The obtained ordered mesoporous Ag/TiO₂ composites exhibit excellent solar-light-driven photocatalytic performance for degradation of phenol. This is attributed to the synergistic effects of the formation for small Ag clusters acting as traps to effectively capture the photogenerated electrons, and the surface plasmon resonance of Ag clusters promoting the absorption of visible light. This study really realizes the high-efficiency utilization of noble metals and fabricates high-performance solar-light-driven photocatalyst.

KEYWORDS
mesoporous TiO₂, Ag cluster, confinement effect, solar-light-driven photocatalysis, surface plasmon resonance

Address correspondence to H. Fu, fuhg@vip.sina.com
1 Introduction

Mesoporous TiO$_2$ materials have attracted great interest due to their promising applications in photocatalysis, dye-sensitized solar cells, sensors, separation and water purification [1-5]. Much work has been done to prepare ordered mesoporous anatase TiO$_2$ and they exhibited excellent photocatalytic performance due to their extraordinarily large surface areas and well-arranged mesopores or channels in favor of mass transfer within networks [6-8]. However, the wide band-gap (3.2 eV) of anatase TiO$_2$ reduced the utilization of solar light, as well as the low quantum yield largely restricted the overall photocatalytic efficiency, and thus limited the application [9-11].

To extend the photo-response of mesoporous TiO$_2$ to visible light region and promote the separation efficiency of photogenerated charge carriers, numerous strategies have been adopted, such as sensitization, doping, narrow band-gap semiconductor coupling, improving crystallinity and so on [12-15]. In particular, coupling TiO$_2$ with noble metals which could be formed a Schottky barrier at the interface, could effectively promote the separation of photogenerated electron-hole pairs owing to their different work functions and Fermi levels [16-18]. Ismail et al. reported ordered hexagonal mesoporous Pt/TiO$_2$ composites with well dispersed Pt nanoparticles of about 5-12 nm [16]. The excellent photocatalytic activity for photo-oxidation of CH$_3$OH in aqueous suspensions was ascribed to the close contact between Pt and TiO$_2$ formed Schottky barrier. And more than that, the surface plasmon resonance (SPR) of noble metals could absorb visible light to a large extent, and so could increase the utilization ratio of solar light [19-22]. Wang et al. synthesized mesoporous Au/TiO$_2$ nanocomposite microspheres with small Au nanoparticles (~10 nm) stably confined within the microspheres [19]. The incorporation of Au nanoparticles acting as sensitizers promoted the visible-light photogenerated charge carriers separation greatly, owing to their strong SPR. The photocatalytic efficiency was indeed improved obviously. However, the amount of noble metals was high and their sizes were usually large, and then increased the costs greatly, which was disadvantageous of practical applications. Subsequently, how to reduce the amount of noble metals and decrease their sizes in order to increase their utilization efficiency remains challenging.

Recently, the confinement effect of mesoporous channels was proved to be effective to control the size and uniform dispersion of noble metals, which hindered the aggregation and growth of noble metals, resulting in the formation of small and highly monodispersed noble metal nanoparticles [23-26]. These strategies indeed increased the utilization efficiency of noble metals and improved the catalytic performance obviously. And more than that, it also offered new ideas for achieving much smaller noble metals in order to further increase their utilization efficiency. In view of the low-cost and special characteristic of Ag among various noble metals, Ag was good candidate for improving the photocatalytic performance of TiO$_2$. Very recently, our group fabricated ordered mesoporous Ag/TiO$_2$ composites with small Ag clusters and investigated the confinement effect on photocatalytic performance systematically [24]. Small quantity of highly dispersed Ag clusters with coordination number (CN) of Ag-Ag ~3.8 were embedded inside the channels of well-ordered mesoporous TiO$_2$. The separation efficiency of photogenerated charge carriers was notably increased due to the strong interactions between Ag clusters and mesoporous TiO$_2$ pore-walls leading to Ag clusters acted as traps to capture photogenerated electrons effectively. The visible light photocatalytic activity was also enhanced because of the obvious SPR of the metallic Ag clusters. Therefore, the small and uniformly distributed Ag clusters were confirmed to be coupled with mesoporous TiO$_2$ pore-walls effectively and thus improved the photocatalytic performance. From this it can be seen that, in order to increase the utilization efficiency of noble metals and fabricate effective interface coupling between mesoporous TiO$_2$ and noble metals, the requirements of the uniform dispersion and small size for noble metals should be satisfied. Then, along with this mind, whether making the best use of confinement effect of mesoporous TiO$_2$ to further reduce the Ag clusters in order to greatly increase the utilization efficiency of Ag and enhance the photocatalytic performance should be worth considering.

In this work, based on the above consideration, in order to promote the utilization ratio of solar-light, we fabricated the small Ag clusters confined in the channels of ordered mesoporous anatase TiO$_2$: via vacuum-induced assistant wet-impregnated method, utilizing well-ordered large-pore mesoporous anatase TiO$_2$: with high crystallinity and less surface defects as hosts. The small Ag clusters were confined in the channels of mesoporous TiO$_2$: effectively and uniformly. The
high efficiency utilization of Ag was come true through this strategy, which decreased the amount of noble metals obviously and reduced the costs of photocatalysis greatly. The strong Ag-O interactions between Ag clusters and pore-walls of mesoporous TiO$_2$ were existed, which favored the separation of photogenerated charge carriers. The photocatalytic performance of the obtained mesoporous Ag/TiO$_2$ composites was also investigated by the degradation of phenol in the presence of simulated solar-light.

2 Experimental

2.1 Synthesis

The preparation of well-ordered mesoporous anatase TiO$_2$ with remarkably high thermal stability and improved crystallinity (MT) was described elsewhere [3]. The mesoporous Ag/TiO$_2$ composites were fabricated by a vacuum-induced assistant wet-impregnated method. Typically, MT (0.1 g) was firstly dried at 120 °C for 4 h in order to remove the absorbed water, and then placed inside a filter flask, which was sealed by a separating funnel and connected with a vacuum pump. The system was vacuumed at 80 °C for 30 min. Subsequently, freshly prepared AgNO$_3$ aqueous solutions (1 mL) with different concentrations were mixed with 1 mL alcohol, and then placed into the separating funnel and added into the system dropwise seven times. Finally, the powders were washed with distilled water thoroughly to eliminate surface-adsorbed AgNO$_3$ and dried under vacuum at 30 °C overnight, then calcined at 500 °C for 3 h in air. The concentration of AgNO$_3$ solution was 0.5 mM and the corresponding composites were denoted as MTA-In. In addition, MT (0.1 g) was immersed in 0.5 mM AgNO$_3$ solution (1 mL) for 12 h at room temperature (RT), and then treated by wet-impregnaged approach for several times without washing (denoted as MTA-Out). The large air resistance of the channels blocked the entry of the Ag species, so the Ag in the channels of mesoporous TiO$_2$ was negligible. The content of Ag in the composites was about 0.36 wt.% for MTA-In, as measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an Optima 7000DV (Perkin-Elmer Corp.) instrument. In order to investigate the effect of Ag content for the photocatalytic performance, the lower (0.25 mM) and higher concentrations (0.75 mM) of AgNO$_3$ solutions were also chosen to confine in the channels of mesoporous TiO$_2$, and the corresponding composites were denoted as MTA-In-Low (0.179 wt.%) and MTA-In-High (0.545 wt.%), respectively.

2.2 Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer by using CuK$_\alpha$ radiation (λ=1.5406 Å). The transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. Nitrogen adsorption-desorption isotherms at 77 K were collected on a Micromeritics ASAP 2010 nitrogen-adsorption apparatus. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area. Pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherm. X-ray photoelectron spectroscopy (XPS) was performed with AXIS ULTRA DLD. Diffuse reflectance spectroscopy (DRS) was measured on a UV/vis spectrophotometer (Shimadzu UV-2550). The steady-state surface photovoltage spectroscopy (SS-SPS) measurement was carried out with a home-built apparatus equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powders were sandwiched between two ITO glass electrodes, and monochromatic light was passed from a 500 W xenon lamp through a double prism monochromator (SBP300). Transient-state surface photovoltage (TS-SPV) measurement was performed with a self-assembled device in air atmosphere at room temperature. The powders were excited by a 532 nm-laser radiation with 10 ns pulse width from a second harmonic Nd:YAG laser (Lab-130-10H, Newport, Co.). The signals were collected via a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix) with a pre-amplifier. X-ray absorption fine structure (XAFS) spectroscopy was performed at room temperature in transmission mode on beam-line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF),
China. The station was operated with a Si (111) double-crystal monochromator. The synchrotron was operated at energy of 3.5 GeV and the current in the range 150-210 mA. The photon energy was calibrated with Ag foil. Data processing was performed by the program ATHENA. All fits to the EXAFS data were performed by using the program ARTEMIS. The beam-line covered the energy range from 100 to 1000 eV, with an energy resolution of 0.2 eV.

2.3 Photocatalytic activity

The photodegradation of phenol was carried out in an aqueous solution (5 mg L⁻¹) at room temperature. A 150 W Xe lamp was used as a simulated solar-light source. The reactor was open to air in order to reach the air-equilibrated condition. In a typical experiment, 30 mg photocatalyst powder was dispersed in 50 mL phenol solution in a quartz reactor using a magnetic stirrer. The suspension was stirred magnetically for 0.5 h in the dark in order to reach adsorption equilibrium. The mixture was later illuminated for different times and stirred continuously during the irradiation. Prior to determining the concentration of total organic carbon (TOC) by TOC-VCPN (SHIMADZU), the solution was separated from the catalysts by centrifugation and filtration through 0.22 μm nominal pore-size membrane filters. The visible light photocatalytic activity was also performed with a cut-off filter (λ≥420 nm) to remove UV light. Furthermore, a blank experiment without adding catalyst was also conducted and no significant decomposition of phenol was observed under the same irradiation conditions. To demonstrate the stability of photocatalysts, we recycled the used MTA-In for testing other photocatalytic activities under solar-light irradiation. After photocatalytic experiment, the MTA-In was recovered by washing with distilled water three times and drying in an oven overnight to remove the residual reactant and reactivate the adsorption and catalytic performance.

3 Results and Discussion

3.1 Structure and morphology of ordered mesoporous Ag/TiO₂ composite

It is well-known that phase-pure anatase TiO₂ possesses the optimal photocatalytic performance among anatase, rutile and brookite. Therefore, it is of great significance to prepare phase-pure anatase TiO₂ materials. The typical XRD patterns of MT, MTA-In and MTA-Out are shown in Fig. 1. It clearly shows the presence of crystalline phase-pure anatase for all samples, because five high-intensity crystal peaks at 2θ=25.2-55.1° can be observed and could be indexed as (101), (004), (200), (105), and (211), respectively (JCPDS, No. 21-1272). However, the main diffraction peaks for Ag species are not observed clearly for MTA-In and MTA-Out, which might be due to the low content and small size of Ag [27]. The XRD results confirm that the nanocrystalline phase-pure anatase structure maintains well in the composites and the Ag species disperse uniformly in mesoporous TiO₂. In addition, the small-angle XRD (SAXRD) measurements are also performed to reveal the ordered mesostructure (Fig. S-1 in the Electronic Supplementary Material (ESM)). The well-resolved diffraction peaks could be observed clearly for all samples, suggesting a highly ordered 2D hexagonal structure. What's more, the diffraction peaks show no clear changes after the introduction of Ag, indicating the high thermal stability of MT and the well-ordered mesoporous network maintained well in the composites.

![Figure 1 XRD patterns of MT, MTA-In and MTA-Out.](image-url)
these composites all show two obvious peaks, which are centered at about 373.6 and 367.6 eV, ascribed to Ag 3d\textsubscript{5/2} and Ag 3d\textsubscript{3/2}, respectively, with a spin-energy separation of 6.0 eV, assigning to the characteristic of metallic silver (Ag\textsuperscript{0}) [28]. No other valence of Ag could be observed, indicating the Ag\textsuperscript{+} ions are reduced to metallic Ag\textsuperscript{0} in the mesoporous TiO\textsubscript{2} channels during the thermal treatment process [24]. These results suggest that the metallic Ag\textsuperscript{0} dominates the Ag species within the channels of mesoporous TiO\textsubscript{2} and further confirms the formation of mesoporous Ag/TiO\textsubscript{2} composites.

The results suggest the size of metallic Ag in mesoporous TiO\textsubscript{2} channels for MTA-In is the smallest compared with MTA-Out and Ag foil, which is ascribed to the obvious confinement effect of these channels. From Fig. 3B, a very strong peak at 2.85 Å could be observed for all samples, which is assigned to Ag-Ag coordination from the corresponding normalized Fourier transforms of the EXAFS spectra at the Ag K-edge. It further confirms the formation of metallic Ag in the composites. In addition, an obvious peak at about 1.6 Å for MTA-In would be assigned to Ag-O interaction, which maybe originate from interactions between Ag and the pore-walls of mesoporous TiO\textsubscript{2} [24]. The strong Ag-O interaction would construct efficient transfer and separate channels for photogenerated charge carriers, thus favoring improving the photocatalytic performance. However, this peak for MTA-Out sample is absent.

To further reveal the existing form of these Ag species in mesoporous TiO\textsubscript{2} channels, and deeply understand the interaction between Ag species and mesoporous TiO\textsubscript{2} pore-walls, X-ray absorption fine structure (XAFS) spectroscopy, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, was operated in this study. Normalized XANES (A) and normalized Fourier transforms of the EXAFS spectra (B) for MTA-In, MTA-Out and Ag foil at the Ag K-edge are shown in Fig. 3. The normalized XANES of MTA-In and MTA-Out is similar to that of Ag foil (Fig. 3A), indicating the existing form for these Ag species in mesoporous TiO\textsubscript{2} channels is metallic Ag. In particular, all peaks in the spectra for MTA-In and MTA-Out are broader than those of metallic Ag foil, especially for MTA-In samples due to the obvious nanometer effect of Ag. [24]
indicating the weak interactions between metallic Ag nanoparticles and the surface of mesoporous TiO$_2$. The above results indicate that there indeed exist the strong Ag-TiO$_2$ interactions for metallic Ag clusters in mesoporous TiO$_2$ channels. In order to obtain the local structural parameters in the Ag EXAFSs, curve-fitting analyses for samples are performed and shown in Table 1. The coordination number (CN) for bulk silver, MTA-Out and MTA-In is about 10.8, 4.3 and 1.9, respectively. Obviously, the CN for MTA-In is the lowest compared with MTA-Out and bulk silver, suggesting the small size for metallic Ag clusters in mesoporous channels, owing to the confinement effect. From these results, the small Ag clusters (CN ~ 1.9) confined within mesoporous channels are formed for MTA-In. The highly dispersed Ag clusters within mesoporous TiO$_2$ channels would be beneficial for photocatalysis.

Table 1 Local structural parameters in the Ag EXAFSs of MTA-In, MTA-Out and Ag foil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>σ² (10$^{-3}$ Å$^2$)</th>
<th>ΔE$_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag foil</td>
<td>Ag-Ag</td>
<td>10.8±0.5</td>
<td>2.87±0.01</td>
<td>9.8±0.4</td>
<td>1.8±0.3</td>
</tr>
<tr>
<td>MTA-Out</td>
<td>Ag-Ag</td>
<td>4.3±0.3</td>
<td>2.85±0.01</td>
<td>9.3±2.3</td>
<td>-2.9±1.0</td>
</tr>
<tr>
<td>MTA-In</td>
<td>Ag-Ag</td>
<td>1.9±0.3</td>
<td>2.83±0.01</td>
<td>13.6±2.3</td>
<td>-1.1±1.0</td>
</tr>
<tr>
<td>MTA-In</td>
<td>Ag-O</td>
<td>2.1±0.2</td>
<td>2.24±0.01</td>
<td>15.4±3.8</td>
<td>-1.3±1.2</td>
</tr>
</tbody>
</table>

The N$_2$ adsorption-desorption isotherms (A) and the corresponding BJH pore size distribution plots (B) of MT, MTA-In and MTA-Out are shown in Fig. 4. All curves exhibit small hysteresis loops at relative high pressure, which are attributed to type IV isotherms, indicating the mesoporous materials.$^{29}$ The MT presents a narrow BJH adsorption pore size distribution with a mean value of ~10 nm, implying that the materials have very regular pore channels in mesoporous region. It is very important to note that the mesoporous frameworks maintain very well after the introduction of Ag and thermal treatment, further indicating the thermal stability of MT. Both MTA-Out and MTA-In possess narrow BJH adsorption pore size distribution, but the pore size for MTA-In (9.4 nm) decreases due to the loading of Ag clusters in the channels (as shown in Table 2). For MTA-Out, the pore size and pore volume are not declined obviously, indicating the Ag species mainly outside of the channels of mesoporous TiO$_2$. Moreover, the BET surface areas and pore volumes are also decreased (Table 2), implying the efficient loading of Ag clusters in the channels of mesoporous TiO$_2$ because of the vacuum-induced assistant strategy. Interestingly, MTA-In still possesses relative high BET surface area (113 m$^2$ g$^{-1}$), large pore size (9.4 nm) and pore volume (0.16 cm$^3$ g$^{-1}$), which are satisfactory with photocatalysis.

Table 2 The BET surface area, pore size and pore volume of MT, MTA-In, and MTA-Out.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT</td>
<td>122</td>
<td>10.1</td>
<td>0.20</td>
</tr>
<tr>
<td>MTA-Out</td>
<td>116</td>
<td>9.9</td>
<td>0.19</td>
</tr>
<tr>
<td>MTA-In</td>
<td>113</td>
<td>9.4</td>
<td>0.16</td>
</tr>
</tbody>
</table>
The morphology of the ordered mesoporous structure is confirmed by the TEM analysis. Figure 5 shows TEM image (A) for MTA-In, and the corresponding elemental mapping of Ag (B), Ti (C) and O (D), and the magnified TEM image (E) for MTA-In and schematic diagram of the confinement effect for Ag clusters confined in the channels of mesoporous TiO$_2$ (F). The well-ordered mesoporous structure for MTA-In could be observed obviously from Fig. 5A, which is similar to mesoporous TiO$_2$. The ordered mesoporous network with a diameter of about 10 nm and 2D hexagonal mesostructure is not destroyed due to the introduction of Ag clusters, suggesting its high thermal stability of MT. However, the Ag clusters could not be observed obviously for MTA-In in mesoporous channels, which may be ascribed to the confinement effect of mesoporous channels leading to forming very small Ag clusters. These results are consistent with the XAFS analysis. In addition, little big Ag particles can also be seen from Fig. 5A, due to the incomplete wash of the surface adsorbed Ag aggregated into big Ag nanoparticles. In order to further confirm the uniform distribution of Ag clusters in MAT-In, the elemental distributions of Ag, Ti and O are performed by EDS elemental mapping (Fig. 5B-D). Obviously, the Ag clusters are confined within the MT framework with high homogeneity and small size from Fig. 5B. These Ag clusters could contact closely with mesoporous TiO$_2$ pore-walls, favoring the separation of photogenerated electron-hole pairs. The high dispersibility of these Ag clusters in MTA-In further confirms the existence of the confinement effect for mesoporous channels, which could effectively inhibit the aggregation of Ag clusters and realize the formation of Ag clusters. On the contrary, the Ag species out of the mesoporous channels would aggregate into big nanoparticles, as shown in Fig. S-2 in the ESM. Moreover, the elemental Ti and O are also distributed uniformly throughout the samples from Fig. 5C and D, indicating the integrated microstructure of MT.

From the magnified TEM image (Fig. 5E), the Ag clusters could not be observed clearly, further suggesting the very small size of Ag clusters. The schematic diagram of the confinement effect for Ag clusters confined in the channels of mesoporous TiO$_2$ is shown in Fig. 5F. It in vivid details these small Ag clusters confined in mesoporous TiO$_2$ uniformly and the intimate contact between them, which is advantageous of the separation of photogenerated charge carriers. These small Ag clusters with homogenous distribution in mesoporous TiO$_2$ channels would make the best use of noble metal Ag to utilize visible light and favor

![Figure 5](image-url)
the separation of photogenerated charge carriers, and thus enhancing the photocatalytic performance. Figure 6 shows the UV/vis diffuse reflectance spectroscopy (DRS) of MT, MTA-In and MTA-Out. The strong absorption peak between 300-400 nm is attributed to electronic transitions from the valence band to the conduction band \((O_2p-Ti_3d)\) for mesoporous TiO\(_2\) [30]. In addition, the strong and broad absorption in visible light region at about 450-600 nm for mesoporous Ag/TiO\(_2\) samples would be ascribed to the SPR of metallic Ag [31]. These small Ag clusters would absorb visible light effectively, which offers possibility for high-efficient utilization of solar-light. Moreover, the shift of the absorption edge becomes clear while the Ag species outside of the channels of mesoporous TiO\(_2\) from Fig. 6, which may be resulted from the formation of large Ag nanoparticles.

![Figure 6](image_url) UV-vis diffuse reflectance spectra of MT, MTA-In and MTA-Out.

3.2 Photocatalytic activity

The photocatalytic activity for different samples is evaluated by measuring the time-dependent degradation of phenol under simulated solar-light irradiation and shown in Fig. 7. Without adding catalyst, no significant decomposition of phenol can be observed under solar-light irradiation, which confirms the high stability of phenol solution. The photocatalysts are added to the phenol solutions and stirred magnetically for 0.5 h in the dark in order to reach the adsorption equilibrium. Only about 10% phenol could be adsorbed on the surface of photocatalysts for all samples. No obvious difference for the adsorption performance among them could be observed. After being irradiated for different times by simulated solar-light, it can be seen that the degradation ratio of phenol is increased after being loaded the Ag. The photocatalytic activity is the highest when the Ag clusters are confined in the channels of mesoporous TiO\(_2\) (MTA-In). While, once the Ag species are outside of the channels of mesoporous TiO\(_2\) (MTA-Out), the photocatalytic performance decreases obviously. From the TOC detection, the complete mineralization of phenol for MTA-In could be observed after solar-light irradiation for 2 h, which is higher than that of MT, MTA-Out and commercial P25 (~82%). The excellent photocatalytic performance for MTA-In may be attributed to the small Ag clusters confined in mesoporous channels, forming intimate contact between mesoporous TiO\(_2\) pore-walls and highly dispersed Ag clusters within the channels, which favors the separation of photogenerated electron-hole pairs and inhibits their fast recombination. Schematic diagram of the possible mechanism of the photocatalytic reaction for Ag clusters confined in the channels of mesoporous TiO\(_2\) under UV and visible light irradiation is shown in Fig. S-3 in the ESM. Under UV light irradiation, the formed Schottky barrier between these Ag clusters and mesoporous TiO\(_2\) pore-walls would play critical roles. The conduction-band electron could transfer to Ag clusters that are confined within the channels, because the Fermi levels of Ag are lower than that of TiO\(_2\). Therefore, the Ag clusters act in trapping the photogenerated electrons (Fig. 7, bottom 1), which can inhibit the fast recombination of photogenerated electrons and holes, and thus enhance the photocatalytic performance under UV light irradiation. In addition, mesoporous anatase TiO\(_2\) could not be excited by visible light due to the large bandgap (~3.2 eV). But the noble metal Ag could absorb visible light because of the SPR [32]. The visible light irradiation is used a cut-off filter \((\lambda \geq 420 \text{ nm})\) to remove UV light in this study, keeping the intensity constant. Obviously, the visible light photocatalytic performance of mesoporous Ag/TiO\(_2\) composites is also high (~80% for 2 h) due to the strong SPR (Fig. S-4 in the ESM). Under visible-light
irradiation (Fig. S-3 in the ESM), the photogenerated electrons are transferred from the plasmon-excited Ag clusters into the conduction band of TiO$_2$ (Fig. 7, bottom 2), which separate the photogenerated charge carriers efficiently because of the intimate contact between them. Furthermore, the absorption of visible light for the Ag clusters within mesoporous channels is not influenced obviously, because the open mesoporous channels are not affecting the light penetration. It can be seen from this that the improved solar-light-driven photocatalytic performance may be ascribed to the synergistic effects of confinement effect of mesoporous channels, the intimate contact between them, and the SPR of the Ag clusters. The effect of photocatalytic performance for different contents of Ag are also studied and shown in Fig. S-4 in the ESM. Obviously, the content of Ag too low or too high is all disadvantageous of photocatalysis. If the content of Ag is too low, the photogenerated charge carriers are not separated efficiently due to the insufficient contact between them. If the content of Ag is too high excessive Ag would aggregate into relative large Ag clusters, leading to the decrease of BET surface and surface active sites, reducing the utilization efficiency of Ag, then decreasing the photocatalytic performance. Therefore, it is very important for controlling the content of Ag in order to form small Ag clusters, and thus obtain high-performance mesoporous Ag/TiO$_2$ photocatalyst. In order to confirm the role of the small Ag clusters confined in the channels of mesoporous TiO$_2$, the photocatalytic activity is also compared with previous reported relative large Ag clusters (CN of Ag-Ag ~3.8). Interestingly, the photocatalytic performance is raised by ~20% for the former, indicating the high-efficiency utilization of noble metal Ag. More than that, small Ag nanoparticles loaded in mesoporous TiO$_2$ are also performed under the same conditions to compare the photocatalytic activity. The photocatalytic efficiency for these small Ag nanoparticles is declined by ~25%, further indicating the high-efficiency utilization of noble metals for these small Ag clusters in this study. It also confirms that the formation of small Ag clusters in the channels of mesoporous TiO$_2$ is crucial for further increasing the photocatalytic performance.

It is well-known that the surface photovoltage spectroscopy (SPS) is a well-established contactless technique to investigate the photophysical processes of semiconductors, such as charge-transfer and separation, which can be considered as an effective method for quickly evaluating the photocatalytic activity of semiconductor materials [10,33]. In order to illustrate the separation and dynamic processes of the photogenerated charge carriers, SS-SPS and TS-SPV are performed and shown in Fig. 8. The intensity of SS-SPS peak for MTA-In is lower than that of others from Fig. 8A, due to the Ag clusters drills into mesoporous channels acting as traps to capture the photogenerated electrons, and the intimate contact between them inhibiting the fast
recombination of electron-hole pairs efficiently. It is very interesting to note that the intensity of SS-SPS peaks for MTA-In is much weaker than that of MTA-Out (Fig. 8A). This may be ascribed to the Ag aggregate into large nanoparticles for MTA-Out, resulting in the decrease in the traps of photogenerated electrons, which lead to the intensity of SS-SPS peaks increase. The confinement effect of mesoporous channels for MTA-In leads to the formation of the small and uniform Ag clusters (as shown in Fig. 5F), they could form intimate contact between them, which could make the best use of noble metal Ag to separate photogenerated charge carriers. Meanwhile, once these Ag species aggregate into large ones, the utilization efficiency of noble metal Ag would decrease greatly, which is disadvantageous of photocatalytic activity. Therefore, making the full use of noble metal is crucial for photocatalysis. As is known that, for n-type semiconductor TiO₂ nanoparticles, the electron-hole pairs could be generated in the space charge region after being excited by UV light, and would be separated quickly through the built-in electric field, resulting in fast SPV phenomenon (< 10⁻⁵ s) [34]. Besides the built-in electric field, the charge separation is also influenced by carrier diffusion process, mainly contributing to the slow photovoltage response (> 10⁻⁴ s) [35]. Thereinto, the lifetime for charge carriers could be obtained from the transient photovoltage measurements.³⁶ Obviously, the charge carrier lifetime for MTA-In is prolonged compared with MT and MTA-Out, indicating the photogenerated charge separation is greatly improved by the formation of these small Ag clusters confined in the channels of mesoporous TiO₂, which is advantageous of photocatalysis. It is in consistent with the SS-SPS results.

The stability of the photocatalyst is also performed because it is very important for practical applications. From Fig. 9, there is no obvious decrease in photocatalytic activity for MTA-In after 5 cycles, indicating the high stability and durability. Therefore, the recycle utilization of the stable MTA-In is possible and the stability in treating organic contamination is satisfactory.

### 4 Conclusions

In summary, we demonstrated the fabrication of small Ag clusters confined in ordered mesoporous anatase TiO₂ channels with excellent
The Ag clusters dispersed in the channels uniformly due to the obvious confinement effect and formed strong Ag-O interactions between Ag clusters and the high-crystalline pore-walls of mesoporous TiO$_2$ from the EXAFS analysis. The ordered mesoporous Ag/TiO$_2$ composites exhibited excellent solar-light-driven photocatalytic activity for degradation of phenol. The obvious enhancement was ascribed to the intimate contact between Ag clusters and mesoporous TiO$_2$ pore-walls in favor of the separation of photogenerated charge carriers, as well as the strong SPR of these Ag clusters. It realized the high-efficiency utilization of noble metals Ag and decreased the costs of photocatalyst greatly. The composites also presented high stability and durability because they showed high photocatalytic activity even after several recyclies, which was advantageous of practical applications. This novel mesoporous Ag/TiO$_2$ composite would have potential applications in photocatalysis and it also may provide insights for high-efficient utilization of other noble metals in photocatalysis.

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