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Mesoporous Ag/TiO$_2$ nanocomposites fabricated by dealloying/calcination show superior photocatalytic performance under visible light as well as UV irradiation.
Mesoporous Ag/TiO$_2$ nanocomposites with greatly enhanced photocatalytic performance towards degradation of methyl orange under visible light

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Abstract

Ag/TiO$_2$ photocatalysis has received tremendous attention as a potential solution to the worldwide energy shortage and for countering environmental degradation. Here, the combination of dealloying with calcination has been used to fabricate mesoporous Ag/TiO$_2$ nanocomposites with large specific surface area of 90.18 m$^2$/g. In these nanocomposites, the Ag nanoparticles are well dispersed in the mesoporous anatase TiO$_2$ matrix with a 3 dimensional network structure. More importantly, the Ag/TiO$_2$ nanocomposites show greatly enhanced photocatalytic performance for the degradation of methyl orange under visible light as well as UV irradiation, compared to that of P25. The photocatalytic mechanism has been rationalized on the basis of Schottky junction, co-existence of metallic Ag, and large specific surface area. The present Ag/TiO$_2$ nanocomposites show great potentials for photocatalysis under solar light.

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Introduction

Electron-hole pairs can be excited from titanium dioxide (TiO$_2$) under light illumination. Therefore, TiO$_2$ is widely applied as semiconductor photocatalyst. However, the photocatalytic efficiency of TiO$_2$ is poor because the excited state conduction-band (CB) electrons and valence-band (VB) holes will recombine and dissipate the input energy in the form of heat or emitted light.$^1$ To prevent the recombination of electron-hole pairs, the approach that has generally been applied is to load the noble metal (Ag, Au, Pt, Pd, etc.) nanoclusters on the semiconductor surface.$^2$ In general, the noble metal nanoclusters can function as effective cocatalysts, form a Schottky junction and enhance the visible light absorption.$^3$

Conventionally, the noble metal nanoparticles can be deposited onto semiconductor by deposition–precipitation or photodeposition methods.$^{4-8}$ It is well known that the size, loading and morphology of the noble metal nanoparticles on TiO$_2$ matrix are the important parameters for enhancing photocatalytic activity by visible light.$^9,^{10}$ However, these methods appear to be ineffective in these parameters. In order to improve the photocatalytic activity of TiO$_2$, several complex approaches have been used to control the size, loading and morphology of the noble metal nanoparticles. Chen et al.$^{10}$ reported the synthesis of TiO$_2$-supported Ag nanoclusters with excellent control of the cluster size (<5 nm) by one-pot sol–gel method. Yin et al.$^{11}$ have prepared Au/TiO$_2$ with high photocatalytic activity by controlling the Au nanoparticles with the size of 10 nm using the ligand-exchange method. Generally, all of these methods are always difficult to considering both the noble metal
nanoparticles and the TiO$_2$ matrix, any one of which will influence the photocatalytic activity. Therefore, it is highly desirable to develop novel routes to controllably fabricate noble metal-semiconductor nanocomposites with tunable compositions/microstructures and enhanced photocatalytic activity by visible light.

Among all noble metals, Ag is particularly suitable for industrial applications because it is nontoxic and of low cost relative to other noble metals. In addition, the specific surface area is another important factor to explore the photocatalytic efficiency of TiO$_2$. Several approaches have been extensively studied in the past decades, such as hydro- or solvothermal synthesis, sol–gel, microwave-assisted method. As is known to all, the larger the specific surface area photocatalysts have, the better the photocatalytic performance they will get.

Dealloying (selective corrosion) is normally utilized to fabricate nanoporous metals/alloys/nanocomposites. Ever since Erlebacher etc. reported that nanoporous Au can be obtained by the dealloying method, nanoporous metals have been extensively investigated such as nanoporous Cu, Ag, Pd etc. And then nanoporous alloys have also been fabricated using the dealloying method. Nanoporous Au-Pt, Pd-Ni, Pt-Co alloys with excellent performance have been obtained by dealloying different alloy precursors. In addition, nanoporous metal/oxides have attracted wide interests. Nanoporous Cu/(Fe,Cu)$_3$O$_4$ composites, nanoporous Ag/Fe$_3$O$_4$ nanocomposites, nanoporous Ag/Co$_3$O$_4$ ribbons have been successfully fabricated using the dealloying method. Besides, pure oxide materials could also be prepared by dealloying such as WO$_3$, Cu$_2$O, Fe$_3$O$_4$, Mn$_3$O$_4$, Co$_3$O$_4$. 
For nanocomposites like Cu/(Fe,Cu)₂O₄, and Ag/Fe₃O₄, sub-microsized metal oxides disperse in the nanoporous metal matrix. In the inverse scenario, however, no literature is available. That is, nanosized metals are well distributed in a mesoporous oxide matrix.

Here, we developed a novel strategy to synthesize Ag nanoparticles modified mesoporous anatase TiO₂ photocatalysts (Ag/TiO₂ nanocomposites) through the combination of chemical dealloying with calcination on a large scale. The photocatalytic activity of the Ag/TiO₂ nanocomposites was further evaluated by degradation of methyl orange (MO) under both visible light and UV irradiation. The nano-sized Ag decorated mesoporous TiO₂ nanocomposites show excellent photocatalytic activity towards degradation of MO, which has been rationalized based upon the high specific surface area and the formation of Schottky junction.

**Experimental**

The alloying ingots with a composition of Al₉₇.₄Ti₂.₉ or Al₉₇.₄Ti₂.₄Ag₀.₂ (nominal composition, at.%) were prepared by melting pure Al, Ti and Ag metals (purity > 99.9 wt.%) in a high-frequency induction furnace. Using a single roller melt spinning instrument, the pre-alloyed ingot was remelted by high-frequency induction heating and then melt-spun onto a copper roller with a diameter of 0.35 m at a speed of 1000 revolutions per minute in a controlled argon atmosphere. The ribbons obtained were typically 2-5 mm in width, 20-50 µm in thickness and several centimeters in length.
The as-spun Al-Ti or Al-Ti-Ag ribbons were dealloyed in a 4 mol/L NaOH aqueous solution under free corrosion conditions. After dealloying for 2 h at ambient temperature, the Na-titanate or Ag/Na-titanate was obtained. Then the as-dealloyed samples were washed thoroughly with deionized water for several times, in order to remove the residual chemical substances. After drying in air, the as-dealloyed samples were immersed in a 0.1 mol/L HCl aqueous solution at ambient temperature for 2 h and then washed thoroughly with deionized water. The obtained H-titanate or Ag/AgCl/H-titanate samples were calcined under 400 °C for 1 h. Then we could obtain the mesoporous anatase TiO₂ or Ag/ TiO₂ nanocomposites. The AgCl/Ag/TiO₂ nanocomposites were prepared by re-acid treating the Ag/TiO₂ sample in the 0.1 mol/L HCl aqueous solution at ambient temperature for 2 h and then washed thoroughly with deionized water.

All products were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) with selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). In addition, N₂ adsorption-desorption experiments of the samples were carried out at -196 °C with a V-Sorb 2800P surface area and porosity analyzer. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The pore size distribution was measured from the desorption branch of isotherm using the corrected form of Kelvin equation by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetry (TG) was carried out in Ar at a heating rate of 20 °C/min on a thermal analyzer. The UV-vis
diffuse reflectance spectra (DRS) were recorded in a wavelength range of 250-800 nm to study the optical performance of the samples. The X-ray photoelectron spectroscopy (XPS) was utilized to study the chemical composition on the surface of the photocatalyst.

The photocatalytic activity of the samples was evaluated by degradation of MO aqueous solution at room temperature under visible light irradiation, because MO is a kind of chemically stable and persistent containing-nitrogen dye pollutant.\textsuperscript{31, 32} A 300W xenon lamp with 420 nm cut-filter was used as the visible light source. The photocatalytic experiments under visible light irradiation were carried out by adding 20 mg photocatalysts (P25, Ag/TiO\textsubscript{2} or AgCl/Ag/TiO\textsubscript{2} composites) into 25 mL MO solution (20 mg/L). The suspension was stirred in the dark for 30 min to obtain the saturated adsorption of MO before visible light illumination. In addition, a 250 W high-voltage mercury lamp was used as the UV light source. And 5 mg photocatalysts (P25 or Ag/TiO\textsubscript{2} composites) were added into 25 mL MO solution under UV light irradiation. The suspension was stirred in the dark for 30 min to obtain the saturated adsorption of MO before UV light illumination.

At varied irradiation time intervals, the concentration of the MO solution was measured by monitoring the absorbance at 464 nm (the maximum absorbance wavelength of MO) using a UV-Vis spectrophotometer. The catalytic performance was evaluated by the ratio of the concentration of MO after irradiation for different time ($C_M$) divided by the initial concentration ($C_0$) (i.e., $C_M/C_0$).

**Results and discussion**
Fig. 1 shows the XRD patterns of the as obtained samples using the Al$_{97.1}$Ti$_{2.9}$ and Al$_{97.4}$Ti$_{2.4}$Ag$_{0.2}$ precursors. After dealloying the Al-Ti ribbons in the NaOH solution, the XRD pattern (Fig. 1(aI)) of the dealloyed samples is similar to that of Na$_2$Ti$_2$O$_4$(OH)$_2$ (Na-titanate), as noted elsewhere.$^{33,34}$ The H-titanate samples were obtained by acid treating the dealloyed samples and its XRD pattern is shown in Fig. 1(aII). It is clear that a diffraction peak position shifts from 28$^\circ$ to 25.5$^\circ$ after acid treatment in the HCl solution, as marked by an arrow in Fig. 1(a). The XRD pattern of the acid treatment samples (Fig. 1(aII)) is similar to the H$_x$Ti$_{2-x/4}$O$_{4-x/4}$·H$_2$O (H-titanate), here $x$≈0.7, $\gamma$: vacancy, which has been reported in other literature.$^{35,36}$ The formation mechanism of the H-titanate could be elucidated by the cation-exchange mechanism.$^{37,38}$ After calcination at 400$^\circ$C, the H-titanate obtained from the Al-Ti alloy has transformed to the anatase TiO$_2$ (PDF#21-1272) as shown in Fig. 1(aIII).

The Al$_{97.4}$Ti$_{2.4}$Ag$_{0.2}$ was selected as the dealloying precursor for the sake of adding metallic Ag to the anatase TiO$_2$. The XRD patterns of various samples are shown in Fig. 1(b), which are obtained under the same treating conditions with the Al-Ti precursor. After dealloying in the NaOH solution, the XRD pattern (Fig. 1(bI)) shows that the Na-titanate and face-centered cubic (fcc) Ag phase are identified in the dealloyed samples (Ag/Na-titanate). After acid treatment in the HCl solution, the H-titanate presents in the as-treated samples, suggesting the occurrence of cation-exchange. And both the fcc Ag and AgCl phases could be identified in the as-treated samples due to the transformation of partial Ag into AgCl during the acid
treatment in the HCl solution (Fig. 1(bII)). After calcining the Ag/AgCl/H-titanate at 400 °C, only the anatase TiO$_2$ and fcc Ag are distinguished in the as-calcined samples (Ag/TiO$_2$) according to the XRD pattern (Fig. 1(bIII)). On the one hand, the anatase TiO$_2$ can be obtained owing to the dehydrated reaction of H-titanate during the calcination process. On the other hand, all the AgCl phase has transformed to the fcc Ag phase after calcining the Ag/AgCl/H-titanate due to the reaction between the AgCl and H$_2$O at high temperature. The AgCl/Ag/TiO$_2$ sample was prepared by re-acid treating the Ag/TiO$_2$ in the 0.1 mol/ L HCl solution and the XRD pattern is shown in Fig. 1(bIV). The fcc Ag almost transforms to the AgCl phase suggesting the high chemical activity of the Ag nanoparticles.

The FESEM image in Fig. 2(a) shows the microstructure of the Na-titanate samples, which were obtained through dealloying the Al-Ti alloy in the NaOH solution. The Na-titanate exhibits a 3 dimensional (3D) network structure, which results from the selective corrosion of the elemental Al and the complicated reaction of the released Ti with NaOH. The Na, Ti and O elements are detected from the related EDS spectrum (Fig. S2(a)), which verifies the formation of Na-titanate. It should be noted that the elemental H in Na-titanate cannot be identified by the EDS analysis. After acid treatment, the 3D network structure can still be observed in the H-titanate (Fig. 2(b)). And the Na element cannot be detected from the corresponding EDS spectrum (Fig. S2(b)), implying that the cation-exchange occurred during the acid treatment process in the HCl solution (the Na$^+$ ions in the Na-titanate were replaced by the H$^+$ ions). However, this ion exchange does not significantly change
the morphology of the samples. In addition, a large amount of H$_2$O is released in the calcination process as depicted in Fig. S1, suggesting the existence of H element. Fig. 2(c) presents the microstructure of the anatase TiO$_2$ which was obtained by calcination of the H-titanate. The anatase TiO$_2$ shows a 3D network structure, which is inherited from the titanate. The 3D network structure of the anatase TiO$_2$ is beneficial to its photocatalytic performance owing to the enhanced specific surface area. Fig. 2(d) shows the FESEM images of the Ag/AgCl/H-titanate which was prepared by dealloying and further acid treatment of the Al-Ti-Ag precursor. As shown in Fig. 2(d), the Ag/AgCl nanoparticles with sizes of 200-500 nm are distributed in the H-titanate matrix, and several particles are marked by arrows. But it is difficult to distinguish metallic Ag from AgCl. The Ag and Cl elements are detected by EDS except for Ti and O elements (Fig. S2(c)), suggesting the cation-exchange and the transformation of metallic Ag in the dilute HCl solution. The 3D network structure of the H-titanate matrix indicates the additive Ag in the precursor alloy hardly changes the dealloying process. Typically, the Ag nanoparticles grow on the surface of TiO$_2$ to form the Schottky junction. In our case, the as-prepared Ag/TiO$_2$ samples show the analogical microstructure. Fig. 2(e) shows the microstructure of the Ag/TiO$_2$ samples which were fabricated by calcination of the Ag/AgCl/H-titanate at 400 °C. The Ag nanoparticles with sizes of tens to hundreds of nanometers are homogeneously distributed in the anatase TiO$_2$ matrix (some particles are highlighted by arrows in Fig. 2(e)). A spherical Ag nanoparticle is highlighted in Fig. 2(f), and the related EDS spectrum is presented in Fig. S2(d). It is clear that the
Ag element is dominant in the EDS spectrum, confirming the existence of Ag nanoparticles in the Ag/TiO$_2$ nanocomposites. In addition, both Ti and O can also be identified in the EDS spectrum because the spot size for EDS is larger than the Ag nanoparticle. The anatase TiO$_2$ matrix shows a 3D network structure which is similar to that of the pure mesoporous anatase TiO$_2$ (Fig. 2(c)). Fig. 2(g) shows the typical microstructure of the AgCl/Ag/TiO$_2$. After re-acid treatment, the metallic Ag partially transforms to the AgCl phase which exhibits the large particles with the heterogeneous size (Fig. 2(g)). Fig. 2(h) shows the distribution of Ag and Cl elements. Obviously, the same outlines of the Ag and Cl elements indicate the existence of AgCl phase, which is in agreement with Fig. 2(g). The TiO$_2$ matrix (marked by the dashed box in Fig. 2(g)) still presents the 3D network structure (Fig. 2(i)), indicating the stability of the anatase TiO$_2$ in the HCl solution.

Fig. 3 illustrates the TEM, related SAED pattern and HRTEM images of the Ag/TiO$_2$ photocatalyst. Fig. 3(a) exhibits that dispersive Ag nanoparticles with diameter of about tens to hundreds of nanometers are loaded in the anatase TiO$_2$ matrix. The matrix presents a mesoporous structure as depicted in Fig. S3. The corresponding SAED pattern is shown in Fig. 3(a-1), which is consistent with the regular diffraction rings of the anatase TiO$_2$. Besides, bright diffraction spots can also be observed (marked by arrows in Fig. 3(a-1)), and correspond to the fcc Ag phase. The electron diffraction results are in good agreement with the XRD analysis in Fig. 1(bIII). As shown in the enlarged image (Fig. 3(b)), the spherical Ag nanoparticles grow in the anatase TiO$_2$ matrix with the 3D network structure. The lattice spacings of
0.35 and 0.24 nm determined by HRTEM (Fig. 3(c)) correspond to (101) plane of the anatase TiO$_2$ and (111) plane of the fcc Ag phase, respectively. Moreover, the lattice distortion marked by a square at the interface between the TiO$_2$ matrix and Ag nanoparticles is observed, suggesting that the Schottky junction has been achieved.

Specific surface area is an important parameter for photocatalysts. The N$_2$ adsorption-desorption isotherm and BJH pore size distribution curves (inset) of the Ag/TiO$_2$ samples are displayed in Fig. S3. The hysteresis loop in the N$_2$ adsorption-desorption isotherm of the Ag/TiO$_2$ results from the filling of the framework with 3D network structure. The adsorption–desorption isotherm can be classified as a type IV isotherm with a H3-type hysteresis loop due to the presence of mesopores, which agrees with the results of the SEM and TEM. It should be noted that the BET specific surface area of the mesoporous AgTiO$_2$ is as high as 90.18 m$^2$/g. In addition, the specific surface area of the present Ag/TiO$_2$ nanocomposites is much larger than that of P25 (52 m$^2$/g) in other literature.$^{41}$ The BJH pore-size distribution curve indicates that the Ag/TiO$_2$ photocatalysts exhibit a narrow pore-size distribution with two kinds of pore diameters of 2 ~ 5 and 5 ~ 20 nm, which confirm the hierarchically porous structure of the Ag/TiO$_2$ samples. The mesoporous structure supplies the efficient transport pathways for the photogenerated charge carriers, which is propitious to the photocatalytic activity.$^{42,43}$

The fully scanned spectrum (Fig. 4(a)) shows that Ti, O, Ag and C elements exist on the surface of the Ag/TiO$_2$ sample. The C 1s peak at 284.6 eV is ascribed to the adventitious carbon. No other characteristic peaks can be found, suggesting the purity
of the Ag/TiO₂ nanocomposites. The high resolution XPS spectra of Ti 2p, Ag 3d and O 1s are displayed in Fig. 4(b)–4(d) respectively. Fig. 4(b) shows the peaks at 458.75 and 464.65 eV, which correspond to the Ti 2p₃/₂ and Ti 2p₁/₂ respectively. However, the peak positions for Ti 2p in the Ag/TiO₂ photocatalysts shift to the lower binding energy than the bare TiO₂, confirming the strong interface between the metallic Ag and TiO₂. The XPS peaks for Ti 2p can be further divided into different peaks by XPS peak fitting program. The peak at 458.1 eV proves the existence of the Ti³⁺ oxidation state, which is advantageous to the higher photocatalytic activity for TiO₂ under the visible light irradiation. According to the areas of Ti³⁺ and Ti⁴⁺ (Fig. 4(b)), the ratio of Ti³⁺ was determined to be about 28.9% in total TiO₂. The Ag 3d spectrum of the Ag/TiO₂ presents two peaks at 367.9 and 373.9 eV, which are assigned to Ag 3d₅/₂ and Ag 3d₃/₂ binding energies, respectively. The XPS peak separation of 6.0 eV between two Ag 3d states is also the characteristic of metallic Ag. The peak positions of Ag 3d shift to the lower position than the bulk Ag, indicating strong interface interactions between the metallic Ag and TiO₂. The shifted peak positions of the Ti 2p and Ag 3d in Ag/TiO₂ illustrate the Schottky junction between metallic Ag and TiO₂. The O 1s peak (Fig. 4(d)) at about 530 eV is the characteristic of the lattice oxygen of TiO₂. In addition, the wide and asymmetric feature of the O1s spectrum suggests that there exist more than one oxygen component in the Ag/TiO₂ photocatalyst. The O 1s peak can be further fitted into two peaks including lattice oxygen (O₁₁O at 530.1 eV) and surface hydroxyl groups (O₁₁H at 531.7 eV).

For comparison, the photocatalytic activities of commercial P25 nanoparticles,
AgCl/Ag/TiO₂ and mesoporous Ag/TiO₂ were evaluated by photodegradation of MO solution under visible light irradiation. The photocatalytic results under visible light irradiation are shown in Fig. 5. The MO absorbance spectra (Fig. 5(a, b and c)) present the intensity of all the MO peaks decrease with the increase of treatment time indicating all of the photocatalysts can adsorb and degrade the MO solution. And MO degradation efficiency (Fig. 5(d)) illustrates the mesporous AgCl/Ag/TiO₂ and Ag/TiO₂ possess stronger adsorption capacity in dark originating from the mesoporous structure and the large specific area. In order to exclude the photo bleaching, the blank test is shown in Fig. 5(d) indicating the effect of light can be neglected. Of importance, the MO solution could be completely degraded in 120 min by the mesporous Ag/TiO₂ under visible light irradiation, indicating its superior photocatalytic performance. After re-acid treating the Ag/TiO₂ in the HCl solution, the AgCl/Ag/TiO₂ photocatalyst exhibits the poorer photocatalytic activity than the Ag/TiO₂ because of the decrease in the amount of the Schottky junctions. But it is still higher than P25 because the doping or deposition of silver halides onto TiO₂ can further enhance the photocatalytic activity. And the residual Ag nanoparticles could also enhance the photocatalytic activity of the AgCl/Ag/TiO₂ photocatalyst. Under the same conditions, only about 27% of MO can be eliminated in 120 min by P25, showing the worst photocatalystic activity. Besides, the Ag/TiO₂ photocatalyst exhibits the enhanced photocatalytic activity under the UV light irradiation, compared to the commercial P25, as shown in Fig. S4. Therefore, the present Ag/TiO₂ photocatalyst presents excellent catalytic activities under both visible light and UV
irradiation.

In the following, we try to clarify the reasons for the enhanced photocatalytic performance of Ag/TiO₂. Ag/TiO₂ powders are black as shown in Fig. S5(e), which can absorb the visible light in the natural environment. Fig. 6 shows the optical performance of the different photocatalysts by UV-Vis diffuse reflectance. Obviously, a sharp band edge absorption peak of P25 only appears in the UV region and almost has no response in visible light region. Compared to P25, the notable absorption covering the range of 400-600 nm in the visible-light region can be observed in the spectra of Ag/TiO₂ and AgCl/Ag/TiO₂ nanocomposites, which is principally due to the surface plasma resonance effect of Ag nanoparticles. Of importance, the band edge absorption peaks of the prepared photocatalysts shift to the visible light region. The plots of (F(R)E)¹/² versus the energy of absorbed light are converted from the UV−Vis DRS spectra according the Kubelka-Munk function (Fig. 6 (b)). The bandgap energy of Ag/TiO₂ estimated from the intercept of the tangent to the plot is around 2.81 eV and that of the AgCl/Ag/TiO₂ is about 2.98 eV, which are lower than 3.16 eV of P25. As is well known, the narrower energy gap is beneficial to absorb the visible light. The results of the optical performance indicate that the modified TiO₂ by Ag nanoparticles can harvest more photons than pure TiO₂ especially under the visible light, which is in agreement with the results of photocatalytic tests.

Fig. 7 depicts a schematic illustration of enhanced photocatalytic activity by the mesoporous Ag/TiO₂ nanocomposites. It is well known that pure TiO₂ hardly degrades the MO under visible light irradiation owing to the large energy gap. It has
been demonstrated that Ag nanoparticles in the Ag/TiO$_2$ and AgCl/Ag/TiO$_2$ nanocomposites result in the notable response to the visible light (Fig. 6). And the Ag nanoparticles are advantageous to capture the photon.$^{49, 50}$ As for the Ag/TiO$_2$ nanocomposites, the hot electrons are injected into the CB of the TiO$_2$ matrix via the Schottky junction between Ag and TiO$_2$, leaving the holes in Ag nanoparticles under the visible light irradiation$^{51}$ (enlarged section in Fig. 7(a)). And the photogenerated charges would decompose the MO molecule. Under the UV light irradiation, the Ag nanoparticles serve as the scavenging centers for causing photogenerated electron and hole pair separation (Fig. 7(b)). The excited electrons under UV spectrum can be transferred from the CB of TiO$_2$ to the metallic Ag by the Schottky junction (enlarged section in Fig. 7(b)), resulting in the improved photocatalytic activity$^2$. In our experiment, the fcc Ag nanoparticles are distributed in the mesoporous anatase TiO$_2$ matrix with a 3D network structure. This unique microstructure could be used to improve the quantity of the Schottky junction and thus increase the electron transfer pathways with a certain amount of Ag content. After re-acid treating the mesoporous Ag/TiO$_2$ in HCl solution, almost all of the Schottky junctions between Ag and TiO$_2$ are damaged resulting in the decrease of the electron transfer pathways. In addition, the nanosized Ag almost entirely transformed to the AgCl which cannot excite carriers under the visible light irradiation. However, the AgCl phase would be partially reduced to metallic Ag during the photodegradation process as a result of photo-instability of AgCl.$^{50}$ So the AgCl/Ag/TiO$_2$ samples present better photocatalytic performance than P25 in visible light region, but the activity is lower
than the Ag/TiO₂ photocatalyst owing to the decreasing electron transfer pathways between Ag and TiO₂.

Summary and conclusions

Novel Ag/TiO₂ nanocomposites can be fabricated through a new strategy which combines chemical dealloying/acid treatment with calcination. The dealloying of the ternary Al-Ti-Ag precursor leads to the formation of Ag/Na-titanate, and the further acid treatment gives rise to the formation of Ag/AgCl/H-titanate through the cation-exchange and chlorination. The calcination of Ag/AgCl/H-titanate results in the formation of Ag/TiO₂ nanocomposites which are composed of Ag nanoparticles well distributed in the mesoporous anatase TiO₂ matrix. Compared to the commercial P25, the introduction of Ag nanoparticles can greatly enhance the photocatalytic activity of the Ag/TiO₂ nanocomposites under both visible and UV light irradiation. The enhanced photocatalytic activity of Ag/TiO₂ is attributed to the synergistic contribution of the Schottky junction between Ag and TiO₂, the surface plasma resonance effect of metallic Ag nanoparticles and the large specific surface area (90.18 m²/g) originating from the mesoporous structure. Our strategy will provide a novel route to synthesize noble metal (Ag, Au, Pt, etc.)/oxide nanocomposites with enhanced functional properties. Moreover, the loading amount of noble metal in these nanocomposites can be adjusted through facilely changing the composition of ternary precursor alloys (for example, the Ag/Ti ratio in the Al-Ti-Ag precursor). In
addition, the present fabrication strategy can be facilely scaled up (Fig. S5), which is crucial for the commercialization of photocatalysts.

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**Figure captions**

Fig. 1 XRD patterns of the obtained samples using different precursors of (a) Al$_{97.1}$Ti$_{2.9}$ or (b) Al$_{97.4}$Ti$_{2.4}$Ag$_{0.2}$. (I) the as-dealloyed samples, (II) the acid treatment samples, (III) the as-calcined samples, (IV) the re-acid treatment samples.

Fig. 2 FESEM images of (a) Na-titanate, (b) H-titanate, (c) the anatase TiO$_2$, (d) Ag/AgCl/H-titanate, (e and f) Ag/TiO$_2$ and (g, h and i) AgCl/Ag/TiO$_2$.

Fig. 3 (a and b) TEM images of the Ag/TiO$_2$ photocatalyst, (a-1) corresponding SAED pattern and (c) HRTEM image.

Fig. 4 XPS spectra of the Ag/TiO$_2$ sample: (a) survey; (b) Ti 2p; (c) Ag 3d; (d) O 1s.

Fig. 5 (a-c) UV-vis absorption spectra of MO solution under different visible light irradiation time in presence of (a) Ag/TiO$_2$, (b) AgCl/Ag/TiO$_2$, and (c) P25. (d) Comparison of photocatalytic performance of different photocatalysts.

Fig. 6 (a) UV-Vis diffuse reflectance absorption spectra (DRS) of different photocatalysts and (b) plots transformed according to the Kubelka-Munk function versus energy of light for the photocatalysts.

Fig. 7 Proposed photocatalytic schematic illustration of the Ag/TiO$_2$ photocatalyst under (a) visible and (b) UV light irradiation. CB: conduction-band; VB: valence-band.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7

(a) Visible light

(b) UV

Electron

Hole

TiO$_2$

Ag

TVB$^E$

CB

EF

VB