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Physical Chemistry Chemical Physics

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Photoinduced Reversible Shape Conversion of Silver Nanoparticles Assisted by TiO₂†

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Silver nanoprisms were transformed into nanodecahedrons through photoinduction of ultraviolet (UV) light in the presence of titanium dioxide (TiO₂) quantum dots (QDs). Subsequently, the silver
10 nanodecahedrons were reconverted to silver nanoprisms under sodium lamp if there was sufficient citrate in the reaction system. The localized surface plasmon resonance (LSPR) optical properties of silver nanoparticles were tuned during photoinduced shape conversion. Photocatalysis role of TiO₂ QDs assisted the conversion of prism to decahedron by UV light irradiation. Nevertheless, the existence of TiO₂ did not inhibit the photoinduced reconversion from decahedron to prism by sodium light. It was demonstrated
15 that citrate was indispensable in the photoinduction process. In addition, oxygen in solution played a vital role in the reversible shape conversion of silver nanoparticles. Moreover, simulated sunlight can convert silver nanoprisms to nanodecahedrons instead of UV light with assistance of TiO₂ QDs, which would promote the photoinduced reaction of silver nanoparticles based on natural light source.

20 1. Introduction

Anisotropic silver nanoparticles have received considerable attention because of their potential applications in many research fields such as surface enhanced spectroscopy,[1,2] biological sensing,[3] and optoelectronic devices.[4-7] These applications of
25 silver nanoparticles are primarily based on localized surface plasmon resonance (LSPR) arising from interaction between electrons around nanoparticles and incident light.[8-10] The LSPR properties of silver nanoparticles are associated with their size, shape and surrounding.[11,12] A number of approaches for synthesis
30 of silver nanoparticles with well-defined morphologies have been explored to tune their LSPR optical properties.[13-18] Photoinduction method is one of the most popular strategies to control the morphologies of silver nanoparticles.[17-23] Photoinduced conversion from silver seeds to silver nanoprisms was first
35 reported by Mirkin *et al* in 2001.[17] It was demonstrated that the photoinduced growth process was driven by surface plasmon excitations.[18,24] The photoinduced fabrication of silver nanoprisms was proved to involve the reduction of silver cations by citrate on the silver particle surface and the oxidative dissolution of small
40 silver particles.[24] Besides, Wu *et al.* also proposed a similar mechanism of photoconversion from citrate stabilized silver seeds to nanoprisms.[25] They suggested that the photoinduced process involved photooxidation of citrate by "hot holes" from the plasmon

dephasing on nanoparticle surface, oxidative etching of silver and
45 selective reduction of silver ions on crystalline prisms. In addition to the growth of silver nanoparticles by photoinduction, the shape conversion after formation of silver nanoparticles was also achieved through a photoinduced method. Yin *et al.* employed UV light to change silver nanoprisms into silver nanodisks and tuned
50 precisely the LSPR optical properties of silver nanoplates in a wide range of wavelength *via* the UV-light-induced shape reconstruction.[26] Additionally, in our previous study, sodium light was used to convert silver nanoprisms with low concentration of citrate to silver nanodisks that were reconstructed to silver
55 nanoprisms after addition of more citrate under sodium light irradiation.[27] A series of shapes of silver nanoplates were realized through controlling the concentration of citrate in reaction system during the photoinduced process involving sodium light. However, it is difficult to accomplish the reversible shape conversion using
60 photoinduced approaches.

Additives can influence the photoinduced process of silver nanoparticles through their interaction with silver nanoparticles. For example, reduced graphene oxide (RGO) from graphene oxide (GO) could accelerate the photoinduced growth of silver
65 nanoprisms, due to electron transfer between RGO and silver nanoparticles.[28] Titanium dioxide (TiO₂) is a well-studied and stable photocatalyst capable of degrading organic molecules via electron hole pairs that are formed upon irradiation with UV light exceeding the band gap of materials.[29] TiO₂ as one of the most

popular photocatalysts is widely applied in decontamination of water and self-cleaning coatings due to its strong oxidizing capacity for organic pollutants, chemical stability, non-toxicity and low cost.[29-32] Noble metal nanoparticles, in particular silver nanoparticles, have been combined with TiO$_2$ nanoparticles to enhance the efficiency of photocatalysis.[33-35] Metal nanoparticles prevented the recombination of the hole–electron pairs from TiO$_2$ under light irradiation and promoted the separation efficiency of photo-generated electron–hole pairs.[33-35] In addition, silver nanoparticles loaded photocatalytically on TiO$_2$ nanoporous films exhibited multicolor photochromism.[36-40] Silver ions were reduced to silver nanoparticles in the TiO$_2$ nanoporous structures under ultraviolet (UV) light. Plasmonic excitation of the silver nanoparticles placed on TiO$_2$ by visible or near-infrared light resulted in their oxidation due to plasmon-induced charge separation.[41] The interconversion between plasmonic silver nanoparticles and silver ions with assistance of TiO$_2$ under light irradiation, resulted in reversible color changes.[38] Variation in the particle size distributions photoelectrochemically induced by monochromatic excitation caused spectral changes, leading to multicolor photochromism of silver nanoparticles.[37, 38] The photoinduced oxidation of silver nanoparticles could be used to control their size, shape, and aspect ratio.[41] However, to our knowledge, the photoinduced shape conversion of silver nanoparticles assisted by TiO$_2$ was rarely reported in literature.

In the present study, reversible shape conversion of silver nanoprism to nanodecahedrons was realized with assistance of TiO$_2$ quantum dots (QDs) under different light sources. TiO$_2$ promoted transformation from prism to decahedron by UV light irradiation. The obtained silver nanodecahedrons were reconverted to silver nanoprisms through the photoinduction process under sodium light. The spectral changes in the photoinduction process were monitored to understand shape conversion of silver nanoparticles. Morphologies of silver nanoparticles were characterized in the different reaction periods. The influence of citrate and dissolved oxygen on shape conversion was investigated. Moreover, the simulated sunlight was also employed to induce the shape conversion from prism to decahedron in the presence of TiO$_2$. Furthermore, the effect of TiO$_2$ on photoinduced reaction is discussed.

2. Experimental section

2.1 Materials

AgNO$_3$ (>99%), trisodium citrate (≥99.0%), sodium borohydride (>98%), Titanium(IV) butoxide (TBT, 97%), poly(vinylpyrrolidinone) (PVP, average Mw = 40,000) and acetic acid (≥99.7%) were purchased from Sigma-Aldrich. All the chemicals were analytical grade and used as received.

2.2 Photoinduced synthesis of initial silver nanoprisms

A typical experiment was carried out by a photoconversion process. First, silver seeds were prepared by dropwise addition of NaBH$_4$ solution (8.0 mM, 1.0 mL) to an aqueous solution of AgNO$_3$ (0.1 mM, 100 mL) in the presence of trisodium citrate (1.0 mM) under vigorous stirring. The yellow silver seed solutions were obtained. The silver seed solutions were then placed under a

sodium lamp (NAV-T 70 model from Osram China Lighting Co., Ltd.). The color of silver colloids changed from yellow, to green, and finally to blue during the irradiation process. The obtained blue colloid was used as initial silver nanoprism solution in subsequent photoinduced process.

2.3 Preparation of TiO$_2$ quantum dots (QDs)

Anatase TiO$_2$ QDs were prepared by the following method. In a typical procedure, 1.0 mL of TBT was dissolved in 10 mL of ethanol by ultrasonication for 5 min, and followed by dropwise adding 4.0 mL acetic acid under vigorous stirring to form a transparent solution. The obtained solution was dropwise added into 20 mL of ethanol containing 0.5 g PVP. The mixture was diluted to 50 ml by ethanol to form a clear light yellow solution, and then transferred to a 100 mL autoclave. This reaction system was kept at 150 °C for 10h and then cooled slowly to room temperature. The PVP-capped TiO$_2$ QDs were flocculated from ethanol by the addition of hexane (40 mL of hexane/10 mL of reaction mixture) and subsequently separated by centrifugation at 7000 rpm for 10 min. The TiO$_2$ QDs were washed with ethanol/hexane mixture 3 times. Finally, TiO$_2$ QDs were dispersed in water and the concentration of obtained TiO$_2$ QD solution was 10.12 mg/mL.

2.4 Photoinduced shape conversion from prism to decahedron

TiO$_2$ QD solution (90 μL, 10.12 mg/ml) was added into 20 mL of initial silver nanoprism solution in a quartz beaker under stirring. After 3 min, the beaker containing initial silver nanoprism solution with TiO$_2$ QDs (4.55×10^{-2} mg/mL) was covered with a quartz dish and placed in an UV light box. In the meantime, the initial silver nanoprism solution without TiO$_2$ QDs in a quartz beaker coved by a quartz dish was also irradiated by UV light. The extinction spectra of the samples at different periods were recorded by UV-vis absorbance spectrometer. The changes in color of reaction solutions were observed.

2.5 Reconversion of silver nanoprisms from nanodecahedrons

Subsequently, the silver nanoparticle solution obtained through UV light induction was transferred for light irradiation under sodium lamp after the concentration of citrate in solution was adjusted. The optical properties and morphologies of silver nanoparticles were characterized in the photoinduction process.

26 Characterization

Extinction spectra of silver nanoparticle solutions were recorded using a Varian Cary 3E UV/vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 with an acceleration voltage of 200 kV. Samples for TEM analysis were prepared by dripping a drop of silver nanoparticle solutions onto the copper grids with thin carbon films and drying them in the air at room temperature. UV light was obtained from self-built UV light box equipped with TL 20W/12 RS UVB tube from Philips. Suntest instrument (SUNTEST XLS+ from Atlas Material Testing Technology LLC) was used to produce simulated sunlight for photoinduced conversion of silver nanoparticles. Emission spectra of light sources were obtained using an Ocean Optics USB4000 spectrometer.

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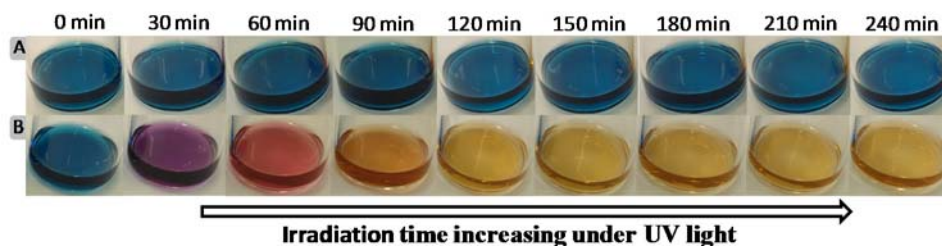
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Fig. 1 Photographs of silver nanoprism solutions without (A) and with (B) TiO$_2$ irradiated for different time by UV light.
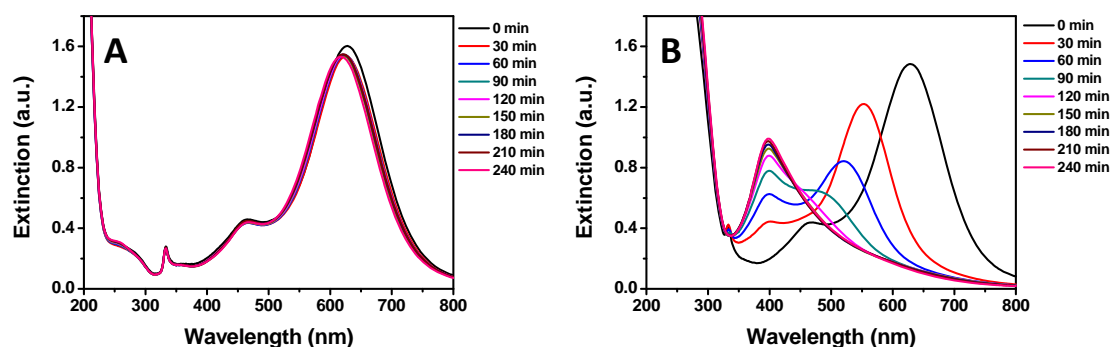

Fig. 2 Evolution of extinction spectra of silver nanoprism solutions without (A) and with (B) TiO$_2$ irradiated for different time by UV light.

3. Results and discussion

The silver nanoprisms were synthesized from sliver seeds (0.1 mM of AgNO$_3$ and 1.0 mM of citrate) through photoinduction under sodium lamp. The as-synthesized silver nanoprisms were stable under irradiation of UV light. The color silver nanoprisms solution did not change visibly (Fig. 1A). The extinction spectra of silver nanoprism solution varied slightly at the beginning of UV light irradiation (30 min), and remained nearly unchanged after further irradiation (30 ~ 240 min) (Fig. 2A). As can be inferred, it is difficult to convert the morphologies of these silver nanoprisms. Yin et al. reported that the silver nanoprisms were transformed to silver nanodisks by UV light.[26] It should be noted that the silver nanoprisms in that study were prepared through reduction of silver ions by sodium borohydride in the presence of citrate and PVP at room temperature under vigorous stirring, and the silver nanoprisms were different from the ones in this study. In a previous paper, the silver nanoprisms with low concentration of citrate were converted to silver nanodisks under sodium lamp.[27] It was suggested that the shape conversion of prism to disk was due to limited stability of lower concentration of citrate (0.1 mM of citrate). The silver nanoprisms with high concentration of citrate (1.0 mM of citrate) could not be transformed to nanodisks by sodium light.[27] Photoinduced conversion of silver nanoparticles was restricted by many influencing factors including shape of nanoparticle, concentration of stabilizer and photoinduction wavelength. As can be seen from Fig. 1A and 2A, it is hard to change shape of the silver nanoprisms by UV light. The citrate (1.0 mM) in silver nanoparticle solution might provide sufficient stabilizing ability to nanoprisms.

The color of initial silver nanoprism solution changed during UV light irradiation after TiO$_2$ QDs were added into the solution. The blue silver nanoprism solution changed to purple, red, orange and finally yellow under irradiation of UV light (Fig. 1B). The color change is generated from LSPR optical properties of silver nanoparticles in solution. Figure 2B shows the evolution of extinction spectra of silver nanoprism solution with TiO$_2$ as the irradiation time of UV light was prolonged. The extinction spectra of silver nanoparticles with TiO$_2$ changed noticeably during UV light irradiation. The extinction spectrum of the initial silver nanoparticles presents three bands centered at 332, 465 and 630 nm, ascribed to the out-of-plane quadrupole, in-plane quadrupole, and in-plane dipole plasmon resonance modes of triangular silver nanoplates, respectively.[17, 18] The broad absorbance under 350 min is due to existence of TiO$_2$ QDs in solution. The main LSPR band at 630 nm blue-shifted to 553 nm and decreased in intensity after the initial solution was irradiated for 30 min (Fig. 2B). Meanwhile, a new band at 400 nm appeared. The band at long wavelength continued to blue-shift and decrease with an increase in irradiation time. The new LSPR extinction band at 400 nm increased with irradiation time. The wavelength of the new extinction peak remained constant though its intensity kept increasing, which reveals formation of a new kind of silver nanoparticles from silver nanoprisms. It is speculated that that the new silver nanoparticles
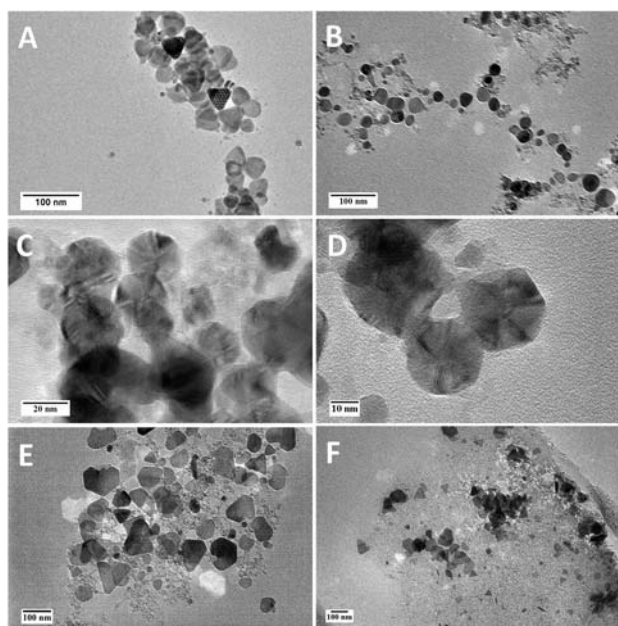
Fig. 3 (A-D) TEM images of silver nanoprisms with TiO₂ irradiated by UV light for different time: (A) 0 min, (B) 60 min, (C, D) 240 min. (E, F) TEM images of silver nanoparticles obtained from the samples corresponding to (C, D) through 7 h of irradiation under sodium lamp after addition of more citrate.

were produced when silver nanoprisms were changed in morphology. The LSPR band at long wavelength disappeared after the silver nanoparticle solution was irradiation by UV light for 150 min. The extinction spectra of silver nanoparticles changed little after 150 min of irradiation by UV light (Fig. 2B). The results manifest that the silver nanoprisms were converted to other morphologies by UV light under assistance of TiO₂ QDs.

To shed light on the effect of irradiation of UV light on silver nanoparticles, TEM characterization was performed to observe morphological changes of nanoparticles. It can be seen that nearly all the initial silver nanoparticles before light irradiation were nanoprisms (Fig. 3A), which is consistent with deduction from LSPR extinction spectra. The silver nanoprisms were transformed to silver nanodisks when the initial silver solution was irradiated by UV light for 60 min (Fig. 3B). The process of shape transformation from nanoprism to nanodisk was similar to those reported in the previous studies.[26, 27] However, it was found the most silver nanoprisms were converted to silver nanodecahedrons after 240 min of irradiation by UV light (Fig. 3 C and D). It can be inferred that the new LSPR band at 400 nm was attributed to the formation of silver nanodecahedrons (Fig. 2B). The photocatalysis effect of TiO₂ in the UV region (especially less than 350 nm) provided an effective route to convert silver nanoprisms to silver nanodecahedrons in the same colloid system. Interestingly, the silver nanodecahedrons from UV light irradiation were reconverted to silver nanoprisms when silver nanodecahedron solution was irradiated under sodium lamp after adding more citrate in solution (Fig. 3E and F). The yellow silver nanodecahedron solution with addition of more citrate changed to blue after it was irradiated by sodium light (Inset in Fig. 4A). The extinction spectrum of silver nanoparticle solution exhibited three LSPR bands centered at 332, 515 and 656 nm when silver nanodecahedron solution was irradiated for 7 h under sodium lamp
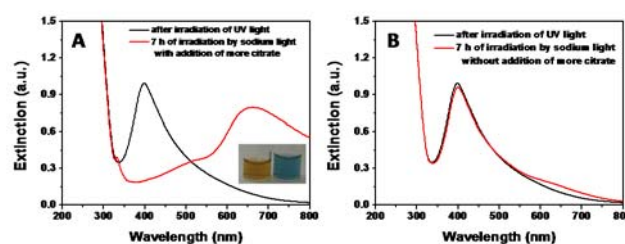

Fig. 4 (A) Extinction spectra of silver nanodecahedron solution and silver nanoparticles from nanodecahedron with addition of more citrate after 7 h of irradiation by sodium lamp. Insert: Photograph of corresponding silver nanoparticle solutions before and after light irradiation. (B) Extinction spectra of silver nanodecahedron solution before and after irradiation for 7 h by sodium lamp without addition of more citrate.

(Fig. 4A), which displays the characteristic LSPR modes of silver nanoprisms.[17, 18] These results indicate that the silver nanodecahedrons were reconverted to silver nanoprisms through photoinduction of sodium light in the presence of additional citrate. However, the extinction spectrum of silver nanodecahedron solution without addition of more citrate changed slightly even after the solution was irradiated for 7 h by sodium light (Fig. 4B), which implies that the silver nanodecahedrons could not be transformed into other morphologies in the absence of enough citrate. To make clear the essential amount of additional citrate for the shape conversion, the concentration of citrate in the nanodecahedron solution was increased by different values (0.1 ~ 1.0 mM) before irradiation by sodium light. Figure S1 displays the extinction spectra of silver nanoparticle solutions with additional citrate after irradiated for 15 h by sodium light. When concentration of additional citrate was 0.1 mM, the LSPR band ascribed to nanodecahedron still existed in the final extinction spectrum of silver nanoparticle solution even after 15 h of irradiation by sodium light (Fig. S1), implying shape conversion from decahedron to prism were not completed with 0.1 M of additional citrate in solution. All the extinction spectra of silver nanoparticle solutions were almost consistent and exhibited the characteristic LSPR bands of silver nanoprism after irradiated for 15 h by sodium light when the concentration of additional citrate was in the range of 0.2 ~ 1.0 mM. The results indicate that the shape conversion from decahedron to prism can be completed under irradiation by sodium light if the concentration of additional citrate should be more than or equal to 0.2 mM. It was demonstrated that citrate as a stabilizer and reducing agent played a crucial role in the photoinduced synthesis of silver nanoprisms.[24, 25] During the conversion process of nanoprism to nanodecahedron, citrate was consumed by UV light through photocatalysis with assistance of TiO₂ QDs. Due to lack of citrate in the reaction system, the obtained silver nanodecahedrons were not reconverted to silver nanoprisms by sodium light.

The concentration of citrate in the initial silver nanoprism solution was increased to 2.0 mM to further gain insights into the influence of citrate concentration on the photoinduced reaction. Similarly, it was found from extinction spectra and colors of solution that the initial silver nanoprisms in the presence of TiO₂ QDs were transformed into silver nanodecahedrons (U3h) through 3 h of irradiation of UV light (Fig. 5). The silver nanodecahedron solution (U3h) was placed under sodium lamp for photoinduction without addition of more citrate. The silver nanodecahedrons were
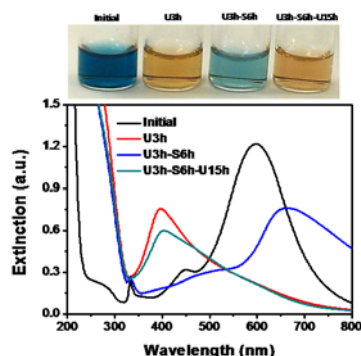
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Fig. 5 Photograph (upper panel) and extinction spectra (bottom panel) of initial silver nanoprism solution (Initial), silver nanodecahedron solution obtained after UV light irradiation for 3 h (U3h), silver nanoprisms from
5 U3h through 6 h of irradiation under sodium lamp (U3h-S6h), and silver nanoparticles from U3h-S6h after 15 h of irradiation by UV light (U3h-S6h-U15h).

converted to silver nanoprisms (U3h-S6h) after irradiation for 6 h by sodium light. No additional citrate was needed to transform
10 nanodecahedrons to nanoprisms, which may be due to existence of adequate citrate in initial silver nanoprism solution. Significantly, the silver nanoprisms (U3h-S6h) from nanodecahedrons could be reconverted to silver nanodecahedrons (U3h-S6h-U15h) when U3h-S6h was placed to UV light again for 15 h of irradiation (Fig.
15 5), which verifies that reversible photoinduced shape conversion of silver nanoparticles is feasible in the presence of sufficient citrate and TiO$_2$ QDs.

In order to examine the influence of further UV irradiation on shape of silver nanoprisms, the initial silver nanoprism solution
20 without TiO$_2$ was irradiated for 24 h by UV light. The extinction spectra and TEM images were measured to observe the changes of silver nanoparticles after UV irradiation. Although the LSPR extinction band at long wavelength blue-shifted in position and decreased in intensity after 24 h of UV light irradiation, the
25 characteristic LSPR extinction spectral profile corresponding to nanoprism did not changed after light irradiation (Fig. S2A), revealing further UV light irradiation did not significantly the shape of silver nanoparticles. Most of silver nanoparticles were triangular silver nanoplates after 24 h of UV light irradiation in the
30 TEM image (Fig. S2B), which further demonstrated that prolonged UV light irradiation did not convert prism to other shape. In addition, to investigate the effect of sodium light irradiation on silver nanoprisms with TiO$_2$, the extinction spectra of silver nanoparticles in presence of TiO$_2$ after irradiated for 24 h under
35 sodium was measured (Fig. S3A). Comparing with the extinction spectrum of initial silver nanoprisms, the band intensity at long wavelength of silver nanoparticles decreased after 24 h of sodium light irradiation. Whereas, the extinction spectrum of silver nanoparticles still displayed characteristic LSPR bands of
40 nanoprisms, which implies that the sodium light irradiation cannot convert silver nanoprisms to nanodecahedrons even though the TiO$_2$ are present in the reaction system. TEM characterization also testified that the morphologies of silver nanoprisms was not changed significantly by sodium light irradiation in the presence
45 of TiO$_2$ (Fig. S3B).

To probe into the influence of TiO$_2$ concentration on the shape conversion rate of silver nanoparticles, the extinction spectra of silver nanoprism solution with different concentrations of TiO$_2$
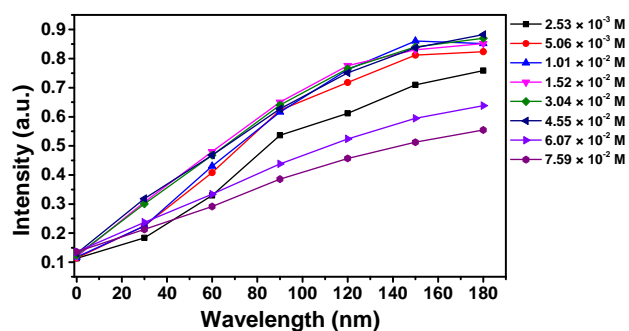

50 **Fig. 6** Plots of intensity of extinction band at 400 nm of silver nanoprism solutions with different concentrations of TiO$_2$ as a function of irradiation time during UV light irradiation.

$(2.53 \times 10^{-3} \sim 7.59 \times 10^{-2}$ mg/mL) during UV light irradiation were recorded (Fig. S4). As can be inferred from extinction spectra, the
55 silver nanoprisms were converted to silver nanodecahedrons after 150 min of UV light irradiation when the concentration of TiO$_2$ was in the range of $2.53 \times 10^{-3} \sim 4.55 \times 10^{-2}$ mg/mL. Nevertheless, the shape conversion rate slowed down when the TiO$_2$ concentration was increased to 6.07×10^{-2} mg/mL. Figure 6 depicts
60 the plots of intensity of extinction band at 400 nm as a function of irradiation time of UV light. The LSPR band assigned to silver nanodecahedrons increased with irradiation time. The shape conversion rate increased as an increase in concentration of TiO$_2$ among $2.53 \times 10^{-3} \sim 1.52 \times 10^{-2}$ mg/mL. The plots of intensity of
65 the extinction band at 400 nm *vs* irradiation time kept unchanged when the TiO$_2$ concentration increased to 4.55×10^{-2} mg/mL from 1.52×10^{-2} mg/mL. The result indicates that shape conversion rates of silver nanoparticles are consistent in a certain range of TiO$_2$ centration, which may be due to constant photocatalytical ability.
70 However, the shape conversion rate decreased as the concentration of TiO$_2$ increased within $4.55 \times 10^{-2} \sim 7.59 \times 10^{-2}$ mg/mL (Fig. 6). It is well known that TiO$_2$ possesses both photocatalysis and optical absorption properties under UV light.[32, 42] The excessive TiO$_2$ in reaction system absorbs much UV light, which may reduce
75 the interaction between UV light and silver nanoparticles. Although the photocatalytical effect from TiO$_2$ promoted the shape conversion of silver nanoparticles under UV light, the dose of light acting on silver nanoparticles decreased due to presence of much TiO$_2$ in solution. It is referred from the results that the optimal
80 shape conversion of silver nanoparticles under UV light could be obtained with TiO$_2$ concentration in the range of $1.52 \times 10^{-2} \sim 4.55 \times 10^{-2}$ mg/mL.

It was noted that the LSPR band at 400 nm appeared at the beginning of irradiation when the silver nanoprisms with TiO$_2$
85 were irradiated by UV light (Fig. 2B). The wavelength of this new LSPR band did not change in wavelength though the LSPR band at long wavelength blue-shifted. It is possible that the silver nanodecahedrons were formed from decahedral separate seeds.[22, 43-45] To investigate the interaction between TiO$_2$ QDs and UV light,
90 the TiO$_2$ QDs were characterized. Figure S5A depicts the UV-vis absorbance spectrum of TiO$_2$ QD solution. The TiO$_2$ QDs have no visible absorbance in the region above 380 nm. While, the absorbance intensity of TiO$_2$ QDs increased dramatically at short wavelength from 350 nm. The optical absorbance property of TiO$_2$
95 results in that TiO$_2$ QDs only interact with UV light. TEM images

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of TiO$_2$ QDs manifest that the size of TiO$_2$ QDs was 3.6±0.6 nm (Fig. S5B and C). In addition, the X-ray diffraction (XRD) patterns of the TiO$_2$ QDs used in the present study show the X-ray diffraction peaks at the 2θ values of 25.3º, 37.9º, 47.9º, 54.3º, 62.5º, 69.5º and 75.3º corresponding to the (101), (004), (200), (211), (204), (116)/(220) and (215) crystal planes of anatase TiO$_2$, respectively (Fig. S6).[33, 46, 47] The anatase TiO$_2$ has been demonstrated to exhibit higher photocatalysis than rutile TiO$_2$.[48-50] The emission spectrum of UV lamp presents a main emission band in the range of 280 ~ 360 nm (Fig. S7). The absorbance wavelength of TiO$_2$ QDs was consistent with the emission wavelength of UV lamp, leading to close interaction of TiO$_2$ and UV light. TiO$_2$ as catalysts was extremely effective to degrade dye molecules through photooxidation under UV light, which provides a promising strategy to reduce the organic load of an actual textile wastewater.[51] It was proposed that both photocatalytic oxidative and reductive reactions occur simultaneously on the TiO$_2$ nanoparticles.[52] In the present study, UV light induced the conversion from silver nanoprisms to silver nanodecahedrons assisted by TiO$_2$, including dissolution of prism and formation of decahedron. Herein, a plausible mechanism of this conversion process is proposed. Charge carriers including hole and electron are generated on TiO$_2$ nanoparticle when the nanoparticle absorbs UV light corresponding to the band gap.[33, 52-55] Hydroxyl radicals (•OH) are formed on the surface of TiO$_2$ through reaction of holes in the valence band. In the stage of dissolution of silver nanoprisms, the citrate stabilizing silver nanoparticles were oxidized by the photogenerated holes and the hydroxyl radicals. The silver nanoprisms with less citrate were facile to be etched by UV light.[26, 27] Moreover, the photogenerated valence band holes and conduction band electrons could either recombine to release heat, which may promote the dissolution of silver nanoprisms.[56, 57] Meanwhile, the photo-generated electrons react with molecular oxygen and H$_2$O on the surface of the TiO$_2$ QDs and produce superoxide radical anions (O$_2$•$^-$). In the stage of formation of silver nanodecahedrons, the photogenerated electrons and superoxide radical anions may assist the reduction of the silver ions from dissolution of silver nanoprisms on special facets of decahedral silver seeds, which facilitates the formation of silver nanodecahedrons.

It has been reported that oxygen in solution displayed a pivotal effect in the shape conversion of silver nanoparticles. Oxygen was proved to etch the twinned silver particles to promote the fabrication of single crystal silver nanostructures in the polyol synthesis route of silver nanoparticles.[58-60] In addition, it was demonstrated that the oxygen in solution assisted the shape conversion from prism to disk under heating condition due to its etching role in the previous study.[57] In this research, the initial silver nanoprism solution was bubbling for 30 min using nitrogen gas to reduce the influence of dissolved oxygen on shape conversion. Compared with the original silver nanoprism solution, the shape conversion of silver nanoprisms after bubbling with nitrogen gas became much slower. There was a very small new LSPR at 400 nm assigned to silver nanodecahedron appearing in the extinction spectrum of the nitrogen gas bubbled silver nanoprism solution even after the solution was irradiated for 6 h by UV light (Fig. 7). The silver nanoprisms without removing
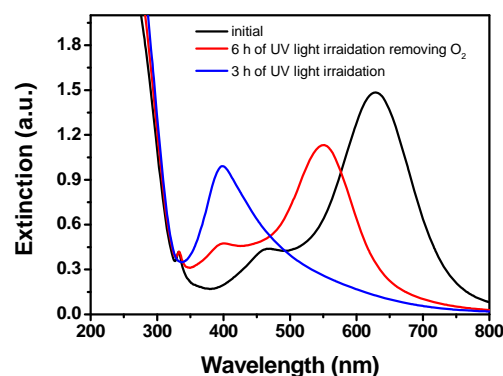
Fig. 7 Extinction spectra of (A) initial silver nanoprism solution, (B) silver nanoprism solution irradiated for 6 h by UV light after bubbling for 30 min using nitrogen gas, and (C) silver nanoprism solution after irradiation for 3 h by UV light without removing oxygen.

oxygen were completely converted to silver nanodecahedrons after only 3 h of UV light irradiation (Fig. 7). Obviously, in addition to the catalysis role of TiO$_2$ QDs, the oxygen in solution assisted the shape conversion of silver nanoparticles under UV light.

The shape reconversion from decahedron to prism was realized through photoinduction under sodium lamp. The wavelength of the irradiation light is important to control the final shape of silver nanoparticles in photoinduced reaction.[18, 61-65] An emission spectrum of the sodium lamp used for photoconversion of decahedron to prism is shown in Fig. S8, with a main emission band in the range of 560 - 620 nm.[27] . No peaks were seen in the UV region. All the emission peaks were located in the visible range. The morphology transformation of silver nanoparticles could be controlled by the wavelength of irradiation light.[61, 66] It can be found that the absorbance band of TiO$_2$ QDs was far from the emission of sodium lamp, implying that TiO$_2$ did not interact with sodium light directly. Sodium light can transform silver seeds into silver nanoprisms due to LSPR excitation from photoinduction.[24, 25, 27, 67] The presence of TiO$_2$ QDs in solution did not hinder the fabrication of silver nanoprisms from transformation of silver nanodecahedrons. Additionally, in the shape conversion of silver nanodecahedron to silver nanoprism under sodium lamp, citrate was necessary to transform the decahedrons to prisms through photo-oxidation process.[24, 25] It was suggested that LSPR excitation of silver nanoparticles under light irradiation induced the formation of "hot holes" on nanoparticles, causing the oxidization of adsorbed citrate. The electrons from photo-oxidation of citrate reduced selectively the silver ions from oxidative etching of silver by dissolved oxygen on particular planes of nanoparticles, leading to formation of silver nanoparticles based on plasmon dephasing on the nanoparticle surface.[24, 25] Therefore, enough citrate is essential to accomplish the shape conversion of decahedron to prism through photoinduction by sodium light.

Besides UV light, the simulated sunlight containing UV and visible light was employed to perform the shape conversion of silver nanoprisms. The spectrum of simulated sunlight is in the range of 300 ~ 800 nm (Fig. S9). The main emission band is located in 450 ~ 600 nm. The color of silver nanoprisms solution without TiO$_2$ QDs changed little after irradiation of simulated sunlight (Fig. S10). The silver nanoprism solutions with TiO$_2$ QDs changed
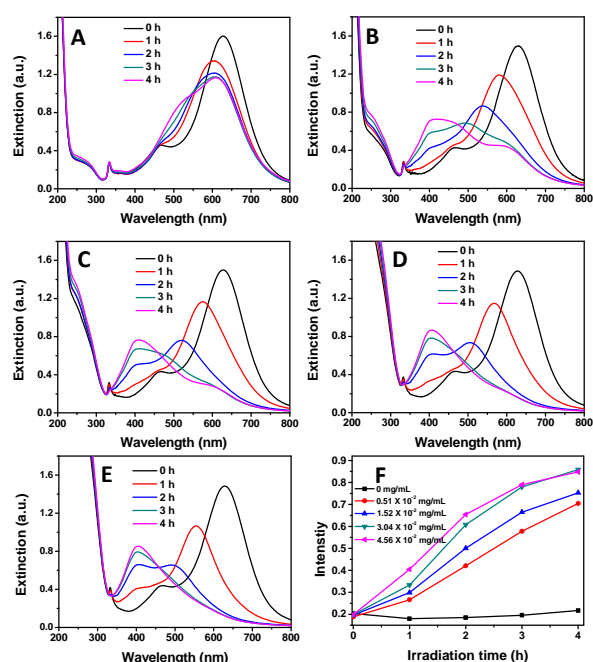
Fig. 8 Evolution of extinction spectra of silver nanoprism solutions during irradiation by simulated sunlight with 250 W corresponding to different concentrations of TiO_2: (A) 0 mg/mL, (B) 5.06×10^{-3} mg/mL, (C) 1.52×10^{-2} mg/mL, (D) 3.04×10^{-2} mg/mL, and (E) 4.55×10^{-2}. (F) Plots of intensity of extinction band at 400 nm as a function of irradiation time of simulated sunlight.

visibly in color during irradiation by simulated sunlight (Fig. S10), which indicates that simulated sunlight can induce the shape conversion of silver nanoprisms with assistance of TiO_2. Figure 8 shows the evolution of extinction spectra of silver nanoprism solutions with different concentrations of TiO_2 QDs. The extinction spectra of silver nanoparticle solution without TiO_2 changed in the bands at long wavelength. Whereas, the intensity of extinction band at 400 nm remained unchanged during simulated sunlight irradiation (Fig. 8A and F). The extinction spectra of silver nanoprism solution with TiO_2 changed dramatically during irradiation by simulated sunlight (Fig. 8B-E). The LSPR band at 400 nm assigned to silver nanodecahedrons increased with an increase in irradiation time. It is found that the change rate of the intensity at 400 nm increased as the concentration of TiO_2 QDs in solution increased (Fig. 8F). The wavelength of absorbance band of the TiO_2 nanoparticle solution was less than 350 nm. The wavelength of simulated sunlight interacting with TiO_2 is within a short region (300 ~ 350 nm). The emission intensity of simulated sunlight in this region is very low (Fig. S9). However, the simulated sunlight still can convert the silver nanoprisms to silver nanodecahedrons under assistance of TiO_2, suggesting the high photocatalytic capacity of TiO_2 QDs. The shape conversion of silver nanoparticles under simulated sunlight in the presence of TiO_2 would aid development in shape controlled synthesis of silver nanoparticles under natural sunlight.

4. Conclusions

The reversible shape conversion from silver nanoprism to nanodecahedron was realized with assistance of TiO_2 quantum dots (QDs) through photoinduction by different light sources. UV light transformed silver nanoprisms into nanodecahedrons in the presence of TiO_2. It was suggested that photocatalysis of TiO_2 promoted the dissociation of silver nanoprisms. Meanwhile, UV light induced the formation of silver nanodecahedrons through photoreduction of silver ions in solution. The nanodecahedrons with plenty of citrate were reconverted to silver nanoprisms by photoinduction of sodium light. Furthermore, the final silver nanoprisms could be reconverted to silver nanodecahedrons under irradiation of UV light. In the present study, the photocatalyst (TiO_2), stabilizer and reducing agent (citrate) and irradiation light (UV light and sodium light) were necessary to accomplish the series of shape conversion. Moreover, it was found that dissolving oxygen in solution assisted the conversion of prism to decahedron during irradiation of UV light. In addition, the shape transformation from prism to decahedron could be achieved under simulated sunlight, which provides a path to develop application of sunlight in controlled photoinduced synthesis of silver nanoparticles.

Notes and references

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† Electronic Supplementary Information (ESI) available: UV-vis absorbance spectrum, TEM image and X-ray diffraction pattern of TiO_2 QDs, and emission spectra of different light sources. See DOI: 10.1039/b000000x/

Acknowledgements

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