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# Facile synthesis of Ag/AgCl hybrid nanostructures with tunable morphologies and compositions as advanced visible light plasmonic photocatalysts

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This paper describes a simple and fast aqueous-phase route to the synthesis of Ag/AgCl hybrid nanostructures. These hybrid nanostructures were synthesized by reduction of AgCl nanoparticles with controlled shapes prepared by reacting  $Ag^*$  with  $Cl^-$  in the presence of polyethyleneimine (PEI) in an aqueous-phase. We could easily control the morphology and composition of the nanostructures by varying the experimental conditions, including the reaction temperature and the amount of reducing agent. The as-synthesized Ag/AgCl hybrid nanostructures exhibited enhanced photocatalytic activity and stability during the degradation of methyl orange under visible light irradiation because of their strong surface plasmon resonance (SPR) effect.

#### Introduction

Noble metal nanostructures including Au, Ag, and alloy-based Au or Ag have been investigated as enablers for a variety of applications involving light because of their plasmon resonance.<sup>1-4</sup> With tight control over the nanostructures in terms of size and morphology, the phenomenon of plasmon resonance gives rise to important applications such as colorimetric sensors,<sup>5</sup> conversion of water to clean hydrogen gas by photocatalytic water splitting,<sup>6</sup> conversion of carbon dioxide to gaseous hydrocarbons,<sup>7,8</sup> creation of self-cleaning surfaces<sup>9</sup> and oxidation of organic contaminants.<sup>10</sup> A photocatalyst, which can absorb light and accelerate a photoreaction, is the most important part of photocatalysis. Photocatalysts also ideally have high absorption of sunlight or visible light, high reactivity, are non-toxic, photostable, and chemically inert.<sup>11</sup> Typically, photocatalysts are solid semiconductors with the ability to create electron-hole pairs when irradiated by light.

Recently, TiO<sub>2</sub>-based photocatalysts have been intensively investigated since the discovery of its water electrolysis behavior.<sup>12</sup> TiO<sub>2</sub>-based photocatalysts have a large band gap, larger than 3.2 eV, which enables them to be chemically stable but restricts their response to the UV fraction of solar energy (about 4%) at the same time, leading to low efficiency in visible and near infrared regions.<sup>13,14</sup> Furthermore, the fast recombination rate of photogenerated electron-hole pairs also decreases the catalytic efficiency of TiO<sub>2</sub>-based

photocatalysts.<sup>15,16</sup> Over the past decades, considerable efforts have been devoted to engineering photocatalysts to enhance their visible light absorption coefficient, including ion doping,<sup>17,18</sup> noble metal deposition,<sup>19</sup> and anchoring organic dye molecules on the surface of photocatalysts.<sup>20</sup> Although there has been some progress enhancing visible light photocatalytic efficiency, the limited amount and the easy leaching of dopants may adversely affect the activity and chemical stability of photocatalysts.<sup>21-23</sup> In addition, dyesensitized photocatalysts often suffer from self-degradation of the dye molecules.<sup>24</sup> Besides TiO<sub>2</sub>-based photocatalysts, some research groups have fabricated novel visible light catalysts such as Bi<sub>2</sub>WO<sub>6</sub>,<sup>25</sup> CFe<sub>2</sub>O<sub>4</sub>/TaON,<sup>26</sup> and Cu<sub>2</sub>(OH)PO<sub>4</sub>.<sup>27</sup> However, these photocatalysts still have some drawbacks such as low activity and poor stability. Therefore, developing a new efficient visible light photocatalyst with good activity, stability, and recyclability still remains a significant challenge.

Plasmonic nanoparticles of noble metals with high absorption coefficients in the visible region can serve as an alternative class of sensitizers to enhance the absorption of semiconductors, which are mainly influenced by size and morphology.<sup>28,29</sup> Moreover, the resulting composite catalysts resist degradation during the photoreaction. Various research on noble metal/supporting material composite photocatalysts has been reported, for instance, Ag/TiO<sub>2</sub>/graphene,<sup>30</sup> Au/TiO<sub>2</sub>,<sup>31</sup> Ag/ZnO,<sup>32</sup> and Ag/AgCl.<sup>33-36</sup> Among them, Ag/AgCl promises high activity and enhanced stability as a metal/semiconductor composite photocatalyst because of their fast separation and transportation of photogenerated electron-hole pairs.<sup>37</sup> Multifarious approaches have been designed to fabricate Ag/AgCl composite material such as an ion-exchange reaction between  $Ag^+$  and  $Cl^-$  followed by UV or laser light reduction,<sup>36,38</sup> polyol reduction,<sup>37</sup> hydrothermal synthesis,<sup>39</sup> and thermal decomposition in ionic liquid.<sup>40</sup>

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However, most of these reported procedures require tedious reaction steps, long reaction times, high reaction temperatures, or have poor control of the size and morphology of the Ag/AgCl structures due to the high reaction speed between the silver and the chloride ions. In addition, controlling the composition of Ag and AgCl in the composite material is the most challenging aspect of obtaining high visible light absorbability of AgCl as well as catalytic activity in Ag nanomaterials. To our knowledge, the maximum level of Ag in the Ag/AgCl hybrid structures is limited to 80% in all previous reports.

Herein, we report a simple, economic, and fast aqueousphase route for the shape-controlled synthesis of AgCl nanoparticles and their transformation to Ag/AgCl hybrid nanostructures, which are efficient, stable visible light photocatalysts. These hybrid nanostructures are synthesized by reducing AgCl nanoparticles with controlled shapes prepared by reacting  $Ag^+$  with  $CI^-$  in the presence of PEI in an aqueous-phase. The synthesized Ag/AgCl hvbrid nanostructures were composite structures with 5-25 nm nanoparticles decorating 150-350 nm-sized particles or hollow structures with boxes and cages. We could easily control the morphology and composition of the nanostructures by varying the experimental conditions, including the reaction temperature and the amount of reducing agent. Interestingly, we were able to control the Ag level in the Ag/AgCl hybrid nanostructure at an Ag level up to 97.4% within 5 min of reaction time. The as-synthesized Ag/AgCl hvbrid nanostructures exhibited enhanced photocatalytic activity and stability during the degradation of methyl orange under visible light irradiation because of their strong surface plasmon resonance (SPR) effect.

#### **Experimental section**

#### Synthesis of AgCl nanoparticles

In a typical synthesis, PEI (40 mg, MW 750,000, 50 wt% solution in water, Aldrich) was dissolved in deionized water (10 mL) and heated to 30 °C under magnetic stirring, and 0.1 mL of 1 M aqueous AgNO<sub>3</sub> (Aldrich) solution was added to the reaction solution. Then, 1 M aqueous solution of NaCl (0.25 mL, Aldrich) was added into the reaction solution rapidly using a pipette. The resulting mixture was heated and stirred for 3 min, resulting in the formation of milky dispersions containing AgCl nanoparticles. The products were collected by centrifugation and washed with deionized (DI) water three times.

#### Synthesis of Ag/AgCl hybrid nanostructures

The as-synthesized AgCl nanoparticles were re-dispersed in 5 mL of DI water, and a 10 mM aqueous solution of NaBH<sub>4</sub> (0.1 mL to 2.0 mL) was then added under magnetic stirring at room temperature. The color of the resulting solution immediately changed from red to green, showing the formation of Ag/AgCl. After 2 min, the product was collected by centrifugation.

#### Characterization

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The morphology and composition of the sample were recorded by SEM (LEO SUPRA 55) and EDS (INCA, Oxford Company). TEM images were captured using a JEM-2100F microscope operated at 200 kV. The UV-vis spectra were recorded using a Jasco UV-vis spectrophotometer. FT-IR spectra were taken using a Jasco FT-IR-6100. The powder XRD patterns were obtained using a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. XPS measurements were conducted using a Thermo Scientific K-Alpha spectrometer with an Al K $\alpha$  X-ray source. TGA was performed using a TGA Q5000 IR thermal analyzer.

#### **Evaluation of photocatalytic activity**

Methyl orange (MO) was chosen as the target organic compound to probe the visible light driven photocatalytic performance of various prepared photocatalysts. 30.0 mg of the respective photocatalysts were dispersed in 50 mL of MO aqueous solution (20 mg/L). The mixture was stored in darkness while being stirred for 30 min to establish an adsorption-desorption equilibrium of MO molecules on the photocatalysts. The photocatalytic test was performed under visible light irradiation using a 200 W mercury xenon lamp (Raynics, Korea) with a UV cut-off filter (> 400 nm). Aliquots of the suspension (2.0 mL) were taken out from the reaction system at different reaction times, and centrifuged at 10,000 rpm for 5 min to remove the photocatalysts from the solution. Supernatants were transferred to a UV-vis cuvette for measuring their absorption spectra in the range of 300-800 nm. For recycling experiments, the photocatalysts were centrifuged, washed, and collected. For subsequent recycling tests, all the procedures were the same as the first cycle.

#### **Results and discussion**

The AgCl nanoparticles were synthesized via a precipitation reaction between AgNO3 and NaCl in the presence of polyethyleneimine (PEI) as a stabilizer in an aqueous-phase at different reaction temperatures. Fig. 1a-d show scanning electron microscopy (SEM) images of the AgCl nanoparticles synthesized at 30 °C, 50 °C, 70 °C, and 90 °C, indicating that these nanoparticles have semi-spherical, spherical, truncatedcubic, and cubic shapes, respectively. The colors of aqueous dispersions of the AgCl nanoparticles were milky (30 °C), dark pink (50 °C), amber (70 °C), and dark yellow (90 °C), respectively (Fig. S1<sup>+</sup>), and all the nanoparticles exhibited a strong absorption peak at 241 nm which corresponds with a direct bandgap of AgCl (5.15 eV) and a weak peak from an indirect bandgap (382 nm, 3.25 eV), as shown in Figure S2<sup>+,41</sup> Average sizes of the AgCl nanoparticles were 154.2 ± 26.3 nm for semi-spheres synthesized at 30 °C, 191.2 ± 28.4 nm for spheres synthesized at 50 °C, 204.7 ± 29.8 nm for truncated cubes synthesized at 70 °C, and 344.2 ± 44.4 nm for cubes synthesized at 90 °C, revealing that the size of the AgCl nanoparticles gradually increased with increasing reaction temperature (Figure S3<sup>†</sup>).<sup>42</sup> Powder X-ray XRD patterns of the AgCl nanoparticles show the presence of diffraction peaks at 27.9°, 32.3°, 46.3°, 54.9°, 57.5°, and 67.4°, which can be



**Fig. 1** a–d) SEM and HRSEM (inset) images of the AgCl nanoparticles prepared by reacting  $AgNO_3$  with NaCl in the presence of polyethyleneimine (PEI) at different reaction temperatures; a) 30 °C, b) 50 °C, c) 70 °C, and d) 90 °C. e–h) SEM images of Ag/AgCl hybrid nanostructures synthesized by reacting AgCl nanoparticles (Fig. 1a–d, respectively) with 2.0 mL of NaBH<sub>4</sub> (10 mM).

assigned to (111), (200), (220), (311), (222), and (400) planes of face-centered cubic (fcc) AgCl (Figure S4†, *Fm3m*, a = 5.5491Å, Joint Committee on Powder Diffraction Standards (JCPDS) file no. 31-1238), respectively.

Fourier transform infrared (FT-IR) transmission spectrum of the AgCl nanoparticles exhibited a distinct band at 1645 cm<sup>-1</sup>, which was assigned to bending modes of amine groups (-N-H). The absorption peaks at 1260 and 1022 cm<sup>-1</sup> were assigned to the stretching bands -C-H, and -C-N, respectively (Fig. S5a†). Thermal gravimetric analysis (TGA) results of the AgCl nanoparticles show around 21% weight loss at as high as 600 °C, with the weight remaining stable afterwards (Fig. S5b†). Both FT-IR and TGA analysis confirm the presence of PEI on the surface of the AgCl nanoparticles.



**Fig. 2** Schematic illustration of reaction pathways for the synthesis of Ag/AgCl hybrid nanostructures.

In a recent report on the synthesis of Ag nanoparticles using PEI as a stabilizer, it was demonstrated that non-bonding electrons of the amine group in PEI interacted with Ag<sup>+</sup> to form a PEI-Ag<sup>+</sup> complex in the aqueous phase, thus controlling the growth rate of the Ag nanoparticles (Fig. 2).<sup>4,43</sup> In the present research, we believe that PEI serves as a multi-functional stabilizer to modulate the reaction rate between Ag<sup>+</sup> and Cl<sup>-</sup> by formation of a PEI-Ag<sup>+</sup> complex and nano-sized AgCl particles by capping the surface of the particles. To validate the existence of coordination, FT-IR analysis of PEI without Ag<sup>+</sup> was performed (Fig. S5a<sup> $\dagger$ </sup>). In the absence of Ag<sup> $\dagger$ </sup> a weak band at 1652 cm<sup>-1</sup> was observed. When PEI was mixed with AgNO<sub>3</sub>, we found small shifting of the absorption bands of -N-H bending (from 1652 to 1645 cm<sup>-1</sup>) and -C-N stretching (from 1043 to 1022 cm<sup>-1</sup>). There observation were well matched with previous reports on the formation of amine-metal  $\operatorname{complexes.}^{44,45}$  When the synthesis was conducted in the absence of PEI, micrometer-sized agglomerated AgCl particles were formed, demonstrating that PEI played a pivotal role in the formation of AgCl nanoparticles (Fig. S6<sup>†</sup>).

The morphologies of the AgCl nanoparticles changed from semi-spheres to cubes when the reaction temperature was increased from 30 °C to 90 °C while keeping other experimental conditions unchanged (Fig. 1a). In order to obtain better understanding, we compared the intensity ratio of  $I_{(200)}/I_{(111)}$  in the XRD data of the AgCl nanoparticles. In the JCPDS file, the intensity ratio of  $I_{(200)}/I_{(111)}$  is about 2.0 (JCPDS file no. 31-1238). The peak intensity ratio of the AgCl semi-spheres synthesized at 30 °C was 1.95, while the AgCl nanocubes exhibited a ratio of around 35.6, supporting the

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SEM images (Fig. S4<sup>†</sup>). These SEM and XRD analyses suggest that the AgCl nanoparticles grow mainly along the <100> direction at higher temperatures because the {100} facets of AgCl possess minimum surface energy and Cl<sup>-</sup> ions in the {100} facets are saturated by Ag<sup>+</sup> ions.<sup>36</sup>

To fabricate the Ag/AgCl hybrid nanostructures, we reduce AgCl nanoparticles using NaBH<sub>4</sub> at room temperature (Fig. 2). Fig. 1e-h show the SEM images of Ag/AgCl hybrid nanostructures prepared by reacting 2.0 mL of NaBH<sub>4</sub> (10 mM) with AgCl nanoparticles, as shown in Fig. 1a-d. The SEM image shown in Fig. 1e shows the formation of hollow cages with sizes around 132.3 ± 18.2 nm. In Fig. 1f-h, we observed the formation of decorated hybrid structures exhibiting morphologies that include spherical (167.9 ± 23.8), truncated cube (185.6 ± 27.2), and cube (315.7 ± 41.6) with 10-25 nmsized small Ag nanoparticles, respectively. The XRD patterns of these Ag/AgCl hybrid nanostructures shows the presence of additional (111) and (200) planes of face-centered cubic (fcc) metallic Ag (Fm3m, a = 4.086 Å, JCPDS file no. 04-0783), indicating the formation of Ag and AgCl crystal structures (Fig. S7†).

The morphology and composition of the Ag/AgCl hybrid nanostructures could be easily controlled by varying the concentration of the reducing agent. SEM images in Fig. 3a-f show the morphology change of the Ag/AgCl hybrid nanostructures synthesized by reacting different volumes of 10 mM NaBH<sub>4</sub> solution with AgCl semi-spheres synthesized at 30 °C (The volumes of 10 mM NaBH<sub>4</sub> solution were 0.1 mL, 0.3

0.3 mL of NaBH<sub>4</sub> solutions reacted with the AgCl nanoparticles, we found that small Ag nanoparticles with sizes of 5-10 nm (Ag/AgCl-0.1) and 15-25 nm (Ag/AgCl-0.3) were attached on the surface of AgCl nanoparticles. They looked like dendrite structures (Fig. 3a and b). Upon further increasing the amount of reducing agent to 0.5 mL and 1.0 mL, a small portion of hollow sphere and hollow cage particles started to be observed while the major product still consisted of Ag nanoparticles decorating AgCl nanoparticles (Fig. 3c and d). Under the reaction conditions using 1.5 mL and 2.0 mL of NaBH<sub>4</sub> solution as a reducing agent, the SEM images show the formation of only nanostructures with hollow interior morphology (Fig. 3e and f). A transmission electron microscopy (TEM) image and energy dispersive X-ray (EDX) elemental mapping data of the Ag/AgCl-2.0 clearly show the formation of hollow cages at high NaBH<sub>4</sub> concentration (Fig. 3g-i).

The composition of the Ag/AgCl hybrid nanostructures was analyzed using energy dispersive X-ray spectroscopy (EDS).<sup>37</sup> The atomic ratio of Ag to AgCl increased from 0 (AgCl nanoparticles) to 36.61 (Ag/AgCl-2.0), indicating that around 97.34% of the AgCl was reduced to Ag (Table S1†). The optical absorption spectra taken from an aqueous suspension of the synthesized Ag/AgCl hybrid nanostructures show the presence of strong plasmon resonance peaks (SPR) around 415–420 nm (Fig. S8†). The absorption peak rises in intensity from Ag/AgCl-0.1 to 2.0, showing more absorption of visible light due to the enhanced Ag. Metallic Ag nanostructures could have a strong interaction with incident light because the conduction



**Fig. 3** a–f) SEM images of Ag/AgCl hybrid nanostructures prepared by reacting the AgCl semi-sphere shown in Fig. 1a with different volumes of NaBH<sub>4</sub> (10 mM); a) 0.1 mL (Ag/AgCl-0.1), b) 0.3 mL (Ag/AgCl-0.3), c) 0.5 mL (Ag/AgCl-0.5), d) 1.0 mL (Ag/AgCl-1.0), e) 1.5 mL (Ag/AgCl-1.5), and f) 2.0 mL (Ag/AgCl-2.0). g) TEM image, h and i) EDX elemental mapping analysis data of Ag/AgCl-2.0 shown in Fig. 3f. j) Powder XRD patterns of the Ag/AgCl hybrid nanostructures, as shown in Fig. 3a–f.

mL, 0.5 mL, 1.0 mL, 1.5 mL, and 2.0 mL, respectively, and these products are noted as Ag/AgCl-0.1 to 2.0). When 0.1 mL and

electrons on the metal surface undergo a collective oscillation upon excitation with incident light, known as surface plasmon

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resonance. Due to this strong SPR-effect, Ag nanoparticles can have upto 10-fold effective extinction cross section than their physical cross section.  $^{46}$ 

The XRD patterns of the Ag/AgCl hybrid nanostructures show the presence of (111) and (200) planes of face-centered cubic (fcc) metallic Ag (JCPDS file no. 04-0783), indicating the formation of Ag and AgCl crystal structures (Fig. 3j). Interestingly, the diffraction peaks of AgCl gradually decreased in intensity and the peak from the (111) plane of AgCl finally disappeared in the Ag/AgCl-2.0, while that of Ag at 38.1° (111) rose from Ag/AgCl-0.1 to 2.0. The atomic percentages of Ag and Cl in the nanostructures were also calculated through normalization of peak areas and values were, 50 and 50 % for AgCl, 82.36 and 17.64 % for Ag/AgCl-0.5, and 97.73 % and 2.27 % for Ag/AgCl-2.0, respectively, which were well matched with EDS analysis.



**Fig. 4** XPS spectra of a–b) the AgCl nanoparticles, as shown in Fig. 1b, c–d) Ag/AgCl-0.5, as shown in Fig. 2c, and e–f) Ag/AgCl-2.0, as shown in Fig. 3f.

These observations were further confirmed by X-ray photoelectron spectroscopy (XPS) investigations. As shown in Fig. 4a, two distinct peaks at 367.3 and 373.2 eV corresponding to the binding energies of the Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  core levels were observed in the AgCl nanoparticles prepared at 30 °C, indicating ionic Ag<sup>+</sup> was a major species in the product. The Cl 2p core level spectrum included a Cl  $2p_{3/2}$  peak at 197.6 and a Cl  $2p_{1/2}$  peak 199.2 eV, respectively, which can be assigned to Cl<sup>-</sup> (Fig. 4b). In the Ag 3d XPS core level spectrum of Ag/AgCl-0.5, two sets of 3d peaks were observed (Fig. 4c). One set consisted of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  peaks at 367.5 and 373.5 eV,

respectively, which corresponds to  $Ag^+$  in the AgCl. The other set included a Ag  $3d_{5/2}$  peak at 368.0 and a Ag  $3d_{3/2}$  peak at 374.2, which can be assigned to metallic Ag.<sup>47</sup> In addition, the intensity of XPS peaks of Cl<sup>-</sup> decreased compared with those of the AgCl nanoparticles, indicating a low portion of AgCl in the product (Fig. 4d). In the Ag/AgCl-2.0, the intensity peaks of Ag were much higher than those of the Ag<sup>+</sup> species, and the peaks for Cl<sup>-</sup> species also decreased to a minimum (Fig. 4e and f). The corresponding XPS spectra indicates that the atomic percentages of Ag and Cl on the surface of the samples were 54 and 46 % for AgCl, 85.02 and 14.97 % for Ag/AgCl-0.5, and 99.6 % and 0.4 % for Ag/AgCl-2.0, respectively.

The photocatalytic performance of the Ag/AgCl hybrid nanostructures was studied during the degradation of methyl orange (MO) under illumination by visible light (Fig. 5a). We investigated the kinetic process of photodegradation by monitoring the intensity of the absorption peak at 464 nm associated with MO as a function of time. Fig. S9† shows the photodegradation curves of MO when using Ag/AgCl-0.5 as a photocatalyst. After adding the photocatalyst, the absorption peak at 464 nm rapidly dropped in intensity as the photocatalytic reaction proceeded, revealing that MO molecules can be effectively decomposed under visible light illumination in the presence of Ag/AgCl hybrid nanostructures.



**Fig. 5** a) Schematic illustration of the proposed degradation mechanism of MO using Ag/AgCl plasmonic photocatalysts. b–c) Photocatalytic degradation of MO using the Ag/AgCl hybrid nanostructures. b) Normalized concentration of MO as a function of reaction time in both the linear and logarithmic scale. c) The normalized concentration of the MO for different photocatalysts on a linear scale. d) Photodegradation kinetics of MO for five consecutive cycles with the same batch of Ag/AgCl-0.5.

After adding the photocatalyst, the absorption peak at 464 nm rapidly dropped in intensity as the photocatalytic reaction proceeded, revealing that MO molecules can be effectively decomposed under visible light illumination in the presence of Ag/AgCl hybrid nanostructures. Organic dyes in aqueous solution often form aggregates of dimers or high polymers, which are absorbed in the short wavelength region, and

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sometimes the polymer or surfactants detach from the surface of the catalysts, which often affects the photocatalysis process.<sup>34</sup> We could not observe any absorption feature of the degradation products of MO molecules in the scanned spectral region during the degradation process, indicating good structural integrity of our PEI-stabilized Ag/AgCl hybrid nanostructures during the harsh photocatalytic environment. Fig. 5b plots the dependence of the concentration (C) of MO normalized against the concentration (C<sub>0</sub>) at the start of the reaction using Ag/AgCl-0.5 as photocatalysts, showing that the decomposition reaction of MO has first order kinetics:

$$dC/dt = -kC,$$
(1)

 $\ln(C/C_0) = -kt$ 

(2)

where k is the rate constant. The rate constant was estimated to be 0.1638  $\mathrm{min}^{-1}$  for MO degraded using Ag/AgCl-0.5. For comparison, we also carried out decomposition of MO using Ag/AgCl-0.1, 0.3, 1.0, and commercial TiO<sub>2</sub> (P-25) which is a reference photocatalyst under visible light irradiation (Fig. 5c). The rate constants were estimated to be 0.0108 min-1 for Ag/AgCl-0.1, 0.0324 min<sup>-1</sup> for Ag/AgCl-0.3, 0.0074 min<sup>-1</sup> for Ag/AgCl-1.0, and 0.0001 min<sup>-1</sup> for P-25 (Fig. S10<sup>†</sup>). Moreover, the decomposition rate of MO by Ag/AgCl-0.5 was faster than Ag/AgCl-0.1, 0.3, 1.0, and P-25 by factors of 15, 5, 22, and 1638, respectively. These results indicate that Ag/AgCl-0.5 exhibits the best performance. The excellent visible light driven photocatalytic performance of Ag/AgCl-0.5 hybrid nanostructures can be attributed to the positively synergistic effect between metallic Ag and semiconducting AgCl. Although Ag/AgCl-1.0 contains a large amount of metallic Ag (~ 92.58%) compared with Ag/AgCI-0.5, the lower level of semiconducting AgCl would limit MO degradation.<sup>48</sup>



**Fig. 6** a) SEM image and b) XRD patterns of the Ag/AgCl-0.5 photocatalyst after five successive photocatalytic reactions.

In addition to efficiency, stability and/or recyclability, photocatalysts are also important for applications because photocatalysts often lose their performance due to photocorrosion.<sup>35</sup> To test the stability of the Ag/AgCl-0.5 hybrid nanostructures, recycling photodegradation experiments for MO were carried out five times (Fig. 5d). The catalyst did not show a significant decrease in photocatalytic performance after repeated use. The SEM image and XRD pattern of Ag/AgCl-0.5 recycled five times are almost identical to the original samples (Fig. 6). These observations indicate that neither the morphology nor the phase composition is changed during recycling tests, and the Ag/AgCl hybrid nanostructures exhibit good stability against photo-corrosion.

We also investigated the photocatalytic performance of Ag/AgCl hybrid nanostructures using degradation of Rhodamine B (RhB). The photocatalytic conducting parameters were the same as that of MO, as shown in Fig. 5b. The rate constant was estimated to be 0.1894 min<sup>-1</sup> (Fig. 7), indicating that the Ag/AgCl hybrid nanostructures could be used as catalyst in various photocatalytic degradation reaction.



**Fig. 7** a) UV-vis absorption spectra for photocatalytic degradation of RhB molecules over Ag/AgCl-0.5 hybrid nanostructures under visible light irradiation. b) Normalized concentration of RhB as a function of reaction time in both the linear and logarithmic scale.

#### Conclusions

In summary, we presented a simple, economic, and fast aqueous-phase route to shape controlled synthesis of AgCl

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nanoparticles and their transformation to Ag/AgCl hybrid nanostructures that are efficient and stable visible light photocatalysts. The shapes, sizes, and morphology of AgCl nanocrystals can be easily controlled by varying the reaction temperature, and the Ag/AgCl hybrid nanostructures were easily synthesized by reducing the AgCl nanoparticles at room temperature during a 5 min reaction time. We could easily the morphology and composition of control the nanostructures by varying the experimental conditions, including the reaction temperature and the amount of reducing agent. The as-synthesized Ag/AgCl hybrid nanostructures exhibited enhanced photocatalytic activity and stability during the degradation of methyl orange under visible light irradiation. Furthermore, we expect that this control over the morphology and composition of the Ag/AgCl hybrid nanostructures makes it a promising material for environmental remediation because of the strong surface plasmon resonance (SPR) effect, which will allow clean energy production for applications such as solar cells, water disinfection, and hydrogen production.

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#### **Graphical Abstract**

Ag/AgCl plasmonic photocatalysts are synthesized by a simple and rapid method in an aqueous-phase. We could easily control the morphology and composition of the nanostructures by varying the experimental conditions. The Ag/AgCl hybrid nanostructures exhibited enhanced photocatalytic activity and stability toward the degradation of methyl orange under the visible light irradiation because of their strong surface plasmon resonance (SPR) effect.



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