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# Controllable synthesis of coloured Ag<sup>0</sup>/AgCl with spectral analysis for photocatalysis†

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Broad spectrum absorption of semiconductor photocatalysts is an essential requirement to achieve the best values of solar energy utilization. Here, through precise surface state adjustment, coaxial tri-cubic Ag<sup>0</sup>/AgCl materials with distinct apparent colours (blue and fuchsia) were successfully fabricated. The reasons for the different colour generation of the Ag<sup>0</sup>/AgCl materials were investigated by performing corresponding spectrum analysis. It was revealed that Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia crystals could efficiently boost the photon energy harvesting, spanning from the UV to near-infrared spectral region (250–800 nm), and achieved 2.6 and 5.4 times the wastewater degradation efficiency of AgCl-white. Simultaneously, these two fresh coloured candidates were demonstrated to have preferable photocatalytic CO<sub>2</sub> photoreduction capability, with yields of ~3.6 (Ag<sup>0</sup>/AgCl-fuchsia) and 2.6 (Ag<sup>0</sup>/AgCl-blue) times that of AgCl-white. It is expected that this work will provide a beneficial perspective for understanding the solar absorption feature at both the major structure modulation and particular surface state regulation level.

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## Introduction

Sunlight-driven semiconductor photocatalysis has long been considered as a “green strategy” in environmental remediation as well as energy conversion, including organic dye decomposition, inorganic ion degradation, reduction of water into renewable hydrogen, and CO<sub>2</sub> reduction.<sup>1–5</sup> In both the environmental and energy fields, the successful application of photocatalysts mainly relies on their light-response range, charge-carrier separation, and energy band location for redox reactions.<sup>6–10</sup> In particular, it should be noticed that the power source of photocatalysis comes from solar irradiation, with visible light taking up 50%. Therefore, it is a key challenge to acquire ultrahigh photon energy capture properties of photocatalysts, especially in the visible light region.<sup>11,12</sup>

High-photon reactive photocatalysts under visible light should absorb the main range of the solar spectrum, even including the poor illumination of interior lighting. Generally, two main approaches have been applied as handy solutions to extend or strengthen the light capturing region of wide bandgap semiconductors, including element-doping and composition

with a narrow bandgap semiconductor.<sup>13–16</sup> Unfortunately, few methods have been developed to broaden the spectral absorption range of a single semiconductor alone without the introduction of extra substances. In previous studies, black-coloured TiO<sub>2</sub> displayed an extended photoresponse from the UV to visible light region, and achieved high light absorption to gain promoted photocatalysis.<sup>17,18</sup> These types of black-coloured TiO<sub>2</sub> materials were prepared from self-modification, such as high-pressure reduction by hydrogen and self-doping with Ti<sup>3+</sup> bulk species, all of which led to an extended light absorption range.<sup>17,19</sup> It is well known that colourful substances always exhibit more intensive solar absorption than white ones. Thus, surface-colour engineering should become a crucial strategy for optimizing the solar light harvesting capacity of photocatalysts.

In the meantime, a distinct coloured silver chloride with promoted light absorption was discovered in our lab during a photocatalytic investigation.<sup>20,21</sup> However, such colour appearance did not receive enough attention due to the unexplained origin of its production. Herein, through a precise surface state control strategy we have succeeded in the synthesis of two gorgeously coloured Ag<sup>0</sup>/AgCl nanoparticles (fuchsia and blue) and investigate their improved photocatalytic performance both in methyl orange and phenol degradation. Compared with the intrinsic AgCl-white crystal, the coloured Ag<sup>0</sup>/AgCl nanoparticles exhibit a narrowed bandgap and this enables higher photon energy absorption. When irradiated by visible light, remarkable improvements have been achieved in the light-excited photocurrent conversion: Ag<sup>0</sup>/AgCl-fuchsia > Ag<sup>0</sup>/AgCl-blue > AgCl-normal. In view of their photocatalytic

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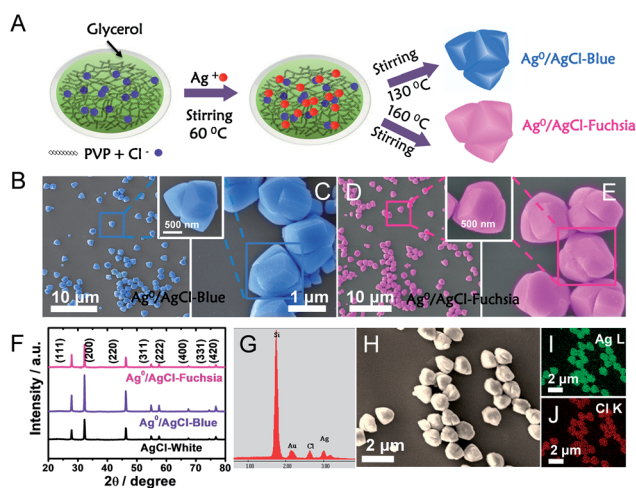
performance,  $\text{Ag}^0/\text{AgCl}$ -fuchsia and  $\text{Ag}^0/\text{AgCl}$ -blue presented considerable activity improvements both in water decontamination and  $\text{CO}_2$  reduction. This work represents a more comprehensive investigation and provides details on how to achieve improvements towards the internal and surface modulation of crystal photocatalysts.

## Results and discussion

A detailed description of the synthesis of the two-colour  $\text{Ag}^0/\text{AgCl}$  composites has been provided in the preparation part (ESI<sup>†</sup>). In a typical experiment in Fig. 1A, polyvinylpyrrolidone (PVP) as a capping agent was added to glycerol solution, and this combination would retard the reaction rate of  $\text{Cl}^-$  and  $\text{Ag}^+$ . Thus, uniform and regular coaxial tri-cube nanostructures of  $\text{AgCl}$  could be achieved at  $130^\circ\text{C}$  and  $160^\circ\text{C}$ , which appeared light blue and fuchsia coloured, respectively. Actually, after comparative analysis in the latter context, the apparent light blue and fuchsia colours were generated from the trace amount of metallic  $\text{Ag}^0$  on the surface of  $\text{AgCl}$ . In the preparation process, PVP and glycerol both play vital roles in realizing the  $\text{AgCl}$  surface colour. It is well known that PVP is a homopolymer with imide groups linking each individual unit, in which the N and O atoms have been proved to provide a strong affinity for silver ions on the crystal surface.<sup>22,23</sup> In addition, both PVP and glycerol display reducibility, especially at high temperature.<sup>20</sup> Equipped with these principles and conditions, temperature changes would control the reduction degree of  $\text{Ag}^+$  to  $\text{Ag}^0$  located on the crystal surface in the presence of PVP and glycol,

the plasma effect of which could achieve a saturated colour. Furthermore, typical SEM images of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia with various resolutions are provided in Fig. 1B–E. It can be observed that the  $\text{Ag}^0/\text{AgCl}$ -coloured crystals display a similar uniform coaxial tri-cubic morphology whether synthesized at  $130^\circ\text{C}$  (Fig. 1B and C) or  $160^\circ\text{C}$  (Fig. 1D and E), which dismissed the possibility of the crystal colour appearance being attributed to the morphology. At the same time, the crystal diameters of the  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia crystals were calculated to be about  $1.36\ \mu\text{m}$  (inset of  $\text{Ag}^0/\text{AgCl}$ -blue) and  $1.40\ \mu\text{m}$  (inset of  $\text{Ag}^0/\text{AgCl}$ -fuchsia), indicating that the contribution of diffraction to the colour origin was negligible. X-ray diffraction (XRD) analysis has been used to determine the crystallographic structure of the as-prepared  $\text{Ag}^0/\text{AgCl}$ -fuchsia,  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{AgCl}$ -white materials in Fig. 1F. The XRD patterns of the three sample structures displayed similar and distinct peaks ( $2\theta$ ) at about  $27.9^\circ$ ,  $32.4^\circ$ ,  $46.3^\circ$ ,  $54.8^\circ$ ,  $57.7^\circ$ ,  $67.6^\circ$ ,  $74.5^\circ$  and  $76.8^\circ$  corresponding to the (111), (200), (220), (311), (222), (400), (331) and (420) crystal phases, which could be assigned to diffractions of fresh crystalline  $\text{AgCl}$  (JCPDS file: 31-1238).<sup>24,25</sup> However, no noticeable peaks of  $\text{Ag}^0$  nanoparticles could be detected from the XRD spectra of the two coloured  $\text{Ag}^0/\text{AgCl}$  materials due to the too small amount and tiny crystal size of the  $\text{Ag}$  crystals generated in the synthesis process. In addition, no other organic form or impurity characteristic peaks were found in the three crystal structures, which implied that the obtained products were clearly extracted. The energy-dispersive X-ray analysis (EDAX) spectra (Fig. 1G) and the corresponding element mapping (Fig. 1I and J) of  $\text{Ag}^0/\text{AgCl}$ -fuchsia demonstrated that  $\text{Ag}$  and  $\text{Cl}$  were the main elements constituting the resulting production. In Fig. 1G, the Si element came from the Si wafer substrate used to load the  $\text{AgCl}$  sample. Fig. 1H is the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image as a template to perform mapping scanning. In order to prove whether there is generation of  $\text{Ag}^0$ , we determined the element content of  $\text{Ag}$  and  $\text{Cl}$  in  $\text{Ag}^0/\text{AgCl}$ -fuchsia through energy-dispersive X-ray analysis spectra (EDAX) ZAF quantification in Table S3.<sup>†</sup> From the molecular structure of  $\text{AgCl}$ , we can figure out that the atomic ratio of  $\text{Ag}$  and  $\text{Cl}$  should be 1 : 1. However, as shown in the results of EDAX ZAF quantification, the atomic ratio of  $\text{Ag}$  (29.92%) is higher than that of  $\text{Cl}$  (28.32%), indicating that a small portion of the  $\text{Ag}$  element has been reduced into metallic  $\text{Ag}^0$ . This can be taken as an effective way to confirm the existence of  $\text{Ag}^0$ .

X-ray photoelectron spectroscopy (XPS) analysis was performed as another strategy to investigate the chemical states and composition of the as-prepared  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia. The complete survey XPS spectra of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia (Fig. 2A) confirmed that their two main ingredients are  $\text{Ag}$  and  $\text{Cl}$ , in good agreement with the element mapping distribution in Fig. 1I ( $\text{Ag}$ ) and Fig. 1J ( $\text{Cl}$ ).<sup>26</sup> Extra elements of O and C might be attributed to the adhesion of oxygen molecules and trace residual organic molecules on the surface of the coloured  $\text{AgCl}$  samples. To investigate the element status of  $\text{Ag}^+$  and the generation of metallic  $\text{Ag}^0$  on the crystal surface in detail, the  $\text{Ag}$  3d spectra were analysed by XPS



**Fig. 1** (A) Schematic illustration of the synthesis of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia in a solution of PVP and glycerol. (B and C) SEM images of the as-prepared  $\text{Ag}^0/\text{AgCl}$ -blue photocatalytic crystals with two resolutions:  $10\ \mu\text{m}$  (B) and  $1\ \mu\text{m}$  (C). (D and E) SEM images of the as-prepared  $\text{Ag}^0/\text{AgCl}$ -fuchsia photocatalytic crystals with two resolutions:  $10\ \mu\text{m}$  (D) and  $1\ \mu\text{m}$  (E). (F) XRD patterns of the  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia crystals in comparison with the  $\text{AgCl}$ -white material. (G) The EDAX result of  $\text{Ag}^0/\text{AgCl}$ -fuchsia. (H–J) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (H) and corresponding electron mapping images for the  $\text{Ag}$  (I) and  $\text{Cl}$  (J) distribution in  $\text{Ag}^0/\text{AgCl}$ -fuchsia crystals.



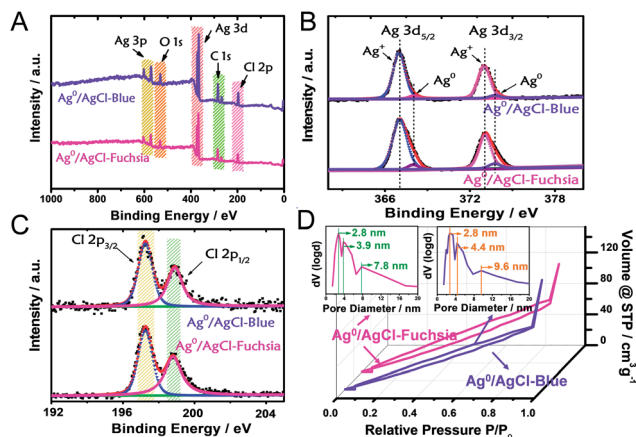


Fig. 2 (A) The complete survey XPS spectra of the  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia crystals. (B and C) XPS characterizations of Ag (B) and Cl (C) of the  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia materials. (D) Nitrogen adsorption–desorption isotherms and the corresponding pore diameter distribution curves of the  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia materials.

as the absolute surface element state technology. In Fig. 2B, two peaks in the Ag 3d spectrum at 367.1 eV and 373.3 eV on  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia were observed, which could be attributed to  $\text{Ag } 3d_{5/2}$  and  $\text{Ag } 3d_{3/2}$ , respectively.<sup>27</sup> Furthermore, the two peaks of  $\text{Ag } 3d_{5/2}$  and  $\text{Ag } 3d_{3/2}$  could be deconvoluted into another four peaks at 367.1 eV, 368.1 eV, 373.1 eV and 373.9 eV, of which the peaks at 368.1 eV and 373.9 eV were ascribed to metallic  $\text{Ag}^0$ , whereas the peaks at 367.1 eV and 373.1 eV were attributed to  $\text{Ag}^+$ .<sup>27–29</sup> Little position discrepancy of the  $\text{Ag } 3d_{5/2}$  and  $\text{Ag } 3d_{3/2}$  peaks of  $\text{Ag}^+$  on  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia could be observed from Fig. 2B, which indirectly confirmed that the  $\text{Ag}^+$  states were not the colour-inducing factor of the  $\text{AgCl}$ -coloured composition. The relative composition was calculated according to the peak area integral of  $\text{Ag}^0$  and  $\text{Ag}^+$  in the XPS spectra, as shown in Table S2.† It can be observed that the content of  $\text{Ag}^0$  was 3.7% and 5.9% in  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia, which again confirms the existence of  $\text{Ag}^0$  and the different amount of  $\text{Ag}^0$  in the two coloured  $\text{Ag}^0/\text{AgCl}$  products. This remarkable distinction of metallic  $\text{Ag}^0$  capacity was in line with the experimental design envisioned and could be accounted as the key cause that brought about the two-coloured  $\text{AgCl}$  compositions. For the Cl element on the surface of the  $\text{AgCl}$  crystals, two peaks at 197.3 eV and 198.9 eV attributed to Cl  $2p_{3/2}$  and  $2p_{1/2}$  were revealed in the  $\text{Ag}^0/\text{AgCl}$ -fuchsia and  $\text{Ag}^0/\text{AgCl}$ -blue samples, respectively.<sup>30,31</sup> The approximate peak positions of Cl  $2p_{3/2}$  and  $2p_{1/2}$  for the  $\text{Ag}^0/\text{AgCl}$ -fuchsia and  $\text{Ag}^0/\text{AgCl}$ -blue samples equally confirmed that the  $\text{Cl}^-$  of  $\text{AgCl}$  did not participate in the colour conversion of  $\text{AgCl}$ . Through the XPS data dissection of the  $\text{Ag}^0/\text{AgCl}$ -fuchsia and  $\text{Ag}^0/\text{AgCl}$ -blue samples, an argument that both the  $\text{Ag}^+$  and  $\text{Cl}^-$  states in  $\text{AgCl}$  have little relationship with the colour change of  $\text{AgCl}$  could be drawn. Meanwhile, the metallic  $\text{Ag}^0$  nanoparticles generated on the surface of  $\text{AgCl}$  have latent energy to change the colour appearance of  $\text{AgCl}$ . The corresponding XPS spectra of Ag 3d and Cl 2p for  $\text{AgCl}$ -white are

shown in Fig. S1.† As shown in Fig. 2D,  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia revealed a similar shape of the  $\text{N}_2$  sorption isotherm, again conforming their analogous physical features. The broad hysteresis loops across the  $\text{N}_2$  sorption isotherm of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia might be attributed to the stacking holes among the particles and the narrow cracks spread on each crystal particle, as shown in Fig. S2.† The Brunauer–Emmett–Teller (BET) specific surface areas of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia investigated through  $\text{N}_2$  absorption/desorption measurement were  $135.5 \text{ m}^2 \text{ g}^{-1}$  and  $131.3 \text{ m}^2 \text{ g}^{-1}$ , respectively. The little difference between the surface areas precluded the effect of area on the colour changes. The pore size distribution (inset) of  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia demonstrated a number of pore sizes of 2.8 nm and 9.6 nm, and 2.8 nm, 3.9 nm and 7.8 nm, respectively, attributed to the cracks on the surface of the  $\text{AgCl}$  crystals.

It is well known that the light absorption capacity of a photocatalyst is directly proportional to its intrinsic colour and the colour thickness, which is the reason why many researchers are seeking multi-colourful photocatalysts.<sup>15,20,32</sup> As shown in Fig. 3A, the pre-synthesized  $\text{AgCl}$  exhibited recognizable fuchsia, blue and white colours in both its dispersed and desiccated forms.

To explore the light-absorption divergence induced by the different colours, the UV-visible diffuse reflectance spectra of pristine  $\text{AgCl}$ -white,  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia were investigated, as shown in Fig. 3B. The light range before 410 nm could be attributed to the intrinsic absorption of  $\text{AgCl}$ ,<sup>30</sup> from which the respective bandgaps of  $\text{Ag}^0/\text{AgCl}$ -fuchsia,  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{AgCl}$ -white could be deduced. With the deepening of the colour, enhanced light-absorption properties were produced in the order  $\text{Ag}^0/\text{AgCl}$ -fuchsia >  $\text{Ag}^0/\text{AgCl}$ -blue >  $\text{AgCl}$ -white. In the visible spectra,  $\text{Ag}^0/\text{AgCl}$ -fuchsia exhibited the most intensive absorption throughout the entire visible light range from 410–800 nm, attributed to the thick colour of fuchsia. Moreover, a remarkable peak at around 540 nm (Fig. 3C) was observed in the absorption curve resulting from metallic  $\text{Ag}^0$  generation.<sup>30,33</sup> The blue coloured  $\text{AgCl}$  showed increased absorption compared to  $\text{AgCl}$ -white (Fig. 3B) and a metallic  $\text{Ag}^0$  absorption peak at 574 nm (Fig. 3C). This is an analysis of light absorption from a colour perspective. Actually, the colour appearance could also be understood through their light-absorption properties. Based on the relation between matter's colour and the colour absorbed in Table S1,† the reasons for the different colour generation of  $\text{AgCl}$  have been investigated. As shown in Table S1,† when the light absorption wavelength ranges from 500–560 nm or 580–600 nm, the matter exhibits the colour of fuchsia or blue, which is consistent with the coloured state of  $\text{AgCl}$  in Fig. 3C. Meanwhile, the appearance of the absorption peak in Fig. 3C was attributed to the emergence of metallic  $\text{Ag}^0$ . As such, we can conclude that the surface generation of metallic  $\text{Ag}^0$  led to the different colour of  $\text{AgCl}$ . Fig. 3D presents the absorption intensity of  $\text{Ag}^0/\text{AgCl}$ -fuchsia,  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{AgCl}$ -white, demonstrating that metallic  $\text{Ag}^0$  generated at higher temperature possessed a stronger absorption intensity. The Kubelka–Munk function plots (Fig. 3E) are transformed from the UV-vis diffuse



reflectance spectra (Fig. 3B), exhibiting different bandgap values of the coloured AgCl. AgCl-white, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia displayed decreasing bandgap values of 2.8 eV, 2.7 eV and 2.4 eV, respectively. According to the literature,<sup>33,34</sup> pristine AgCl has a large bandgap, with a direct bandgap of 5.15 eV and an indirect bandgap of 3.25 eV.<sup>33</sup> However, the AgCl materials synthesized with white, blue and fuchsia colours all possessed a lower bandgap than pristine AgCl. This result may be attributed to metallic Ag<sup>0</sup>, whose generation was inevitable during the AgCl synthesis. The metallic Ag<sup>0</sup> species will strengthen the light absorption of AgCl, which was reflected in the bandgap value of AgCl. On the other hand, the light absorption increases and bandgap narrowing could be observed in the photocurrent conversion (Fig. 3F). TiO<sub>2</sub> anatase is a common semiconductor with a bandgap of 3.2 eV, which has negative light absorption in visible light range.<sup>35–37</sup> Consequently, faint photocurrent was observed on TiO<sub>2</sub>. Due to the existence of metallic Ag<sup>0</sup> species, the light absorption range of AgCl-white, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia moved to the visible light region. According to the light-absorption capacity in the visible light range, Ag<sup>0</sup>/AgCl-fuchsia exhibited the strongest photocurrent, Ag<sup>0</sup>/AgCl-blue followed and AgCl-white was the weakest.

The photocatalytic oxidation performance of Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia in visible light ( $\lambda > 420$  nm, light power

density = 28 mW cm<sup>-2</sup>) was evaluated through the degradation of methyl orange (MO) and the dynamic curves are shown in Fig. 4A. Prior to the photocatalytic degradation process under irradiation, the reaction systems were deposited in dark conditions with continuous stirring for 30 min to achieve an absorption equilibrium state. Due to their similar morphology and dimensions, identical absorption capacities (5%) of Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia were acquired, which can be observed in Fig. 4A. After that, the real-time concentration variation of MO ( $C/C_0$ ,  $C_0 = 10$  mg L<sup>-1</sup>) was investigated *via* the normalized absorption value ( $A/A_0$ ,  $\lambda = 463$  nm) during the photodegradation process at specified time intervals. Through the comparison of the three dynamic degradation curves in Fig. 4A, the photocatalytic capabilities increased in the expected order (AgCl-white < Ag<sup>0</sup>/AgCl-blue < Ag<sup>0</sup>/AgCl-Fuchsia). The increasing order of wastewater degradation performance strongly indicated the important role of colour characteristics in photocatalysis. In order to further monitor the photocatalytic kinetics, apparent reaction rate constants ( $k_{app}$ ) were calculated by means of the transformation of the dynamic degradation curves. The logarithm of the real-time concentration variation of MO ( $\ln(C_t/C_0)$ , corresponding to  $\ln(A_t/A_0)$ , where  $A$  represents the absorbance) exhibited a linear relationship with the photodegradation time, the kinetic study of which followed pseudo-first-order behaviour. The equation could be expressed as follows:

$$\ln(C_0/C_t) = k_{app}t \quad (1)$$

According to the kinetic formula,  $k_{app}$  could be found from the slope of the linear correlation.<sup>38,39</sup> As shown in Fig. S3† and 4B and C, the linear fittings have been captured in light of the corresponding photodegradation curves of AgCl-white, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia, respectively. Furthermore, the  $k_{app}$  values were calculated to be 0.07 min<sup>-1</sup> for AgCl-white (Fig. S3†), 0.18 min<sup>-1</sup> for Ag<sup>0</sup>/AgCl-blue (Fig. 4B) and 0.38 min<sup>-1</sup> for Ag<sup>0</sup>/AgCl-fuchsia (Fig. 4C), which confirmed that the photocatalytic oxidation function was ranked as Ag<sup>0</sup>/AgCl-fuchsia > Ag<sup>0</sup>/AgCl-blue > AgCl-white. Thus, the photocatalytic oxidation abilities of Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia are about 2.6 and 5.4 times higher than that of AgCl-white according to the  $k_{app}$  comparative calculation. The corresponding UV-visible spectra for MO degradation of Ag<sup>0</sup>/AgCl-fuchsia and Ag<sup>0</sup>/AgCl-blue under visible light are provided in Fig. S4.† Significantly, the recyclability and stability of the photocatalysts were considered as another inspection standard, and thus eight successive photodegradation assessments of Ag<sup>0</sup>/AgCl-blue (Fig. 4D) and Ag<sup>0</sup>/AgCl-fuchsia (Fig. 4E) were performed under AM1.5. These outcomes provided favourable evidence to certify the desirable cycling characteristics of both the Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia photocatalyst samples. Besides their brilliant photocatalytic oxidation properties, both Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia have been proven to exhibit promising reducibility for converting CO<sub>2</sub> into liquid fuels under visible light irradiation (>420 nm) and the results are provided in Fig. 4F. As illustrated in Fig. 4F, liquid hydrocarbon fuels of 1.0

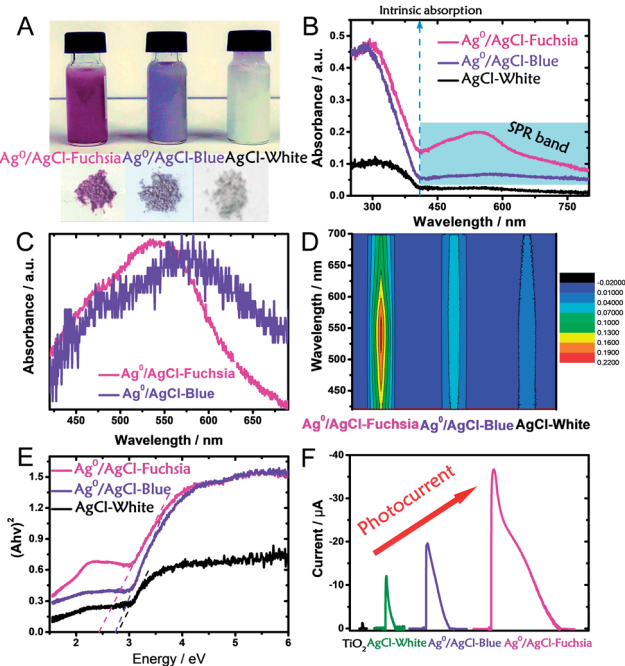


Fig. 3 (A) Digital photographs of dispersed and desiccated Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl. (B) UV-visible diffuse reflectance spectra of Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl. (C) The extracted absorption peak positions of Ag<sup>0</sup>/Ag-fuchsia and Ag<sup>0</sup>/AgCl-blue. (D) The light absorption intensity of Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl-white in the range of 400–700 nm, due to the generation of metallic Ag<sup>0</sup> species. (E) The transformed Kubelka–Munk function plot (*versus* the light energy) of Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl-white. (F) The photocurrent responses of TiO<sub>2</sub>, AgCl-white, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia under visible light.



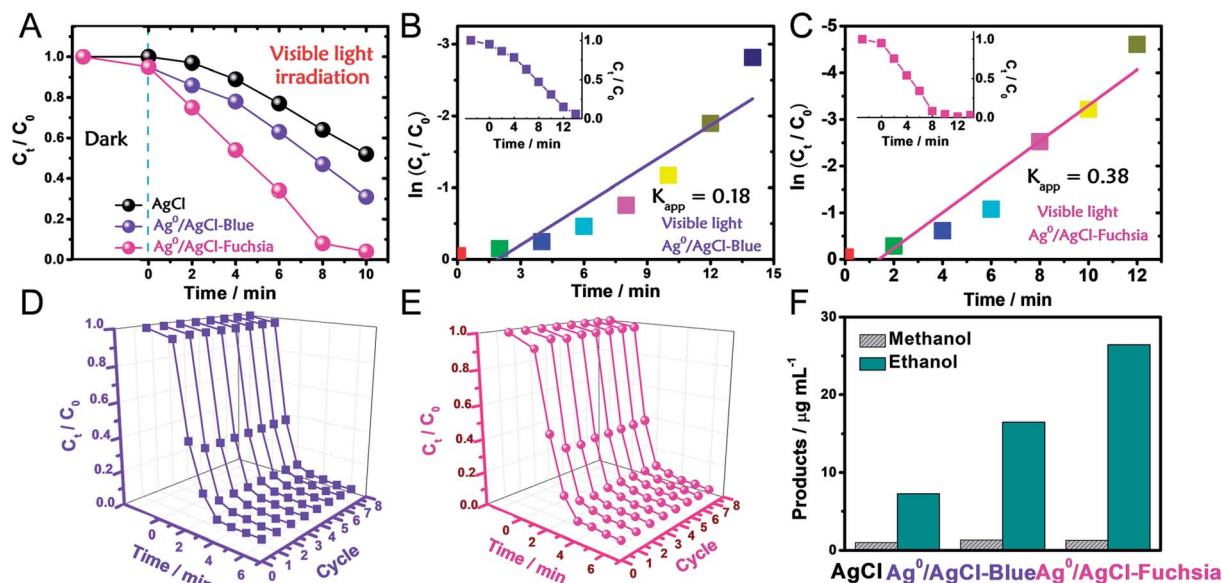


Fig. 4 (A) Photocatalytic evaluation of AgCl, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia for MO degradation under visible light (>420 nm). (B and C) The apparent reaction rate constant ( $k_{app}$ ) of Ag<sup>0</sup>/AgCl-blue (B) and Ag<sup>0</sup>/AgCl-fuchsia (C) under visible light. (D and E) Eight successive photodegradation curves of Ag<sup>0</sup>/AgCl-blue (D) and Ag<sup>0</sup>/AgCl-fuchsia (E) for MO degradation under AM 1.5. (F) The product yields of methanol and ethanol for the AgCl, Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia photocatalysts under visible light.

$\mu\text{g mL}^{-1}$  methanol and  $7.26 \mu\text{g mL}^{-1}$  ethanol for AgCl-white,  $1.34 \mu\text{g mL}^{-1}$  methanol and  $16.48 \mu\text{g mL}^{-1}$  ethanol for Ag<sup>0</sup>/AgCl-blue, and  $1.3 \mu\text{g mL}^{-1}$  methanol and  $26.44 \mu\text{g mL}^{-1}$  ethanol for Ag<sup>0</sup>/AgCl-fuchsia were yielded by CO<sub>2</sub> reduction. This represents a second line of evidence proving that the photocatalytic function was ranked as Ag<sup>0</sup>/AgCl-fuchsia > Ag<sup>0</sup>/AgCl-blue > AgCl-white. The gas chromatography (GC) results of CH<sub>3</sub>OH and CH<sub>3</sub>CH<sub>2</sub>OH generated in CO<sub>2</sub> reduction by Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl-white are provided in Fig. S7 and Table S4.† According to the above experimental results, it was confirmed that the MO molecules could be essentially degraded and CO<sub>2</sub> could be reduced over the Ag<sup>0</sup>/AgCl-blue and Ag<sup>0</sup>/AgCl-fuchsia samples, respectively. Therefore, it was necessary to speculate and analyse the possible photocatalytic mechanism for the purpose of explaining the enhanced photocatalytic activity (Fig. 5). As shown in Fig. 3B, the blue and fuchsia coloured appearance rendered the AgCl with high light capturing capacity for the photocatalytic reaction. The metallic Ag<sup>0</sup> species inducing the colour formation, plus those generated under photocatalytic light irradiation, further enhanced the utilization efficiency of light energy.<sup>33</sup> It is well known that a space charge region with an electric field direction from AgCl to Ag<sup>0</sup> can be formed when a metal is attached to an n-type semiconductor.<sup>40–42</sup> This internal electric field adjoining the surface of the AgCl semiconductor crystals would impede the electron migration from the semiconductor to the metal Ag<sup>0</sup> nanoparticles, which was able to inhibit the growth of Ag<sup>0</sup> nanoparticles. However, as they are plasmon nanoparticles, a large number of electrons could be stimulated over the Ag<sup>0</sup> nanoparticles due to the plasmon resonance effect under illumination and transferred to the conduction band (CB) of AgCl, which would promote the photocatalytic

activity.<sup>26,30</sup> In addition, the exterior colours of the AgCl materials were capable of strengthening the absorption capacity, which could further accelerate the photodegradation process. The hypothesised origin of the colour appearance was deduced to be the existence and state density changes of plasmonic Ag<sup>0</sup> nanoparticles by modulation of their optical properties.

To avoid the sensitization of the dye, we took phenol as a colourless reactant for photocatalytic degradation.<sup>43</sup> As shown in Fig. S5A,† the dynamic degradation curves of phenol show that the photocatalytic oxidation capacities of Ag<sup>0</sup>/AgCl-fuchsia and Ag<sup>0</sup>/AgCl-blue are much better than that of AgCl-white, which is consistent with their performances in MO degradation. Then, through pseudo-first-order linear fitting between  $\ln(C_t/C_0)$  and  $t$ , the apparent reaction rate constants ( $k_{app}$ ) of Ag<sup>0</sup>/AgCl-fuchsia, Ag<sup>0</sup>/AgCl-blue and AgCl-white were calculated to be  $0.025 \text{ min}^{-1}$  (Fig. S5B†),  $0.018 \text{ min}^{-1}$  (Fig. S5C†) and  $0.015 \text{ min}^{-1}$  (Fig. S5D†). This is another parameter that proves the better photocatalytic performance of the coloured samples than normal AgCl-white. Fig. S6† shows the changes in the ultraviolet absorption spectrum of phenol during the photocatalytic degradation process. The phenol has two absorption peaks at 270 nm and 210 nm, which represent the electron transitions from  $\pi \rightarrow \pi^*$  of the benzene structure and  $n \rightarrow \sigma^*$  in the phenol molecules, respectively.<sup>44</sup> The decrease in the intensities of these two peaks indicates that the molecular structure of phenol has been destroyed during the photocatalysis reaction. Here, we take the absorption peak at 270 nm as a reference to calibrate the concentration of phenol.

Therefore, the main driving force for the photocatalytic promotion could be ascribed to three aspects. (i) The featured plasmon effect, which remarkably boosted the electron quantity for photocatalysis. (ii) The intrinsic colour appearance of AgCl,



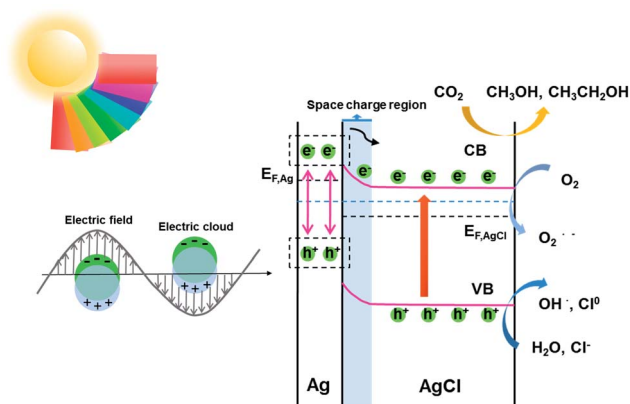


Fig. 5 Schematic diagram illustrating the speculated photocatalytic mechanism of  $\text{Ag}^0/\text{AgCl}$ -fuchsia.

which would enhance the light absorption and promote carrier excitation. (iii) The bandgap narrowing effect exhibited by the coloured  $\text{AgCl}$ . During the degradation, radicals were regarded as the major force to oxidatively degrade the dye molecules.<sup>26,30,45</sup> The excited electrons would react with  $\text{O}_2$  molecules to produce  $\text{O}_2^{\cdot-}$ , and the remaining holes combined with the  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  to generate  $\text{OH}^\cdot$  and  $\text{Cl}^0$ , which has been confirmed in earlier experiments.<sup>27,46</sup> It is worth mentioning that the  $\text{Cl}^0$  atoms could oxidize the MO dye and then be reduced to  $\text{Cl}^-$  ions again.<sup>47</sup> In the whole photoreduction procedure, the electrons on the CB directly engage in the  $\text{CO}_2$  reduction reaction to produce the liquid fuels (methanol and ethanol).<sup>48</sup>

## Conclusion

In summary, under controllable surface state regulation, fresh coloured  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia have been successfully fabricated, which exhibited promoted solar absorption capability compared to  $\text{AgCl}$ -white. Concerning the apparent colours, they are estimated to be provoked by plasma  $\text{Ag}^0$  species on the  $\text{AgCl}$  crystal surface, which could modulate the optical properties through the adjustment of light absorption and reflection. In terms of photocatalytic performance, the apparent kinetic rate constant ( $k_{\text{app}}$ ) of MO photodegradation was calculated over  $\text{Ag}^0/\text{AgCl}$ -blue and  $\text{Ag}^0/\text{AgCl}$ -fuchsia to be about  $0.18 \text{ min}^{-1}$  and  $0.38 \text{ min}^{-1}$ , which was 2.6 and 5.4 times higher than that of normal  $\text{AgCl}$ -white ( $0.07 \text{ min}^{-1}$ ). Simultaneously, they also accomplished  $\sim 3.6$  ( $\text{Ag}^0/\text{AgCl}$ -fuchsia) and 2.6 ( $\text{Ag}^0/\text{AgCl}$ -blue) times the yields of liquid hydrocarbon fuels ( $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ ) compared to  $\text{AgCl}$ -white during  $\text{CO}_2$  photoreduction. In order to more profoundly understand the organic molecule photodegradation and  $\text{CO}_2$  photoreduction, a conceivable reaction mechanism was proposed based on previous studies. It is expected that such a surface state control strategy could represent a beneficial perspective for understanding the solar absorption feature for semiconductor-based photocatalysis.

## Conflicts of interest

There are no conflicts to declare.

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