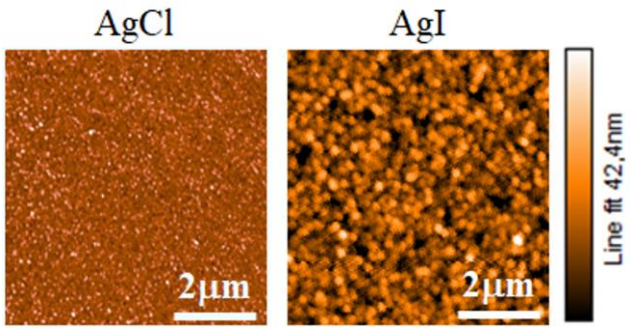
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The AFM images of AgCl and AgI thin film with the thicknesses 50nm are shown in Fig. SI. 1. It is obvious from SI. 1 that AgCl is a smooth film and its surface roughness is lower than 5nm. In contrast, AgI thin film is not smooth and its roughness is higher than 20nm.

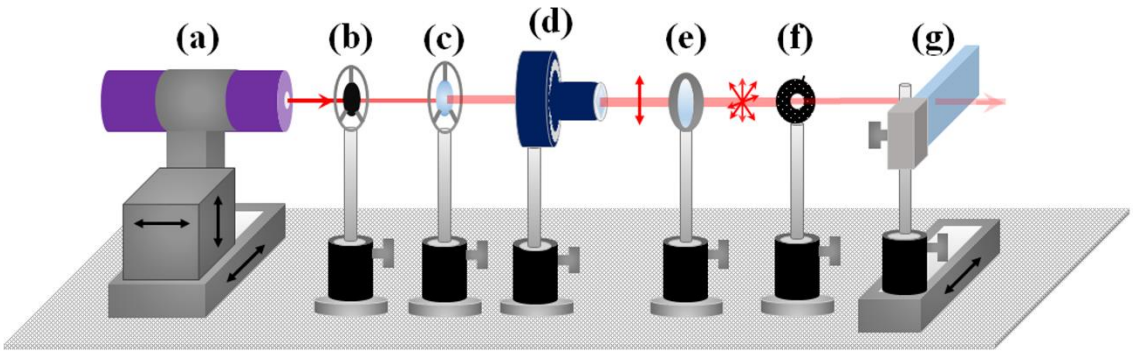


SI. 1 AFM image of AgCl and AgI thin films (thickness is 50nm).

In Fig. S2, the irradiation setup is shown. In part (a), the laser and its holder that is a xyz stage is demonstrated. Three different lasers are used. Therefore, any time the new laser is located on the holder, it must be adjusted again. In part (b) a natural density (ND) filter which decreases the intensity of laser beam is used. The laser beam is diverged by a concave lens in part (c), so that the diameter of laser beam on the sample is about 5mm.

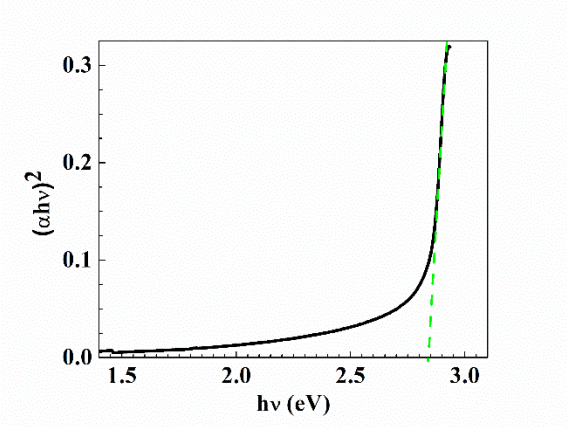
The output laser beams are partially linear polarized. In part (d), a Glan-Taylor calcite polarizer is used to vertically polarize the laser beam and also control the power of the beam. A depolarizer, part (e), is used in front of the polarizer, in case non-polarized beam is needed.

An aperture, part (f), is used to avoid extra light and control the size of the irradiated spot on sample. Part (g) is the the sample and its holder. The Ag-AgCl and Ag-AgI thin films are almost transparent. Therefore, a large percentage of laser beam is transmitted through the samples and only a small percentage will be absorbed and scattered by Ag NPs.



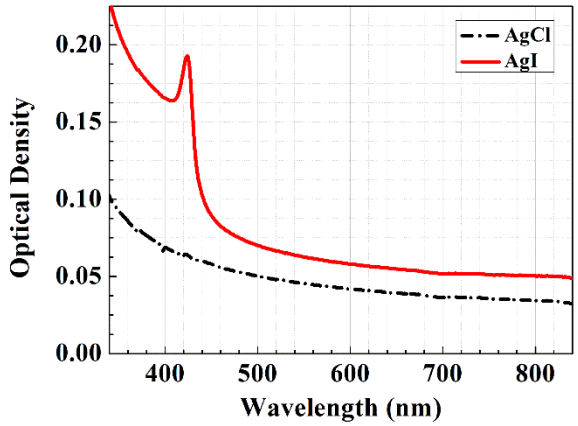
SI. 2 Scheme of the setup used for irradiating the samples: (a) Laser and its xyz stage, (b) ND filter, (c) Concave lens, (d) Glan-Taylor calcite polarizer, (e) Depolarizer, (f) Aperture, (g) Sample and its holder.

In SI. 3 the Tauc plot for determining the band gap energy of AgI thin film is shown. The direct band gap energy is 2.84eV for AgI thin film with the thickness 50nm on glass substrate.



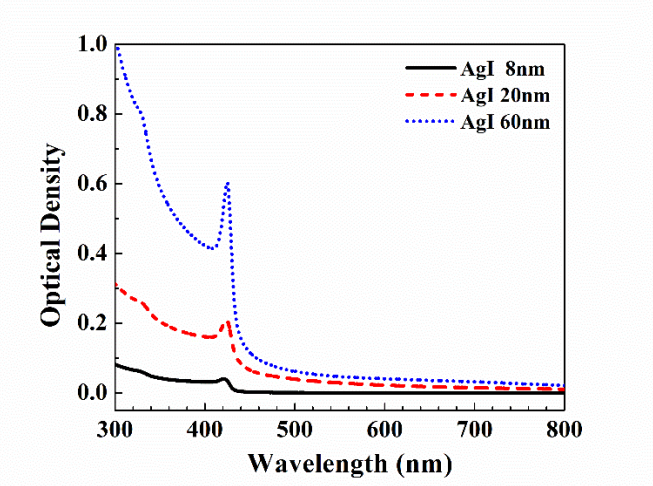
SI. 3 Tauc plot for determining the direct band gap energy of AgI.

The OD spectra of AgCl and AgI thin film with thickness 50nm on glass substrate are shown in SI. 4.



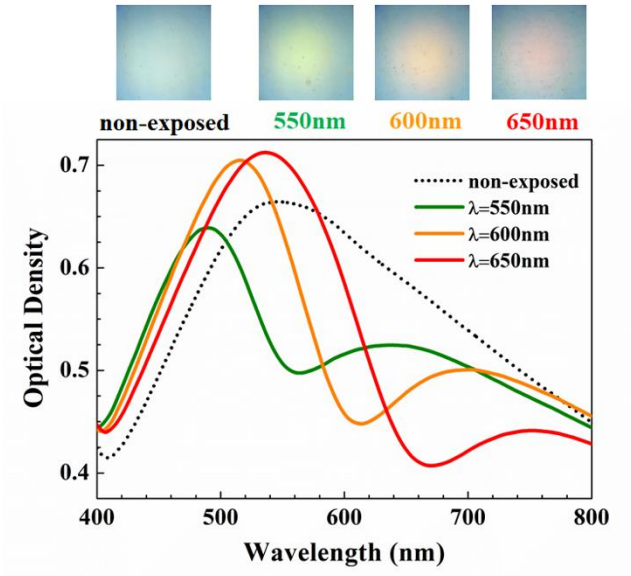
SI. 4 OD spectra of AgCl (balck dash-dotted curve) and AgI (red solid curve).

The OD spectra of AgI with three different thickness (8nm, 20nm and 60nm) on quartz substrate are shown in SI. 5. With the growth of the AgI crystal size, the area under AgI characteristic peak at 423nm is increasing.



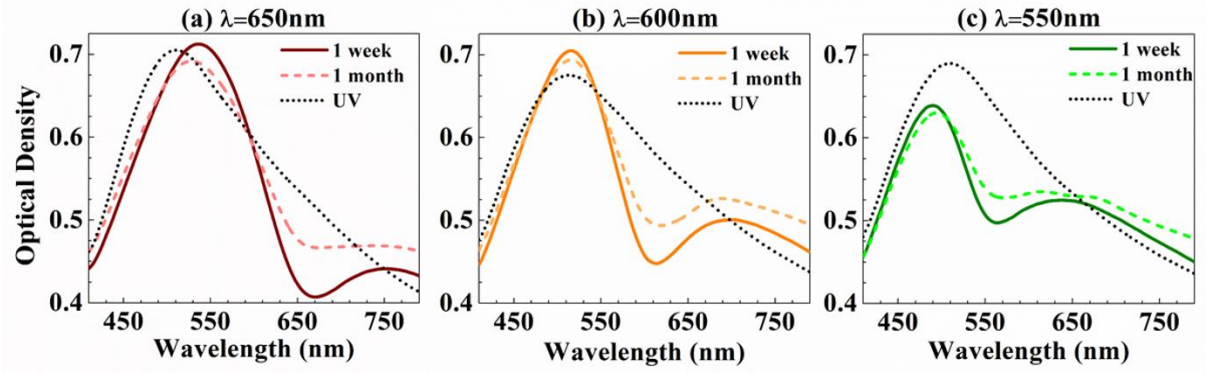
SI. 5 OD spectra of AgI thin films with different thickness 8nm, 20nm and 60nm on quartz substrate.

Fianium white supercontinuum pulsed laser as another light source was used to investigate photochromic behaviour in Ag-AgCl thin film. Ag-AgCl was irradiated with three different wavelengths 550nm, 600nm and 650nm with linewidth 10nm. The output power of the laser beam was about 150 microwatt and repetition rate was 2MHz. The OD spectra of irradiated spots are shown in SI. 6. As it was expected from photochromic materials, a dip is created in related wavelength, comparing with the spectrum of non-exposed sample (black dotted curve). A red-shift in the position of dips is realizable.



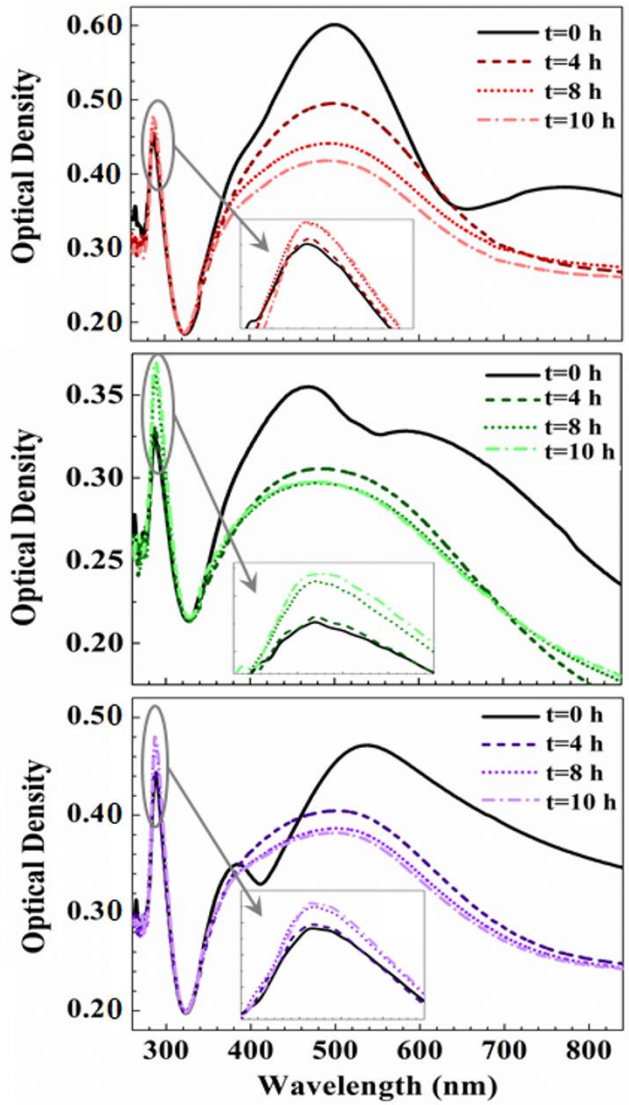
SI. 6 OD spectra of Ag-AgCl thin film before laser irradiation (black dotted curve) and after laser irradiation (solid curves) with different wavelengths 550nm, 600nm and 650nm. The colour spots on Ag-AgCl related to each wavelength is also shown.

To check the colour stability of the spots in SI. 6, the OD spectra of these samples are measured one week and also one month after they were irradiated. In this time interval, the samples are kept in black box in room temperature. Although, after one month the depth of the dips have been decreased, but dips position are not changed. Afterward, the colour spots were irradiated by UV light and their colour is bleached (black dotted curve).



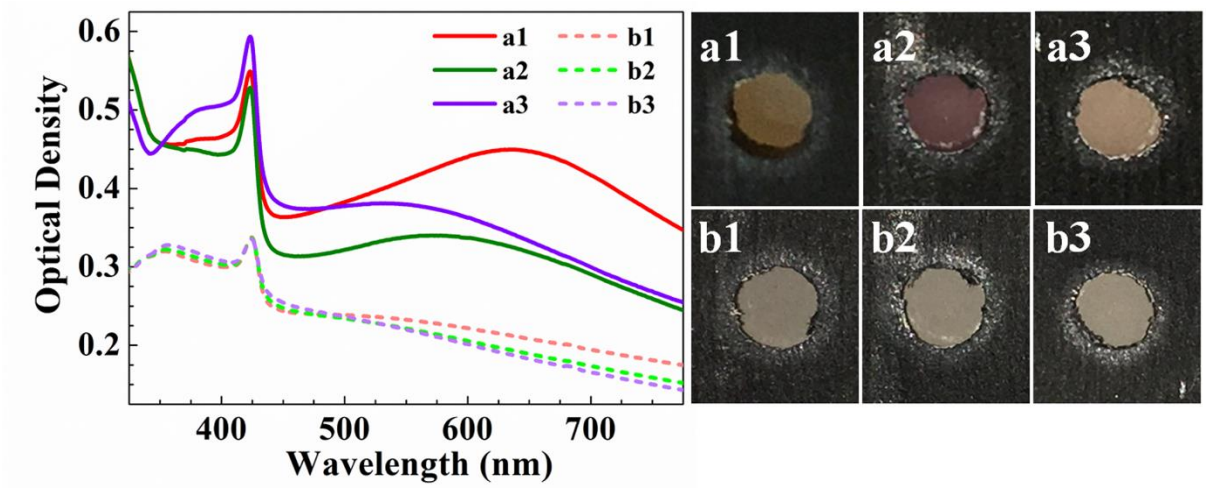
SI. 7 OD spectra of Ag-AgCl thin film after laser irradiation with wavelengths (a) 650nm, (b) 600nm and (c) 550nm. The OD spectra were measured one week after laser irradiation (solid curves) and one month after laser irradiation (dashed curves). The dotted curves are the OD spectra after the sample are irradiated by UV light.

In Ag-AgCl thin film the coloured spots are irradiated by white light in three steps for 4 hours, 8 hours and 10 hours (SI. 8). In each step, the coloured spots became more colourless than the previous step. The OD spectra of the coloured spots is measured in each step. Irradiating white light to coloured spot on Ag-AgCl lead to disappear of the absorption holes. Furthermore, the OD in whole visible region decreases after white light irradiation. The longer duration of white light irradiation leads to more diminution of OD in the visible region and the growth of the absorption peak in the wavelength 290 nm. Irradiation of white light oxidized the Ag NPs to silver ions.



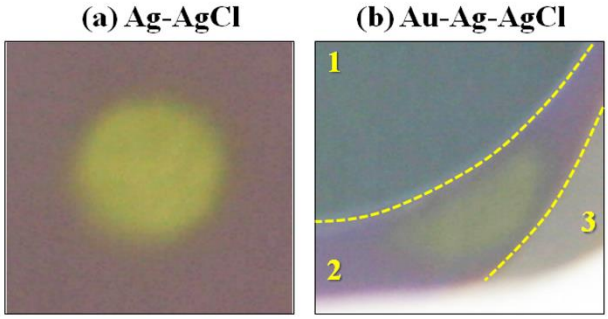
SI. 8 OD spectra of coloured spots on Ag-AgCl thin film irradiated by (a) He-Ne laser (λ=632.8nm), (b) Nd:YAG laser (λ=532nm) and (c) violet diode laser (λ=405nm) before white light irradiation (black solid curves), after three step white light irradiation in 4h, 8h and 10h (coloured curved).

Coloured spots on Ag-AgI thin film are irradiated by white light for 8 hours. The OD spectra of the coloured spot before and after white light irradiation is shown in SI. 9. The SPR peaks between 450nm to 750nm are disappeared by white light. Instead, a peak appears in the vicinity of 360nm after white light irradiation. This peak is the characteristic peak of triiodide ions (I_3^-). In SI. 9 a1 is the sample irradiated by He-Ne laser and b1 is the same sample after white light irradiation. In addition, a2 and a3 are the Ag-AgI sample irradiated by Nd:YAG and violet diode lasers, respectively. After irradiating these samples with white light they are bleached as shown in b2 and b3.



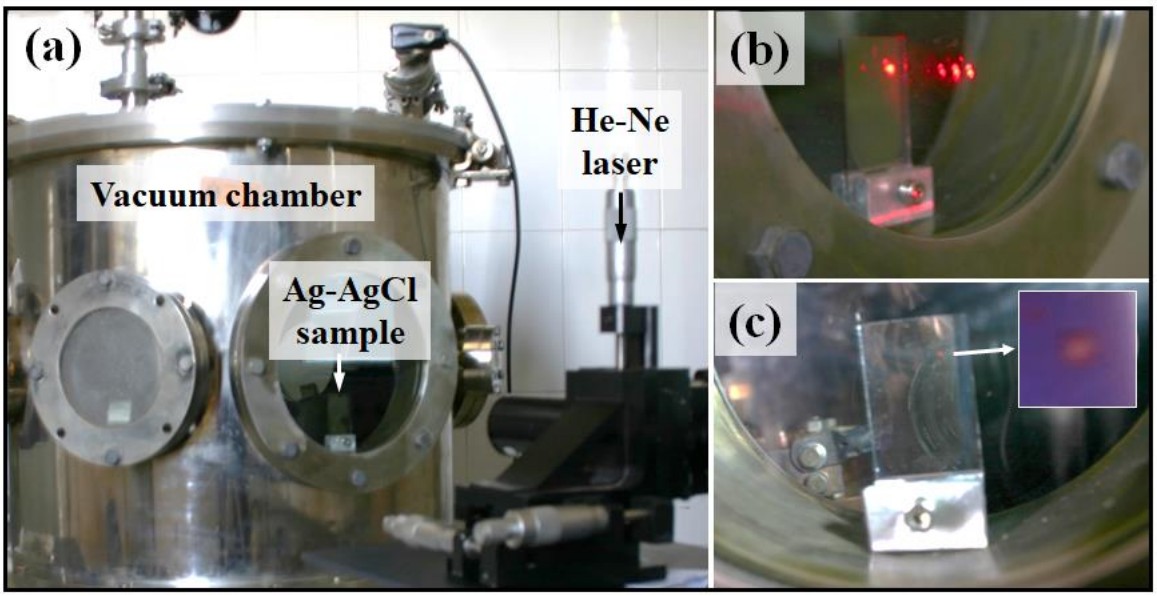
SI. 9 OD spectra of coloured spots on Ag-AgI irradiated by He-Ne laser, Nd:YAG laser and violet-diode laser; before white light irradiation indicated by a1, a2 and a3, after white light irradiation for 8h shown by b1, b2 and b3, respectively.

The gold nanoparticles on AgCl thin film are not showing multicolour photochromic behaviour. To investigate that, a thin film of gold (10nm) is evaporated on Ag-AgCl thin film and no change occurs after laser irradiation. In SI. 10, Ag-AgCl thin film is shown after irradiated by green beam of Nd:YAG laser. In SI. 10b, the part which is determined by 1 is Au-Ag-AgCl thin film, 2 is Ag-AgCl thin fil and 3 is Ag thin film. No colour change is observed in that part 1 which gold nanoparticles exist, while the colour change is obviously seen in Ag-AgCl thin film.



SI. 10 (a) Ag-AgCl sample and (b) Au-Ag-AgCl sample irradiadted by green beam of Nd:YAG laser. In (b) part 1 is Au-Ag-AgCl thin film, part 2 is Ag-AgCl thin film and 3 is Ag thin film.

The Ag-AgCl sample is located in vacuum chamber at pressure 3×10^{-3} mbar and room temperature as shown in SI. 11a. Then the sample is irradiated by He-Ne laser for 10 minutes (SI. 11b). In SI. 11c , it is shown that the colour of sample is changed to red after laser exposure and this phenomenon occurs in the absence of oxygen.



SI. 11 (a) The Ag-AgCl sample is located inside vacuum chamber, (b) He-Ne laser beam is irradiating to Ag-AgCl sample while it is inside the vacumm chamber, (c) after laser irrdaiation the colour change of the sample is obvious**.**