

## Supplementary Information

# Durable Ag/AgCl nanowires assembled in sponge for continuous water purification under sunlight

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## I. Experimental

### *Fabrication of PS@Ag/AgCl NW.*

Polymer sponge pieces were dipped into the ethanol dispersion of AgNWs (7.5 mg/mL) for 5 seconds, then taken out and dried at 60 °C. The obtained AgNWs coated sponge piece was transferred into an oven and heated at 180 °C for 30 min. The resulted AgNWs coated sponge piece was dipped into FeCl<sub>3</sub> solution (0.02 mM) with Polyvinylpyrrolidone (PVP, Mw = 55000, 300 mM) as capping agent under gentle stirring. After 80 min, AgCl NW coated sponge piece was obtained. Finally, the AgCl NW coated sponge piece was irradiated under Xe arc lamp (Perfect Light, 300 W) for 20 min in air to generate welded Ag/AgCl hybrid nanowires coating on the polymer sponge.

### *Fabrication of the flow photoreactor.*

Two pieces of transparent organic glass (made of PMMA, commercial available) with thickness of 1 mm were cut into 7 cm × 3 cm as the sealing plates for the photoreactor. Two holes were drilled in the both ends of the top organic glass and connected with pipes. Silica rubber mats of 7 cm × 3 cm with different thickness (1~7 mm) were cut into rectangular framework with a hollow area of 2 cm × 5 cm. Two comb-like channels were formed on the two ends of the cavity for homogeneous water flow through the sponge. Then a piece PS@Ag/AgCl NW sponge with 5 cm × 2 cm and the same thickness (1~7 mm) as the silica rubber was inserted into the middle cavity of the hollow silica

rubber mats, and sealed by two pieces of organic glass. The resulted construction was fixed by binder clips to prevent the leakage of water during the flow.

### ***Fabrication of AgNWs***

AgNWs were synthesized according to previous work<sup>[1]</sup>. Briefly, 5.8 g of PVP (M<sub>w</sub> = 55000) were dissolved into 190 mL glycerol at 90 °C. 1.58 g silver nitrate powder was added into the above solution after the temperature decreased to 50 °C. Then, a 10 mL glycerol solution containing 59 mg NaCl and 0.5 mL H<sub>2</sub>O was added and heated to 210 °C in 25 min with gentle stirring. When the temperature reached 210 °C, the obtained gray-green solution was transferred to a beaker immediately, water was then added into the solution at a 1:1 ration. AgNPs were removed by stabling the solution for one day. After that, a layer of sediment comprising AgNWs was collected and washed with ethanol two times to remove the residue PVP.

### ***Synthesis of Ag/AgCl NW powder***

The Ag/AgCl hybrid nanowire (Ag/AgCl NW) was fabricated by a two-step procedure as showed in Fig. S3 a, AgCl nanowire was first obtained by in situ oxidation of silver nanowires which was used as both precursor and template by FeCl<sub>3</sub> according to previously reported method<sup>[2]</sup>. Briefly, 18 mL of AgNW dispersion (10 mg/mL in water) and 140 mL of PVP solution (33.3 g/L) were mixed firstly. Then 100 mL of FeCl<sub>3</sub> solution (0.02 mol/L) with PVP (M<sub>w</sub> = 55000, 5.55 g/L) as capping agent was quickly added into the above mixed solution and stirred for 40 min. The resulted mixture was centrifuged and washed with water and ethanol for two times respectively to get AgCl NW. Last, the AgCl NW was re-dispersed in 100 mL of water, and exposed to light irradiation (100 mW/cm<sup>2</sup>, 350 nm~ 780 nm) for 30 min to get Ag/AgCl NW.

### ***In situ chemical recovery of the used PS@Ag/AgCl NW.***

The photoreactor (1 mm thickness of PS@Ag/AgCl NW, and 2.2 mg cm<sup>-3</sup> mass loading of Ag/AgCl

NW, used for the stability test and cycle test in Fig. 4 b and 4c) was first washed with clean water (10 mL), then the recovery solution containing 0.02 mM of FeCl<sub>3</sub> and 300 mM of PVP was injected into the photoreactor at a flow rate of 1 mL min<sup>-1</sup> for 15 min. Finally, the photoreactor washed with clean water (10 mL) again to obtain photocatalytic activity recovered PS@Ag/AgCl NW.

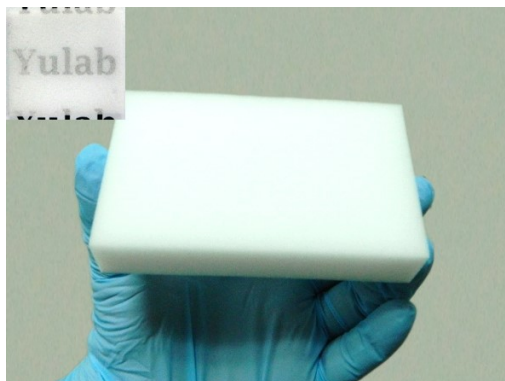
***Performance testing of the fabricated photoreactor.***

The photodegradation experiments was performed under a continuous-recirculation mode (Fig. 4a). 30 mL of methyl orange (MO, 8 mg L<sup>-1</sup>) solution in 100 ml beaker was connected to the inlet of photoreactor by pipes with a small self-priming pump among them. The flow rate can be controlled by tuning the voltage added on the pump. The outlet of the photoreactor was connected back to the beaker by a pipe. Then the photoreactor was localized under a 300W Xe arc lamp (Perfect Light) equipped with an UV-cutoff filter ( $\geq 420$  nm), the light intensity on the photoreactor surface was set at ca. 100 mW cm<sup>-2</sup>. Before visible-light irradiation, the MO solution was first pump though the photoreactor for 30 min in a dark room to reach adsorption equilibrium. Then the MO solution was replaced with 30 mL of fresh MO solution (8 mg L<sup>-1</sup>) and began the photodegradation test. 0.5 mL of MO solution was taken out each time during the reaction for real-time sampling. The MO concentration was measured by UV-vis absorption spectrum. For the evaluation of the photocatalytic activities,  $C$  is the concentration of MO at a real-time  $t$ , and  $C_0$  is the concentration in the MO solution at the beginning of light irradiation. For the stability evaluation of PS@Ag/AgCl NW monolith, the MO solution was degraded by the photoreactor under a once-through mode. The thickness of PS@Ag/AgCl NW monolith is 1 mm, and the Ag/AgCl NW mass loading is 2.2 mg cm<sup>-3</sup>. The MO solution (8 mg L<sup>-1</sup>) was sucked into a syringe, and injected into the photoreactor by a syringe pump at a constant flow rate (1 mL min<sup>-1</sup>). The photoreactor was irradiated under a commercial white LED lamp with a light intensity of 25 mW cm<sup>-2</sup>. The outlet MO concentration was

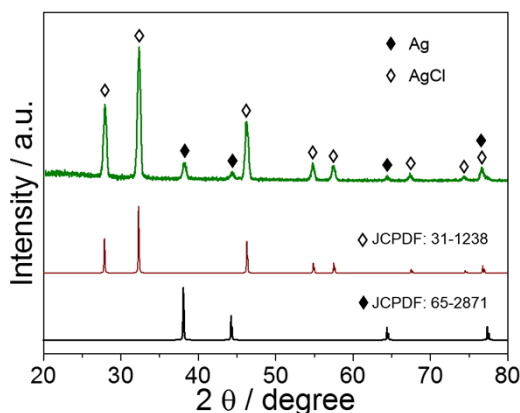
measured by UV-vis absorption spectrum.  $C$  is the concentration of the outlet MO solution at real-time  $t$ ,  $C_0$  is the concentration of original MO solution.

## II. Materials Characterization.

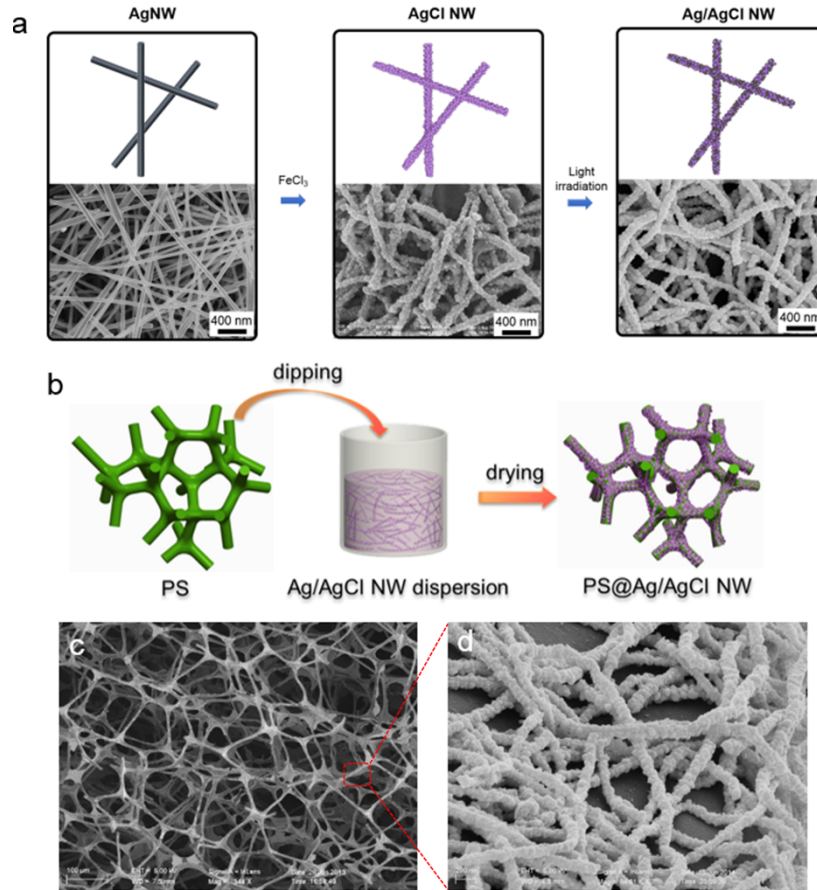
Scanning electron microscopy (SEM) images were obtained from a Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV. X-ray powder diffraction (XRD) was performed on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The X-ray photoelectron spectrometer (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer using Mg K $\alpha$  radiation exciting source.



**Figure S1.** Optical image of commercial polymer sponge (melamine sponge). The inserted image is the polymer sponge piece with 3mm of thickness.



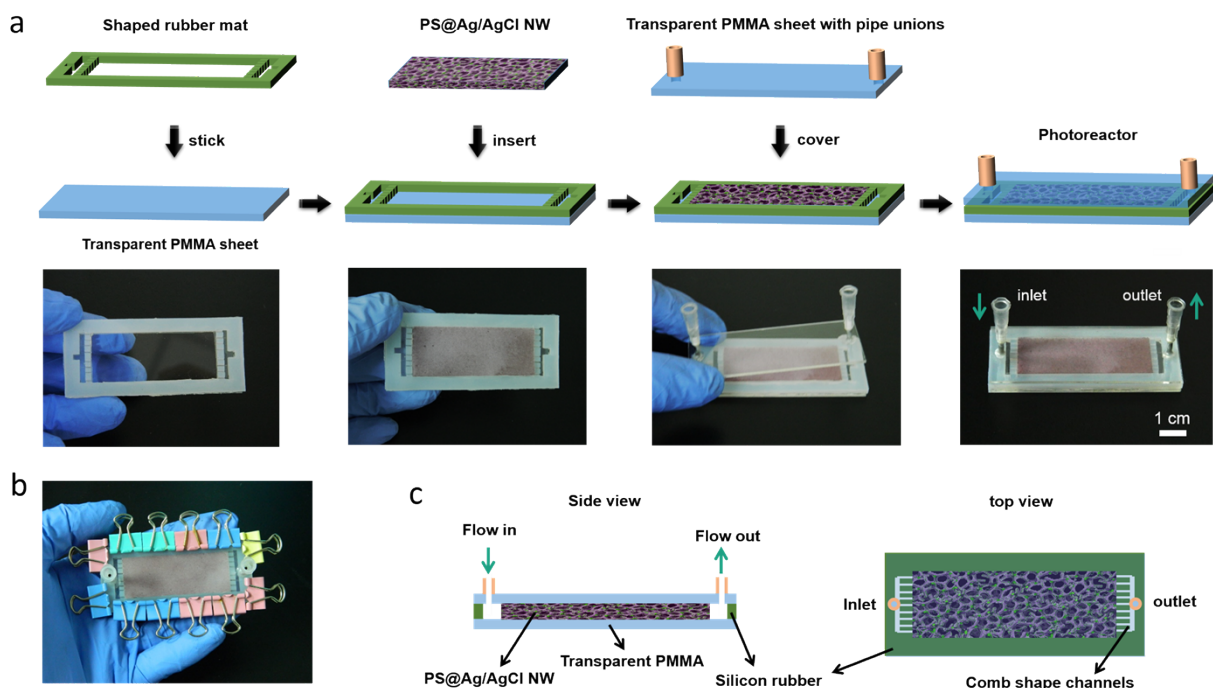
**Figure S2.** XRD patterns of the PS@Ag/AgCl NW monolith. Diffraction peaks from standard JCPDF data of Ag (65-2871) and AgCl (31-1238) are shown for reference.



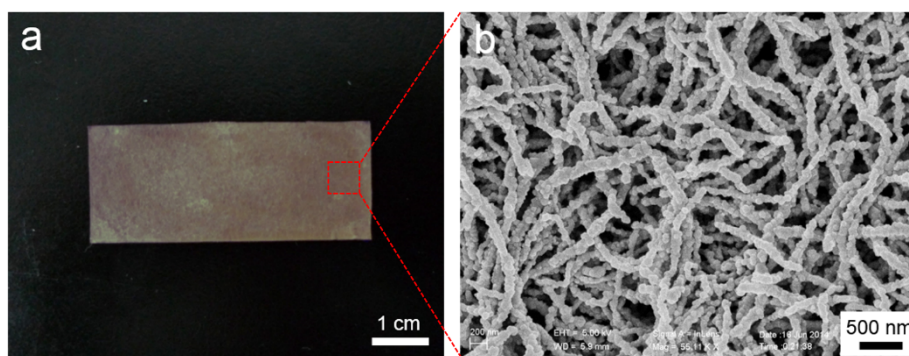
**Figure S3.** (a) Preparation of Ag/AgCl NW in powdered form. (b) Schematic illustration of the PS@Ag/AgCl NW fabricated by direct dip-coating method. The Ag/AgCl NW in powdered form was prepared in advance and dispersed in ethanol. Then the polymer sponge was dipped into the Ag/AgCl NW dispersion for a few second and dried at 60 °C in an oven. (c, d) SEM images of the direct dip-coating processed PS@Ag/AgCl NW in low and high magnification respectively. The Ag/AgCl NW were homogeneously wrapped the fibers of the polymer sponge, and the Ag/AgCl NW network were not welded together at the contact points.



**Figure S4.** Apparatus for the water wash test of PS@Ag/AgCl NW with non-welded and welded Ag/AgCl NW network.

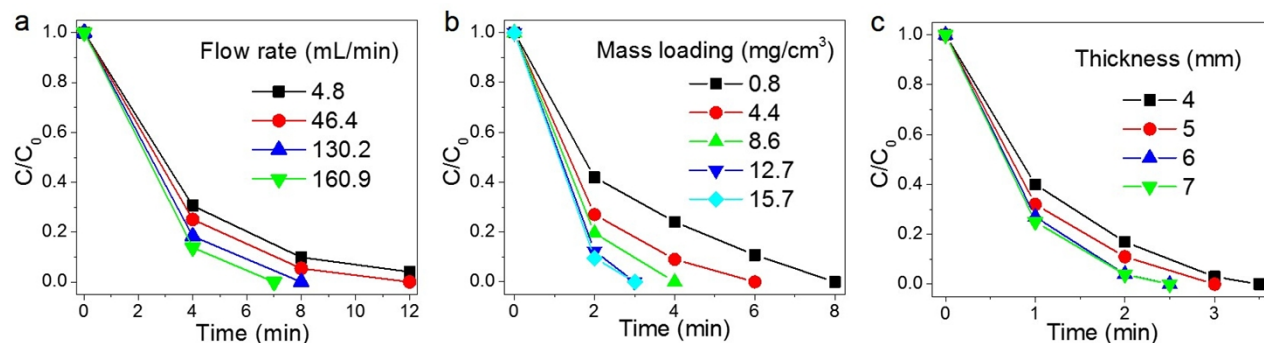


**Figure S5.** (a) Fabrication processes of photoreactor based on 3D Ag/AgCl NW networks with confined flow. Briefly, a silicon rubber mat with patterned cavities was first adhered to a transparent polymethyl methacrylate (PMMA, organic glass) substrate, then a PS@Ag/AgCl NW piece with matched size to the middle cavity of silica rubber was closely embedded into the cavity. After this, an organic glass with inlet and outlet nozzles for the connection of the inner reaction chamber to outside was covered on the topside, and obtained a typical prototype photoreactor with a PS@Ag/AgCl NW piece of 2 cm × 5 cm × 3 mm (Figure 2b). In the actual operation, a pressure should be applied by clamps on the edge of the stack to avoid solution leakage from the contact area between top glass and silicon rubber as showed in (b). (b) Optical images of the PS@Ag/AgCl NW based photoreactor fixed with clamps to avoid solution leakage. (c) Schematic of the closely contact between the sponge piece and the shell of the photoreactor. The comb shape channels are used to ensure that the solution uniformly flow across the sponge piece.

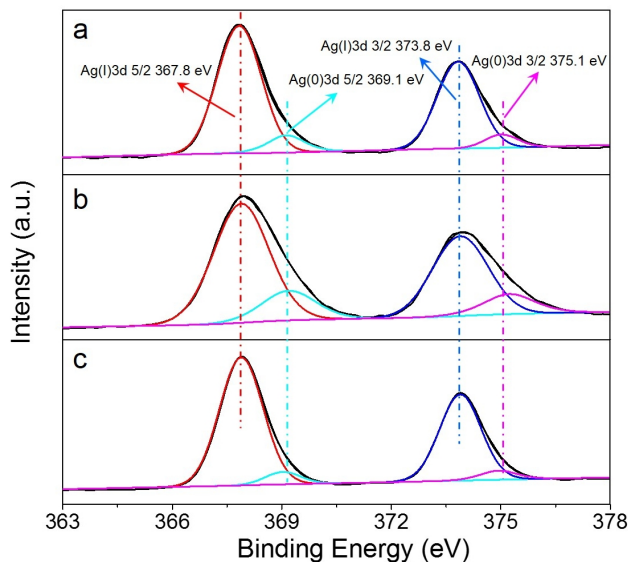


**Figure S6.** (a) Optical image of Ag/AgCl NW film. (b) SEM image of the Ag/AgCl NW film. The fabrication processes of Ag/AgCl NW film was similar to that of weld PS@Ag/AgCl NW. Briefly, AgNW was deposited on a filter paper by vacuum filtration methods, then followed by the same

thermal weld treatment and chemical transformation processes as that in the fabrication processes of weld PS@Ag/AgCl NW monolith.



**Figure S7.** (a) MO degradation by the photoreactor based on 3D Ag/AgCl NW networks with confined flow at different water flow rate under the same light irradiation (300 W Xe arc lamp, 420 nm ~ 700 nm, 100 mW cm<sup>-2</sup>). The PS@AgCl NW piece was 3 mm of thick and had a catalyst load density of 3.6 mg cm<sup>-3</sup>. At the flow rate of 160.9 mL/min, the throughput of the photoreactor reach up to 9600 L h<sup>-1</sup> m<sup>-2</sup>. (b) MO degradation by the above photoreactor (confined flow) with different catalyst loading under the same light irradiation above. The water flow rate was 160.9 mL min<sup>-1</sup>. (c) MO degradation by the photoreactor (confined flow) with different thickness of PS@AgCl NW piece under the same light irradiation above. The catalyst loading density is 12.7 mg cm<sup>-3</sup>. The water flow rate is 90 mL min<sup>-1</sup>. Figure. S7 b shows that the degradation speed increases with the catalysts load, but when the load amount reached 12.7 mg cm<sup>-3</sup>, the photodegradation speed achieved its maximum throughput (720 L h<sup>-1</sup> m<sup>-2</sup>) and would not increase further. This is attributed to the structure of the polymer substrate and working conditions of the photoreaction where the reaction is initiated upon both diffusion of organic pollutant to the catalyst and light photon absorption. When the Ag/AgCl NW coating on the fiber surface is too thick, the top Ag/AgCl NW of the coating will block MO diffusion and photon penetration to the inner Ag/AgCl NW of the coating and therefore the inside Ag/AgCl NWs are inactive. Increasing the thickness of the PS@Ag/AgCl NW monolith also leads to the increase of solar energy utilization. Figure. S7c shows that under the same catalysts mass loading density, the optimal thickness of the PS@Ag/AgCl NW monolith is 5 mm.



**Figure S8.** XPS survey spectrum of a) origin PS@Ag/AgCl NW pieces, b) the PS@Ag/AgCl NW pieces after 2.5h of usage, c) above used PS@Ag/AgCl NW pieces after in-situ chemical recovery treatment. Two bands at ca. 367.8 eV and 372.85 eV are ascribed to Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub> binding energies respectively<sup>[3-6]</sup>. These two bands could be further deconvoluted into two peaks, respectively, at 367.8 eV, 369.1 eV and 373.8 eV, 375.1 eV, where the bands at 367.8 eV and 373.8 eV are attributed to the Ag<sup>+</sup> of AgCl, and those at 369.1 eV and 375.1 eV are ascribed to the metallic Ag<sup>0</sup>. Similar results are reported by other researchers<sup>[3-6]</sup>. The calculated surface mole ratio of metallic Ag<sup>0</sup> to Ag<sup>+</sup> in a, b and c are ca. 1 : 8.4, ca. 1 : 4.1 and ca. 1 : 12.53 respectively.

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