## **Electronic Supplymentary Information (ESI)**

## A Special Ag/AgCl Network-nanostructures for Catalytic Degradation of Refractory Chlorophenol Contaminants

Zaidi Huang,<sup>a</sup> Ming Wen,<sup>a,b,\*</sup> Dandan Wu,<sup>a</sup> and Qingsheng Wu<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, 1239 Siping Road, Shanghai 200092, China.

<sup>b</sup>Shanghai Key Laboratory of D&A for Metal-Functional Materials, Tongji University, 4800 Caoan Road, Shanghai 201804, China

E-mail:

<u>m\_wen@tongji.edu.cn</u> (M. WEN); <u>qswu@tongji.edu.cn</u> (Q.S. WU)

Table S1. Surface properties of network structures.

	network Ag/AgCl NWs	network Ag/AgCl nanospheres
BET Surface Area (m <sup>2</sup> /g)	2.2193	2.4379
Langmuir Surface Area	3.1963	3.7856
(m <sup>2</sup> /g)		

The network-structured Ag/AgCl NWs and network-structured Ag/AgCl nanospheres were prepared under exactly the same condition except PVP. So as-obtained network Ag/AgCl NWs and network Ag/AgCl nanospheres have the same pore channel distribution and content of AgCl in network structures. In Table S1, it can be clearly observed that network-structured Ag/AgCl nanospheres have bigger surface area than network-structured Ag/AgCl NWs.



**Fig. S1** SEM images, XRD patterns and element accounts obtained in the formation process of network Ag/AgCl spheres at 0 min (a), 10 min (b), 30min (c) and 40min (d).

Fig. S1 illustrates the SEM images, XRD patterns and element accounts obtained monitored at different reaction times for the formation of network Ag/AgCl spheres. Only Ag spheres with smooth surface can be observed in Fig. S1Aa at the beginning of the reaction. As the reaction time prolong, some AgCl nanoparticles covered on the Ag spheres and several pores appear in Fig. S1Ba, then more and bigger pores show in Fig. S1Ca. The reaction finally results in the formation of network Ag/AgCl spheres in Fig. S1Da. From the XRD patterns (Ab-Db) and elements accounts (Ac-Dc), the decrease of Ag and the increase of AgCl also can be acquired.



Fig. S2 SEM images of network Ag/AgCl obtained in the temperature of  $150^{\circ}C(A)$ ,  $170^{\circ}C(B)$ ,  $200^{\circ}C(B)$ .

Fig. S2 shows the SEM images monitored at different reaction temperature for the fabrication of network Ag/AgCl nanostructures. When the reaction temperature is lower than 150°C, no products can be obtained. The reaction temperature of 150°C give rise to the network-structured Ag/AgCl irregular polyhedrons with small pores (Fig. S2A). While the temperature went up to  $170^{\circ}$ C, Ag/AgCl network nanostructure with larger macropore (50nm~ 100nm) in well distributed can be observed in Fig. S2B. But if the temperature up to  $200^{\circ}$ C, the networks are loose even collapsed (Fig. S2C). Therefore, we can draw a conclusion that the temperature is one of the important factor for the formation of Ag/AgCl network nanostructures.



**Fig. S3** SEM images of Ag/AgCl nanonetworks were fabricated in deionized water (A) and ethylene glycol (B).

The SEM images in Fig. S3 shows that the network Ag/AgCl obtained in different solvent. Ethylene glycol results in the formation of network Ag/AgCl nanostructures with larger macropores (50nm-100nm) in well distributed (Fig. S3A). When the water is taken place of ethylene glycol, the networks pile up close together, the pores of networks become smaller (Fig. S3B).



**Fig. S4** Typical UV–visible diffuse reflectance spectrum of different nanocatalysts: a) network Ag/AgCl spheres; b) network Ag/AgCl wires; c) P25-TiO<sub>2</sub>.

As-prepared network Ag/AgCl spheres and network Ag/AgCl wires as well as commercial P25- $TiO_2$  were used as our reference photocatalyst, and their UV/Vis diffuse reflectance spectra are compared in Fig. S4. In contrast to P25- $TiO_2$  NPs, the network-structured Ag/AgCl nanocomposites have a strong absorption in visible region due to the plasmon resonance of Ag nanoparticles in network nanostructures. Therefore, network Ag/AgCl nanostructures have excellent photocatalytic performance in visible light towards organic dyes, including methyl orange, methylene blue and rhodamine B, but as for the refractory 4-chlorophenol, photodegradation under visible light is quite difficult to realize, even numbers of catalysts cannot do it under UV irradiation.



Fig. S5 UV-vis absorption spectra of reaction solutions containing no catalysts.

In order to exclude the possibility that the degradation of 4- chlorophenol was caused by the UVlight irradiation, the blank experiment was carried out where only 4- chlorophenol without any photocatalyst was irradiated under UV-light. It can be clearly observed in Fig. S5 that the irradiation does not degrade 4- chlorophenol in the absence of catalysts.



**Fig. S6** UV-vis absorption spectra of reaction solutions containing different catalysts: (A) network Ag/AgCl spheres; (B) network Ag/AgCl wires; (C)P25-TiO<sub>2</sub> nanoparticles; (D)Ag wires.

The photocatalytic performance of our network Ag/AgCl nanostructures was investigated in terms of the photodegradation of 4- chlorophenol pollutants under UV-light irradiation. In Fig. S6, when Ag wires are involved in the reaction system, the photodegradation of 4-chlorophenol can be negligible under UV-light irradiation (Fig. S6D). This can be suggested that the self-photo-sensitized decomposition of 4-chlorophenol under our experimental conditions could basically be ignored. While network Ag/AgCl spheres (Fig. S6A) and network Ag/AgCl wires (Fig. S6B) were used as photocatalysts, different degradation of 4-chlorophenol could be achieved, whose photocatalytic performance are much higher than commercially available P25–TiO<sub>2</sub> (Fig. S6C). So network Ag/AgCl nanostructures display significant advantage owing to its superiority of structure.



Fig. S7 SEM images of network Ag/AgCl after sixth circulation.

In order to investigate the stability and lifetime of the network Ag/AgCl nanostructures, the SEM images of this catalyst over the sixth cycle is shown in Fig. S7. The great mass of the catalysts still keep dispersed distribution, merely some of the structures pulverized in the certain degree. Therefore, the as-obtained network Ag/AgCl nanostructures have the relative good lifetime and stability for the photodegradation of 4- chlorophenol.