Rapid Formation of Ag_nX (X=S, Cl, PO_4, C_2O_4) Nanotubes via an Acid-Etching Anion Exchange Reaction

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Experimental details

Materials Synthesis. All reagents are of analytical grade, purchased from Shanghai Chemical Reagent Factory, and used as received without further purification. Ag_2CO_3 nanorods were prepared via a procedure reported in our previous work.[8] Briefly, 0.085g of $AgNO_3$, 1g of polyvinylpyrrolidone (PVP, MW~ 58K) were dissolved in 20mL of distilled water to form a clear solution, followed by a dropwise addition of 20 mL of pre-prepared $NaHCO_3$ aqueous solution (0.05 M). The solution turned grey after several minutes, indicating the initial formation of Ag_2CO_3 nanorods. The mixture was continuously stirred for 1 h at room temperature and collected by centrifugation. After washing with water and ethanol for three times, the as-prepared Ag_2CO_3 nanorods were dried at 60 ºC for 6 h.

Synthesis of Ag_nX(X=S, Cl, PO_4, C_2O_4) NTs. In a typical procedure, 30 mg of as-obtianed Ag_2CO_3 templates and 60 mg of thioacetamide (TAA) were dispersed in 10mL of ethanol under stirring, followed by a dropwise addition of 5 mL of pre-prepared CH_3COOH (80 μL) ethanol solution. After 10 minutes, the precipitates were collected by centrifugation and washed with water and ethanol for three times, and the as-prepared Ag_2S NTs were dried at 60 ºC for 2 h. In the case of $AgPO_4$ NTs, ethanol was used as the organic solvent. For AgCl and $Ag_2C_2O_4$ NTs, EG was selected to produce as the organic solution.

Synthesis of Ag_2CO_3-Ag_nX yolk-shell nanostructures. The intermediate nanostructures were all prepared with the same method described above except different acid amounts. 20 μL, 40μL and 60 μL of CH_3COOH were used, respectively, to obtain intermediate Ag_2CO_3-Ag_2S yolk-shell nanotubes. For Ag_2CO_3-Ag_nX (X= Cl, PO_4, C_2O_4) yolk-shell nanostructures, 8 μL of HCl, 1μL of H_3PO_4 and 6 mg of $H_2C_2O_4$ were used, respectively.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were recorded by using Cu K_α irradiation on a Philips PW3040/60 X-ray diffractometer operated with a scanning rate of 0.06 deg s^{-1}. Scanning electron microscopy (SEM) analysis was performed with a Hitachi S-4800 scanning electron micro-analyzer using an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted at 200 Kv with a JEM-2100F field emission TEM. Samples for TEM measurements were prepared by dispersing the products in ethanol and placing several drops of the suspension on holey carbon films supported by copper grids.

Photocatalytic test. The photocatalytic activities of the Ag_nX nanotubes were evaluated by degrading of RhB aqueous solution under visible light irradiation from a 500 W Xe lamp equipped with one 420nm cut off filter. The reaction cell was placed in a sealed black box with the top opene, and the cut off filter was placed to provide visible-light irradiation. In a typical process, 10mg of different as-prepared Ag_nX nanotubes as photocatalysts were added into 20mL of RhB solution (concentration: 5 mg/L). After being dispersed in an ultrasonic bath for 5 min, the solution was stirred

for 2 h in the dark to reach adsorption equilibrium and then exposed to visible light irradiation. The photocatalysts were removed by centrifugation at given time intervals, and the RhB concentration was measured colorimetrically at 550 nm using the UV-vis spectroscopy.

Table S1. Different molar ratio of the Ag and S prepared with different volume of CH_3COOH.

CH_3COOH volume (μL)	Atomic (%)		Molar ratio
	Ag	S	(Ag : S)
20	15.35	4.35	3.5
40	17.70	6.64	2.7
60	15.80	7.19	2.2
80	17.30	8.40	2.0

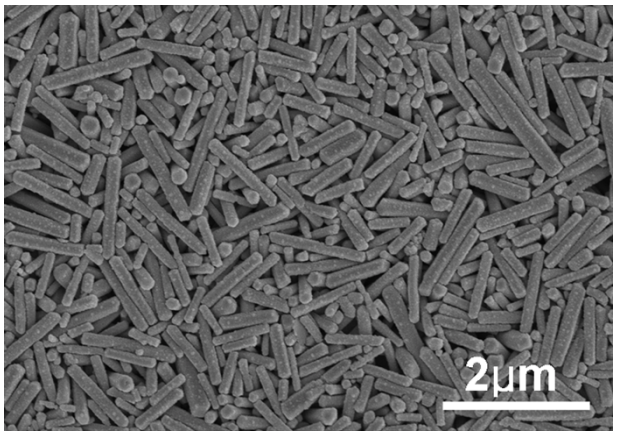

Fig. S1. SEM image of Ag_2CO_3 nanorods.

Fig. S2. SEM images of the as-prepared Ag_nX obtained in water: a) Ag_2S, b) AgCl, c) Ag_3PO_4, d) $Ag_2C_2O_4$.

Fig. S3. SEM images of the as-prepared (a) AgCl (a) and (b) $Ag_2C_2O_4$ obtained in ethanol.

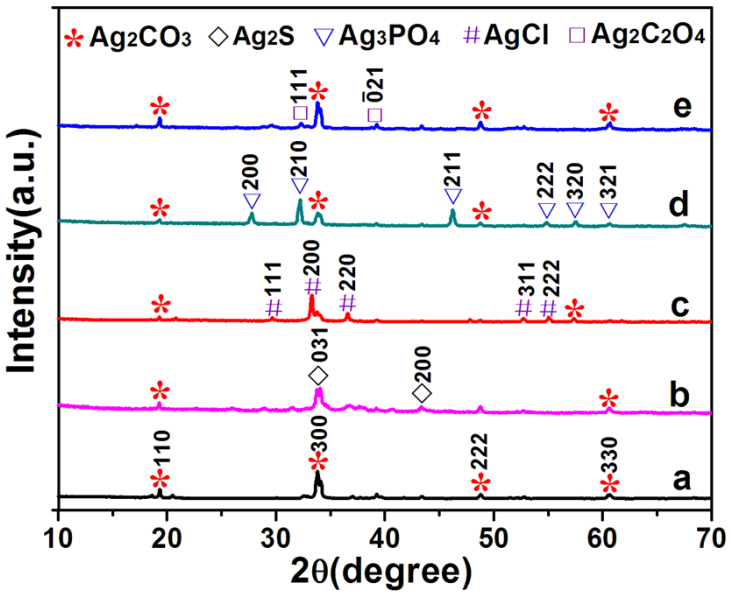

Fig. S4. XRD patterns of (a) the as-prepared pure Ag_2CO_3 nanorods and different Ag_2CO_3-Ag_nX yolk-shell nanostructures: (b)Ag_2CO_3-Ag_2S; (c)Ag_2CO_3-AgCl; (d)Ag_2CO_3-Ag_3PO_4; (e)Ag_2CO_3-$Ag_2C_2O_4$.

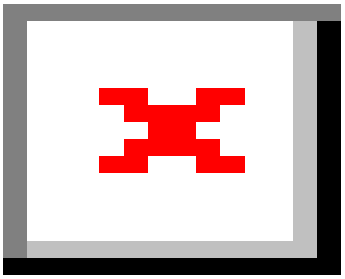

Fig. S5. SEM images of the as-obtained Ag_nX samples with the different salts: (a) Na_2S; (b) NaCl; (c) Na_2HPO_4; (d) $Na_2C_2O_4$.

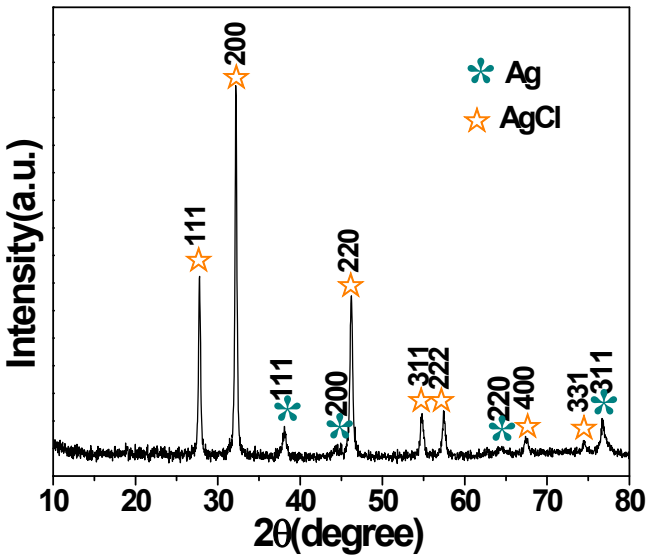

Fig. S6. XRD pattern of the AgCl NTs after six cycles of the photocatalytic test.

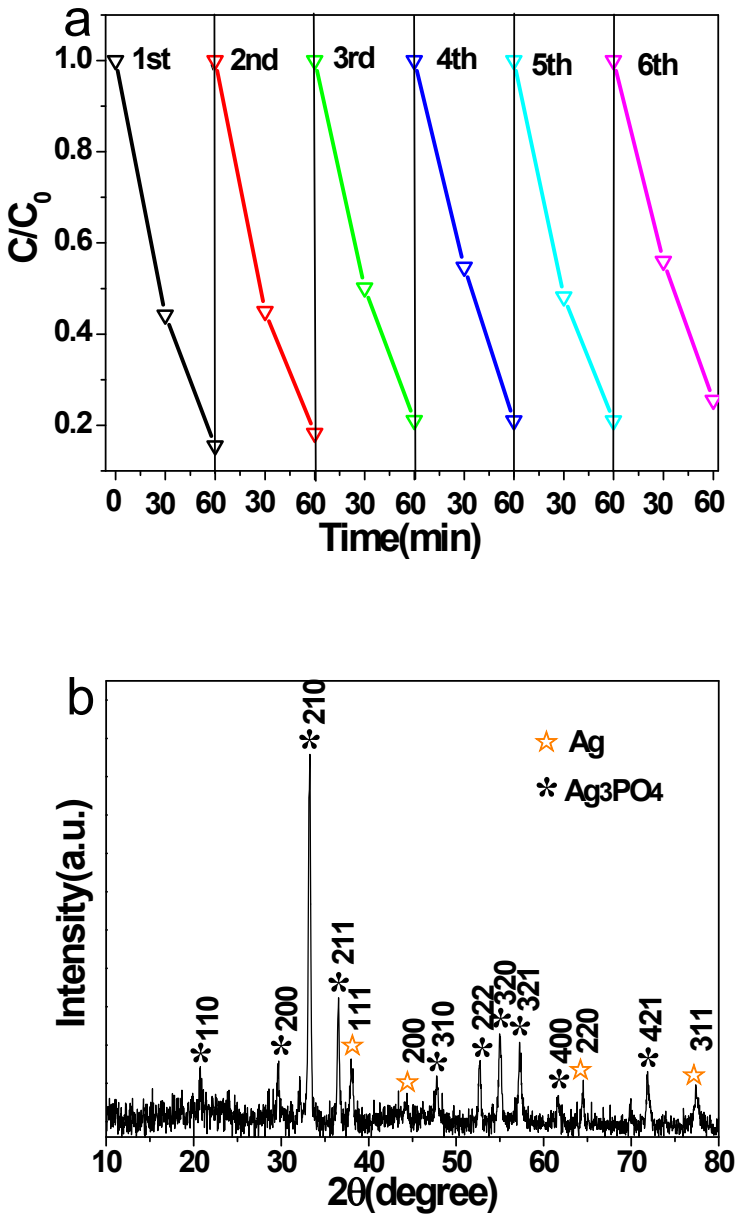

Fig. S7. (a) 6 cycles of degradation of RhB using Ag_3PO_4 NTs as photocatalyst; (b) XRD pattern of the Ag_3PO_4 NTs after six cycles of the photocatalytic test.