

Supporting Information

AgX/ graphite-like C₃N₄ (X=Br, I) hybrid materials for photoelectrochemical determination of copper (II) ion

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Experimental details

Reagents and materials

Dicyandiamide, cupric chloride (CuCl₂·2H₂O), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl₂·6H₂O), calcium chloride (CaCl₂), lead nitrate (Pb(NO₃)₂), nickel dichloride (NiCl₂·6H₂O), iron trichloride (FeCl₃·6H₂O), zinc chloride (ZnCl₂), lithium sulfate (Li₂SO₄·H₂O), cobalt dichloride (CoCl₂·6H₂O) and manganese chloride (MnCl₂·4H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade without further purification. The stock solutions (0.2 M) of Cu²⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Ni²⁺, Zn²⁺, Mn²⁺, Pb²⁺, Co²⁺ and Li⁺ ions were prepared by dissolving suitable amount of compounds like CuCl₂·2H₂O, NaCl, KCl, MgCl₂·6H₂O, CaCl₂, FeCl₃·6H₂O, NiCl₂·6H₂O,

ZnCl₂, MnCl₂·4H₂O, Pb(NO₃)₂, CoCl₂·6H₂O and Li₂SO₄·H₂O in doubly distilled water. Ionic liquid 1-hexadecyl-3-methylimidazolium bromide ([C₁₆mim]Br) and 1-butyl-3-methylimidazolium iodine ([Bmim]I) were purchased from Shanghai Cheng Jie Chemical Co. LTD (China). Phosphate buffer solution (PBS, 0.1 M, pH 7.0) was used throughout the photoelectrochemical (PEC) detection, which was prepared by mixing stock standard solutions of Na₂HPO₄ and NaH₂PO₄, and adjusting the pH with 0.1 M NaOH or H₃PO₄. All aqueous solutions were prepared with doubly distilled water. The indium tin oxide (ITO) glass was cut into 3 cm × 1 cm slices and successively bathed in 1 M NaOH solution for 10 min and acetone for 30 min, then washed with water and dried prior to use. The human hair sample was digested with the mixture of 68% (W/W) nitric acid and 38% (W/W) hydrochloric acid (3:1 V/V). After digestion, the resulting sample solution was diluted and neutralized to pH 7 with 0.1 M NaOH solution prior to detection.

Apparatus. PEC detection and electrochemical impedance spectroscopy (EIS) measurement were performed on a CHI 660B electrochemical workstation (CHI, USA). The inductively coupled plasma (ICP) spectroscopic detection of metal elements in the human hair sample was performed on a Vista-MPX inductively coupled plasma spectrometer (VARIAN Co. USA). The EDS was carried out with a field-emission scanning electron microscope (JEOL JSM-7001F). X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu K_α (λ=1.54 Å). Transmission electron microscopy (TEM) micrographs were taken with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The samples used for TEM were prepared by dispersing some products in ethanol, then placing a drop of the solution onto a copper grid and letting the ethanol evaporate slowly in air.

Preparation of AgX/g-C₃N₄ hybrid materials^{S1}

Graphitic carbon nitride (g-C₃N₄) was synthesized by directly heating dicyandiamide. Typically, 2 g of dicyandiamide powder was put into an alumina crucible with a cover, then heated at a rate of 2.9 °C/min to reach a temperature of 350 °C, and then tempered at this temperature for another 2 h in a flowing-nitrogen atmosphere. This was next followed heated at a rate of 3.3 °C/min to reach a temperature of 550 °C, and then tempered at this temperature for another 2 h in a flowing-nitrogen atmosphere.

AgBr/g-C₃N₄ hybrid materials were synthesized in the presence of ionic liquid [C₁₆mim]Br. The g-C₃N₄ (0.092 g) as the substrate was added to 8 mL of ethylene glycol, and the suspension was sonicated for 20 min. Then, a suitable [C₁₆mim]Br (0.1161 g) was added into the suspension, and the mixture was stirred magnetically for 30 min. Next, AgNO₃ (0.0509 g) was employed as the source of silver and dissolved in 2 mL ammonia aqueous (25%-28%) to obtain a [Ag(NH₃)₂]⁺ solution. The [Ag(NH₃)₂]⁺ and [C₁₆mim]Br solution quickly added to the g-C₃N₄ mixture, and the resulting suspensions were stirred at 90 °C in water bath for 6 h. AgI/g-C₃N₄ hybrid materials were also prepared in the presence of ionic liquid [Bmim]I (0.0798 g) under the same condition.

Photoelectrochemical Measurements

To investigate the photoelectrochemical properties of AgX/g-C₃N₄ hybrid materials, g-C₃N₄ and AgX/g-C₃N₄ hybrid material modified electrodes were prepared. 10 mg of AgX/g-C₃N₄ powder was dispersed ultrasonically in 1 mL of water, and 20 μL of the resulting colloidal dispersion (10 mg/mL) was drop-cast onto a piece of ITO slice with a fixed area of 0.5 cm² and

dried in air at room temperature to form AgX/g-C₃N₄ modified ITO electrode (denoted as ITO/(AgX/g-C₃N₄)). All the photocurrent measurements were performed at a constant potential of -0.2 V (vs. SCE). PBS was used as the supporting electrolyte for photocurrent measurements. The photocurrents were measured in a standard three-electrode system, which employed a Pt wire as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode and ITO/(AgX/g-C₃N₄) as working electrode. A 500-W Xe arc lamp was utilized as the light source. The Nyquist plots were recorded the 100 MHz to 100 kHz frequency range.

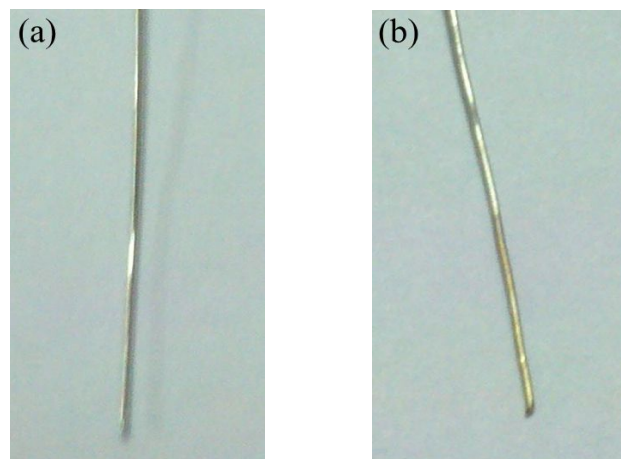


Fig. S1 Photographs of the Pt electrode before detection (a) and after detection (b)

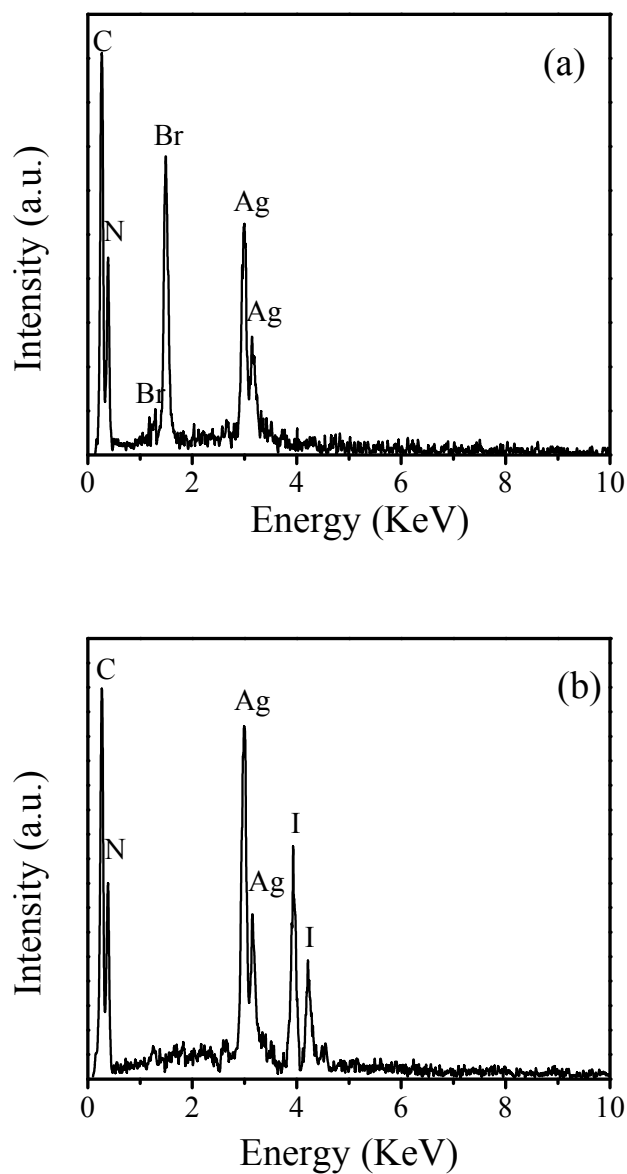


Fig. S2 EDS of the AgX/g-C₃N₄ hybrid materials after detection: (a) the AgBr/g-C₃N₄ hybrid materials, (b) the AgI/g-C₃N₄ hybrid materials

The chemical composition of the hybrid materials after detection was determined by X-ray energy dispersion spectrum (EDS). As shown in Fig.S2, Ag, Br, C and N peaks were observed in spectrum of the AgBr/g-C₃N₄, and Ag, I, C and N peaks were observed in spectrum of the AgI/g-C₃N₄. Moreover, peaks of Cu element at 0.9 eV, 8 eV and 8.9 eV^{S2} were not detected in

two spectrums, suggesting that the reduction of Cu^{2+} did not occur in the $\text{AgX/g-C}_3\text{N}_4$ hybrid materials surface.

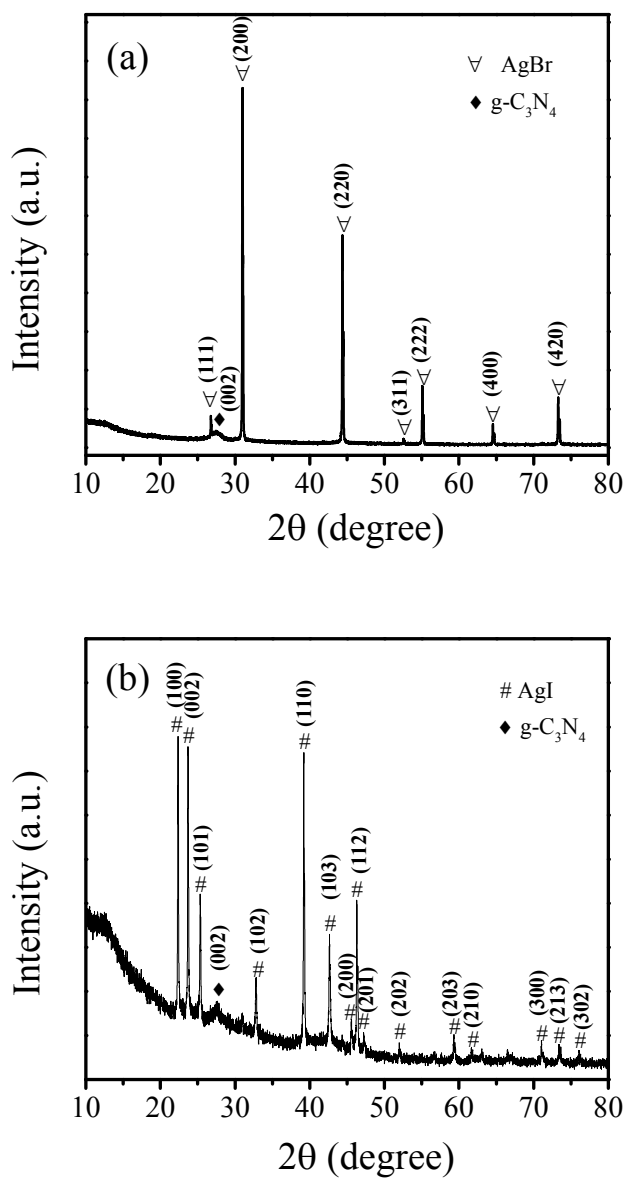


Fig. S3 XRD of the $\text{AgBr/g-C}_3\text{N}_4$ (a) and the $\text{AgI/g-C}_3\text{N}_4$ (b) after detection.

The XRD patterns of the $\text{AgBr/g-C}_3\text{N}_4$ (a) and the $\text{AgI/g-C}_3\text{N}_4$ (b) after detection were shown in Fig.S3. The characteristic peak of $\text{g-C}_3\text{N}_4$ around 27.3° could be clearly identified in two samples, which was indexed as (002) diffraction plane. As shown in Fig.S3(a), the diffraction

peaks at 26.8°, 31.1°, 44.3°, 52.5°, 55.2°, 64.5° and 73.3° gradually appeared and the intensity increased, and the peaks were assigned to the (111), (200), (220), (311), (222), (400) and (420) planes of AgBr crystal (JCPDS file: 06-0438), respectively. In the XRD patterns of the AgI/g-C₃N₄ (Fig.S3(b)), the peaks at 2θ=22.5°, 23.7°, 25.3°, 32.8°, 39.1°, 42.5°, 45.5°, 46.3°, 47.2°, 52.0°, 59.3°, 61.7°, 71.0°, 73.4° and 76.1° were indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (202), (203), (210), (300), (213) and (302) planes of the hexagonal AgI crystal phase (JCPDS file: 09-0374), respectively. Therefore, in the XRD analysis, no impurity peaks were observed, which confirmed that the phase and composition of the AgX/g-C₃N₄ were not changed before and after detection of Cu²⁺. These peaks belonging to Cu₂O or Cu were not detected, which can make sure that the reduction of Cu²⁺ did not occur in the AgX/g-C₃N₄ hybrid materials surface. These XRD results were consistent with the EDS analysis.

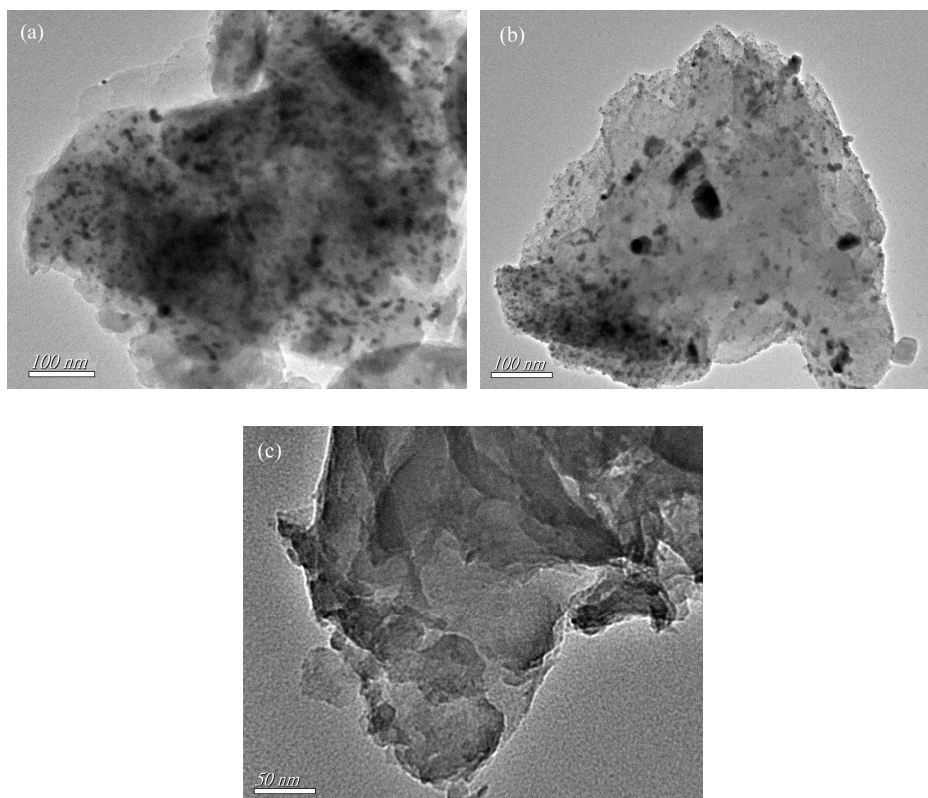


Fig. S4 TEM images of the AgBr/g-C₃N₄ (a), the AgI/g-C₃N₄ (b) and the g-C₃N₄ (c) after detection

The TEM images of the AgBr/g-C₃N₄ (a), the AgI/g-C₃N₄ (b) and the g-C₃N₄ (c) after detection were shown in Fig.S4. It was obvious that the AgX nanocrystals embedded in the g-C₃N₄ layered materials and well dispersed on the the g-C₃N₄ (Fig.S4 (a, b)). The morphology of the pure g-C₃N₄ was the smooth and flat layer. The morphology of the AgBr/g-C₃N₄, the AgI/g-C₃N₄ and the g-C₃N₄ after detection was consistent with our previously reported AgX/g-C₃N₄^{S1}. This result indicated that the structures of the AgX/g-C₃N₄ were not changed before and after detection of Cu²⁺.

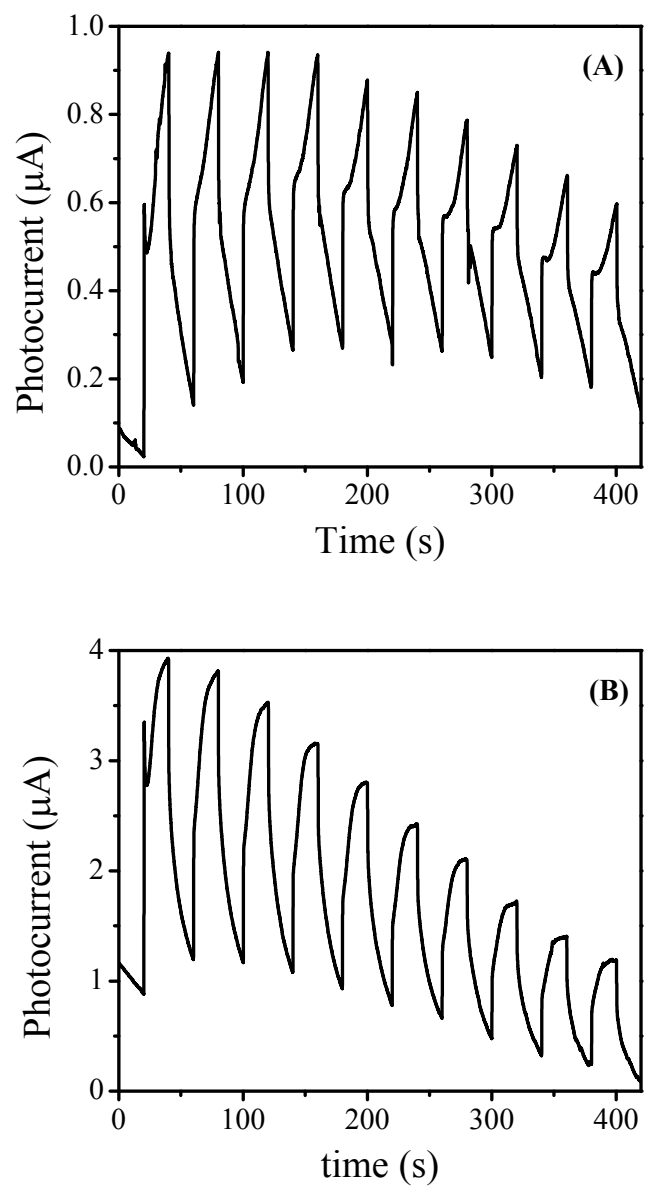


Fig. S5 Time-based photocurrent response of the ITO/AgBr electrode (A) and the ITO/AgI electrode (B) in 0.1 M PBS (pH 7.0)

Table S1 ICP spectroscopic detection results of human hair sample ($\mu\text{g g}^{-1}$)

Element	Content ($\mu\text{g g}^{-1}$)	Element	Content ($\mu\text{g g}^{-1}$)	Element	Content ($\mu\text{g g}^{-1}$)
Al	155.5	Fe	458.5	Na	1169.4
As	4.8	K	199.6	Ni	14.4
Ca	1537.9	Li	0.9375	Pb	4.4
Cu	14.8	Mg	184.6	Zn	428.9
Co	2.384	Mn	14.5		

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