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Speciation Analysis of Silver Sulfide Nanoparticles in Environmental Waters by Magnetic Solid Phase Extraction Coupled with ICP-MS

Supporting Information

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Synthesis and Purification of AgCNPs.

Ag_2S NPs. The Ag_2S NPs were synthesized directly according to a previously published paper.[1] Briefly, 60 mg bis(p-sulfonatophenyl)phenylphosphane dehydrate dipotassium salt (BSPP) was added into 30 mL of freshly dissolved $AgNO_3$ aqueous solution (1mM) to complex with Ag^+. After stirring for 1 h, 1 mL of Na_2S aqueous solution (50 mM) was fleetly added into the BSPP-Ag^I system, which accompanied a series of color changes and finally produced a brown Ag_2S hydrosol.

Ag&Ag_2S NPs. The mixture of AgNPs and Ag_2S NPs were synthesized by part sulfidation of AgNPs following a procedure modified from Li et al.[2] Specifically, under vigorous stirring, 0.6 mL of Na_2S solution (10 mM) was quickly added into 30 mL of commercial AgNP aqueous solution (10 mg/L), which was placed in a septum-sealed 50 mL flask. Afterwards, stirring was continued for another 3 h, while pale yellow color gradually turned fulvous reflecting the formation of Ag_2S NPs.

AgCl NPs. The synthesis of AgCl NPs was accomplished through reaction of $AgNO_3$ with NaCl. Simply, under vigorous stirring, 1 mL of NaCl solution (50 mM) was added dropwise into 50 mL of freshly prepared aqueous solution containing 0.05 mmol $AgNO_3$ and 25 mg TX-114. Then the mixture was stirred for another 30 min.

Citrate-AgNPs. Citrate-AgNPs were synthesized using a previously described method for reducing an aqueous solution of boiling silver nitrate in the presence of trisodium citrate dihydrate with sodium borohydride with slight modification.[3] Briefly, adding 0.43 mL of 58.8 mM $AgNO_3$ and 3.7 mL 34 mM trisodium citrate dihydrate into boiling ultrapure water. After several minutes, 1 mL 50 mM $NaBH_4$ was introduced into the system dropwise under vigorous stirring and stirred for another 30 min.

PVP-3.5-AgNPs. Briefly, 3.4 g $AgNO_3$ was added into 20 mL ultrapure water water, which was pre-heated at 50 ℃ in water bath. Then, a mixture of aqueous solution (125 mL) containing

1.325 g $NaH_2PO_2 \cdot H_2O$, 0.43 g sodium hexametaphosphate, 3.4 g PVP (MW=3,500) and 2.5 mL of H_2SO_4 (l.0 mol/L) was stirred vigorously. Then, the prepared $AgNO_3$ solution was dropped into the mixture with 20-30 drops per minute and stirred vigorously for another 30 min.

PVP-58-AgNPs. To prepare PVP 58-AgNPs, 0.375 g PVP (MW=58,000) was dissolved in 70 mL ultrapure water according to previous study.[4] Then, 2.25 mL of $AgNO_3$ aqueous solution (100 mM) was added into the solution, and the mixture was stirred for 5 min before 2.75 mL of ice-cold $NaBH_4$ (80 mM) was added under vigorous stirring and stirred in ice cold bath for further 30 min.

PVA-protected AgNPs. Poly(vinyl alcohol)-124 (PVA) coated AgNPs were synthesized by reduction of $AgNO_3$ with KBH_4 and stabilized with PVA following the method described by Chio and Hu.[5] Typically, 0.3 mL of PVA aqueous solution (10%, m/v) was added into 50 mL of KBH_4 solution (20 mM) in ice bath. Then, 50 mL of 200 mM $AgNO_3$ solution was rapidly injected into the ice-cooled mixture under vigorous stirring.

GA-protected AgNPs. Following a previous literature,[6] into a boiling solution containing 10 mL of Gum arabic (GA, 10 g/L), 5 mL $AgNO_3$ (100 mM) and 34 mL of ultrapure water was added 1 mL of trisodium citrate dehydrate (100 mM). After 10 min, the system was cooled in an ice-bath.

Purification of AgCNPs. AgCNPs solutions were purified by centrifugal ultracentrifugation through 3 kD membrane (pore size around 1 nm, Millipore, MA) to remove dissolved Ag^+ and soluble byproducts. Specifically, Ag-containing NPs were centrifuged at 9600 rpm for 30 min and further purified by water with three replicates, after which the stock solutions were kept at 4 ^oC in the dark for later use, whereas the stock solutions were quantified by ICP-MS after HNO_3 digestion weekly.

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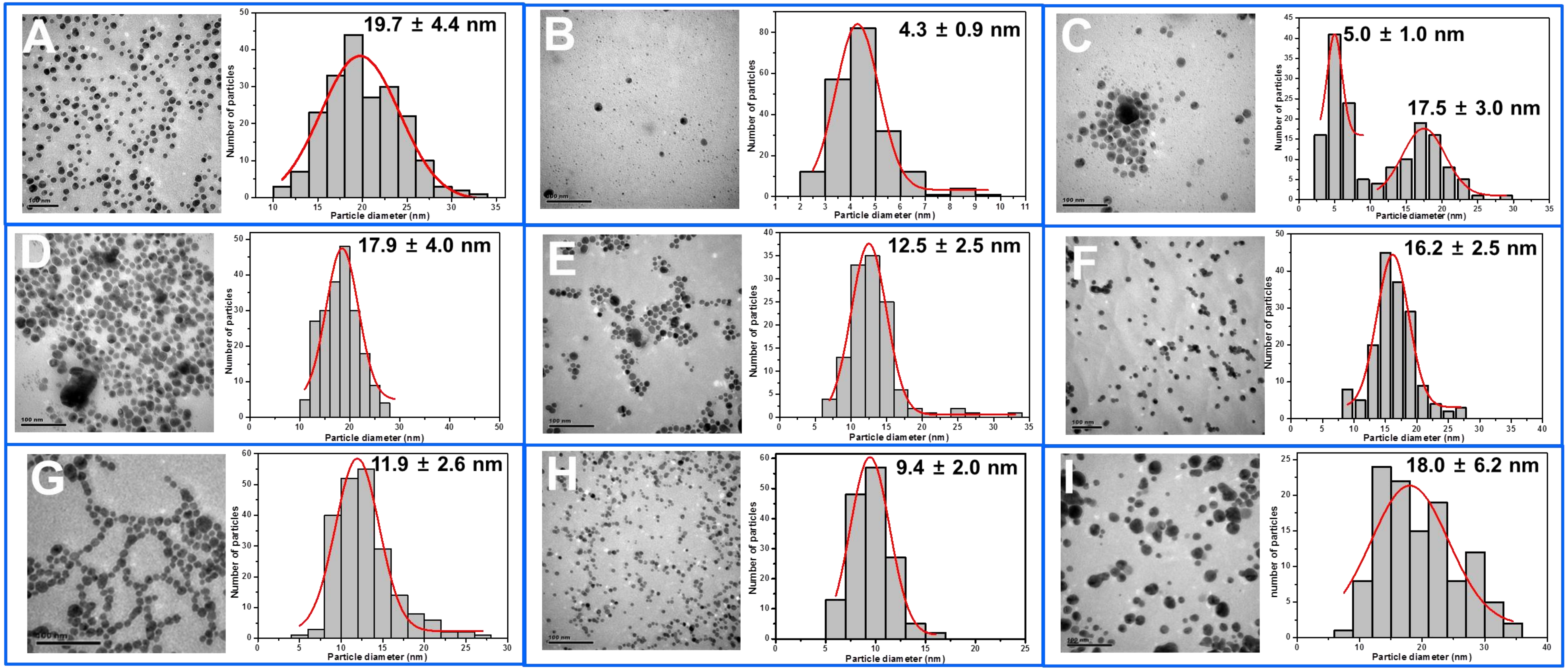

Fig. S1 TEM characterization and size distribution of aged AgCNPs: commercial AgNPs with unknown coating (A); Ag_2S NPs (B); Ag&Ag_2S NPs (C); AgCl NPs (D); Citrate-AgNPs (E); GA-protected AgNPs (F); PVP-3.5-AgNPs (G); PVP-58-AgNPs (H); PVA-protected AgNPs (I).

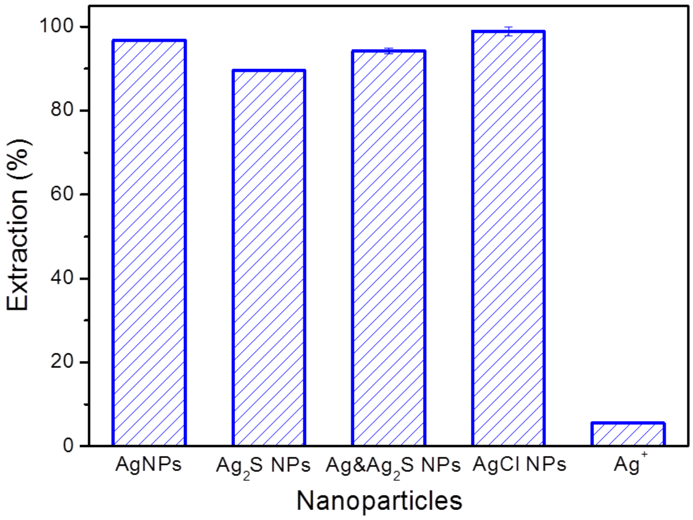

Fig. S2 Extraction efficiency of AgCNPs and Ag$^+$ by the proposed method. Here, 200 μL of IOMP suspension (100 mg/mL) was added to 50 mL HAc/NaAc buffer solution (10 mM, pH 7.0) containing ~ 1 mg/L various AgCNPs. The resulting solution was then shaken at 300 rpm for 1 h.

Table S1 Leaching of Fe after Suspending 20 mg IOMPs in 40 mL of different solutions for 3 h.

	%Fe leached per total Fe	
water matrix	**without aging**	**With aging**
tap water, pH 7.94	0.009 ± 0.001	0.006 ± 0.001
river water, pH 8.24	0.061 ± 0.008	0.050 ± 0.003
lake water, pH 8.35	0.008 ± 0.001	0.007 ± 0.001
WWTP effluent, pH 8.01	0.074 ± 0.001	0.074 ± 0.001
deionized water, pH 6.77	0.084 ± 0.004	0.043 ± 0.005
0.001 M HCl	1.14 ± 0.21	0.33 ± 0.09
0.01 M HCl	1.44 ± 0.20	0.67 ± 0.05
0.1M HCl	1.76 ± 0.16	1.58 ± 0.30
0.5 M HCl	14.4 ± 0.9	10.8 ± 1.4
1 M HCl	45.4 ± 1.7	37.9 ± 0.6
5 M HCl	100	100

Table S2 Analytical Performance of the Proposed Method.

Analyte	Ag_2S NPs
Linear range (μg/L)	0.20 - 100
Calibration curve	$y = 38.31\,x + 10.4$
r^2	0.9967
RSD (%, n = 6)	3.0
LOD (μg/L)	0.068

Table S3 Basic Characteristics of water samples.

Sample	pH	TOC (mg/L)
Tap water	7.94	5.3
River water	8.24	25.8
Lake water	8.35	18.4
WWTP effluent	8.01	36.7