Supplementary Information

Effective and Selective Extraction of Nobel Metal Nanoparticles from Environmental Water through a Noncovalent Reversible Reaction on an Ionic Exchange Resin

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Experimental Section

Materials and Chemicals:

All reagents were of analytical grade and used as received without further purification. Sodium borohydride ($NaBH_4$), $HAuCl_4$, AgNO3 and Na2PdCl4 were purchased from Merck (Darmstadt, Germany). Mercaptosuccinic acid (MSA), polyvinylpyrrolidone (PVP) 10, polyvinylpyrrolidone (PVP) 40, tetra-n-octylammonium bromide (TOAB), sodium hydroxide, sodium bicarbonate, hydrochloride acid, sodium citrate dihydrate and Amberlite IRN-78 (Matrix: styrene divinylbenzene copolymer, functional group: trimethylammonium) used in this study were purchased from VWR International (Leuven, Belgium). 11-Mercaptoundecanoic acid (MUA) and toluidine blue o (TBO) were purchased from Sigma-Aldrich (Steinheim, Germany). Humic acid (Carl ROTH, Karlsruhe, Germany) was used for the DOM test. Methanol was of analytical grade. Ultra pure water (UPW) from a Direct-Qsystem (Millipore, Billerica, USA) with a resistivity of 18.2 MΩ/cm was used for preparation of all solutions. For all experiments, glassware was thoroughly cleaned in a nitric acid steam or with aqua regia solution, rinsed 3-fold with UPW, and oven-dried overnight before use.

Instrumentation:

Instrumentation: UV-vis spectra were recorded using a Cary 50 Scan UV-vis spectrophotometer. The pH of the samples was measured using a Qph 70 pH-meter. The concentrations of NMNPs before and after separation and concentration were determined using a 4100ZL graphite furnace atomic absorption spectrometer (GFAAS, Perkin-Elmer, Germany), equipped with Zeeman-effect background correction, a transversally heated graphite atomizer (THGA) and an AS-71 auto-sampler. Ultracentrifugation was operated in the optima Max-E ultracentrifuge (Beckman, CA, USA) using a TLA-45 rotor. The zeta potential of our samples was determined with a Zeta Potential Analyzer (ZETASIZER Nano series, Germany). TEM images were taken on a JEOL JEM 2010 operating at 120 kV. Scanning electron microscopy (SEM) was performed with JEOL JSM5900LV coupled to an energy dispersive x-ray fluorescence (EDX) (Röntec, Germany) at 15 kV. IR spectra of the samples were recorded on a Varian FTIR-670 spectrometer, using a GladiATR accessory with a diamond ATR element. A more detailed description of IR analysis is provided later.

Synthesis of NMNPs in water:

The citrate-stabilized Au-, Ag- and Pd-NPs were synthesized by reduction of metallic salts with sodium borohydride and stabilized with sodium citrate. Details are described in our previous study. [1]

Preparation of surfactant-stabilized NMNPs in water:

The surfactant-stabilized NMNPs were prepared by the method of *Mahl et al.* [2] with minor modification. We added 5 mL of PVP10 (100 mM), 5 mL of PVP40 (25 mM), or 1 mL of TOAB (10 mM) respectively to 20 mL of citrate-stablized NMNPs suspension. The resulting mixtures were equilibrated at room temperature for at least 2 h before use.

Separation and concentration of NMNPs:

Separation and preconcentration of NMNPs: First, the freshly prepared NPs were modified by MSA; a mixture of 5 mL 0.01 mol L^{-1} MSA and a volume of 45 to 995 mL prepared NPs solution was shaken (200 rpm) for 3 h at room temperature. Then, the MSA-modified NMNPs colloidal solution (pH: 8.0 ± 0.5 by 0.5 M NaOH) was, by means of peristaltic pump, passed through a glass tube with an internal diameter of 20 mm and a length of 9 cm tightly packed (packing length, 2 cm) with 4.5 g of Amberlite IRN-78 nuclear grade ion exchange resin (particle size 500 μm) supplied by Alfa Aesar (Karlsruhe, Germany). The influent rate was controlled between 1.5 and 2.5 mL min^{-1}. Afterwards, the NPs-loaded resin was rinsed with 50 mL methanol and then transferred to 25 mL mixture of formic acid and methanol. The cleavage reaction was conducted using gentle shaking (250 rpm) for different time (2-88 h; it depends on the initial concentration of NMNPs) at room temperature. After settling for 30 min the supernatant containing NPs was collected and concentrated to 5 mL by evaporation under nitrogen.

Analysis of surface carboxyl groups via TBO dye adsorption assay:

The carboxyl groups of MSA on the surface of NPs were analysed by the TBO colorimetric method according to *Sano et al.* [3] with following modifications. Carboxyl groups on the surface of extracted NPs were complexed with 0.5 mM Toluidine Blue O of pH 10 at room temperature overnight. Non-complexed dye was removed with 0.1 mM NaOH and desorption of dye molecules complexed to the carboxyl groups on the surface of extracted NPs was conducted with 50% acetic acid solution. Absorbance was recorded by UV-vis spectroscopy.

Selectivity of separation and extraction of NPs:

In order to study the selectivity of separation and extraction of NPs using the proposed method, the solution of NPs and their corresponding metal ions with MSA was passed through the column. Afterwards, the filtrate was measured by GFAAS, to understand how much of the NPs and ions loaded onto the resin. And then the procedure was operated according to the above-mentioned way.

IR analysis of concentrated NPs:

To remove any free MSA residue, the concentrated NPs suspension was centrifuged at 12000 rpm for 10 min and the deposited NPs were redispersed in fresh formic acid. The centrifuging and redispersing process was repeated three times to ensure complete purification. Thereafter, the purified NPs suspension was analysed by IR spectroscopy.

Equations [4] for calculating separation and recovery efficiencies: The concentration of NPs in the initial suspension (C_i, μg L^{-1}) and filtrate (C_f, μg L^{-1}) were measured by GFAAS and the efficiency of separation was estimated as

$$Efficiency\ (\%) = 100 \times \frac{(C_i - C_f)}{C_i} \qquad Equation\ (1)$$

After the cleavage step, the recovery of NPs was calculated as

$$\mathrm{Recovery}\ (\%) = 100 \times \frac{C_c \times V_c}{(C_i - C_f) \times V_i} \qquad Equation\ (2)$$

where C_c is the concentration of concentrated NPs suspension (μg L^{-1}), V_c is the volume of concentrated suspension (mL), and V_i is the volume of NPs hydrosol source (mL).

References for Supporting Information

[1] L. Li, K. Leopold, *Anal. Chem.* 2012, 84, 4340-4349.

[2] D. Mahl, C. Greulich, W. Meyer-Zaika, M. Köller, M. Epple, J. Mater. Chem. 2010, 20, 6176-6181.

[3] S. Sano, K. Kato, Y. Ikada, Biomaterials 1993, 14, 817-822.

[4] Although the NMNPs-loaded resin was rinsed with 150 mL methanol after the separation, there was no metal found in the methanol using GFAAS. Consequently, we did not consider a loss of metal in the 250 mL methanol when we calculated the separation efficiency (Equation 1).

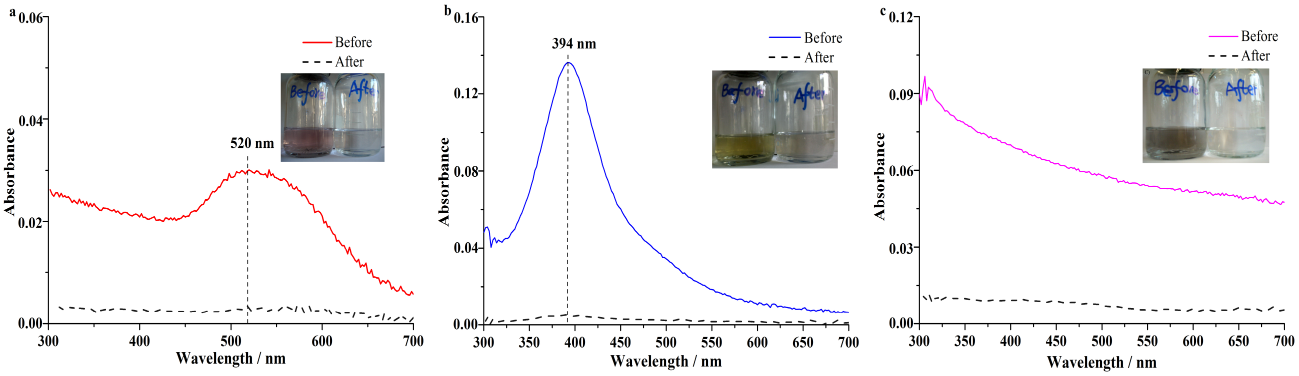

Figure S1. UV-vis spectra of the MSA-modified NMNPs aqueous solution measured before and after adsorption of NPs onto the resin. Inset: visual appearance of samples before and after adsorption. a) Au-NPs, b) Ag-NPs, and c) Pd-NPs.

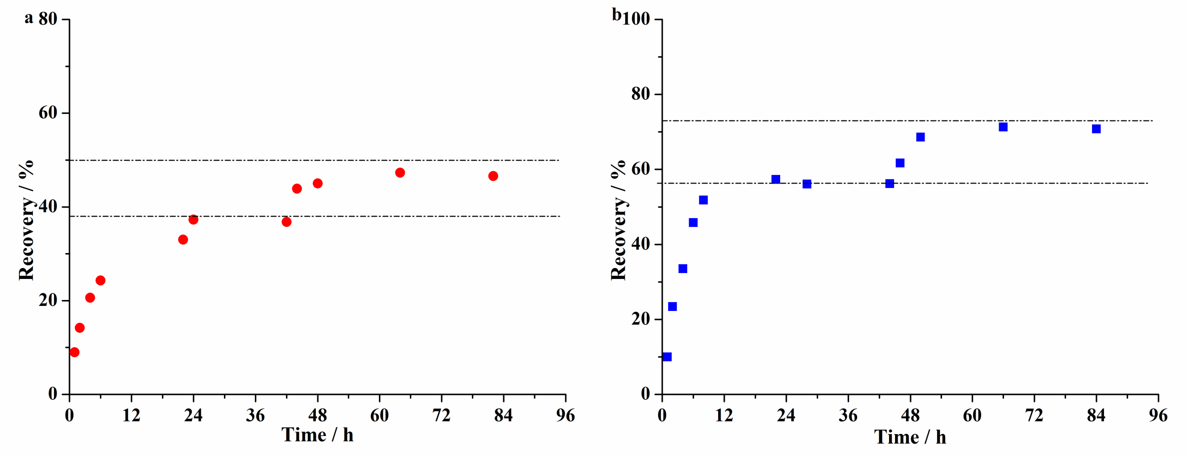

Figure S2. Chemical cleavage reaction of adsorbed MSA-modified Au-NPs (a) and Ag-NPs (b) by 8% formic acid in methanol. The initial concentrations of Au- and Ag-NPs solution are 1 mg L^{-1} respectively. After 42 h, a second equivalent of 8% formic acid in methanol was added.

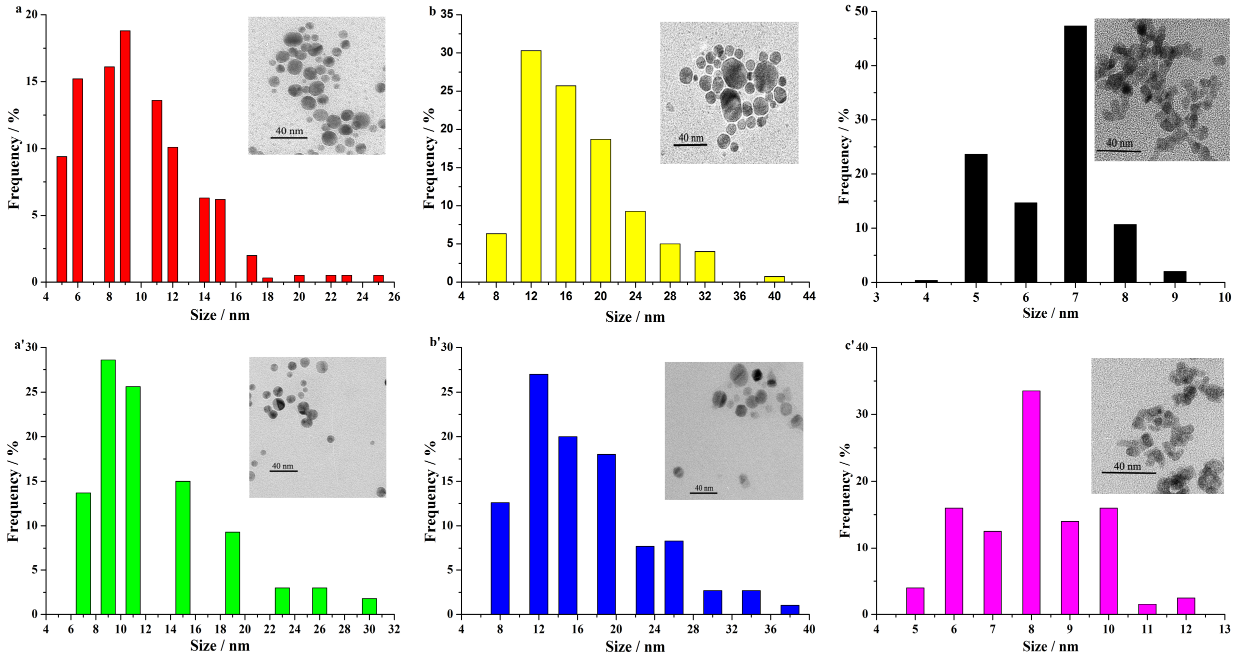

Figure S3. Size distribution of the NPs before (a, b, and c) and after (a', b' and c') the separation and extraction. Inset: TEM images of original and extracted samples. a and a') Au-NPs, b and b') Ag-NPs, and c and c') Pd-NPs.

Table S1. The changes in pH and Zeta potential before and after the NPs passing through the column with resin.

NPs	pH			Zeta potential (mV)		
	Initial hydrosol	Before loading	After loading	Initial hydrosol	Before loading	After loading
Au	2.50 ± 0.20	8.00 ± 0.50	11.46 ± 0.16	-22.8 ± 0.8	-33.3 ± 3.4	-37.2± 0.8
Ag	7.60 ± 0.02		11.72 ± 0.05	-21.5 ± 0.9	-23.8 ± 1.5	-27.3 ± 2.1
Pd	8.21 ± 0.04		11.87 ± 0.09	-16.0 ± 1.5	-29.0 ± 2.7	-35.1 ± 2.5

Table S2. The effect of flow rate on separation efficiency of nanoparticles.

Flow rate mg L^{-1}	Nanoparticles	Separation efficiency (%)
2.5	Au	70.9 ± 1.3
	Ag	68.5 ± 2.7
	Pd	71.5 ± 1.9
2.0	Au	82.7 ± 1.7
	Ag	81.1 ± 0.6
	Pd	79.1 ± 0.8
1.5	Au	97.6 ± 1.1
	Ag	93.0 ± 1.5
	Pd	87.1 ± 1.4

Table S3. Effect of different coatings on the proposed method.

NMNPs	Coating	Separation efficiency (%)		Recovery (%)	
		Witout MSA	With MSA	Without MSA	With MSA
Au	Citrate	41.5 ± 2.9	97.6 ± 1.1	29.7 ± 4.5	105.0 ± 2.4
	PVP10	35.9 ± 1.7	98.3 ± 0.8	32.5 ± 2.7	95.5 ± 1.1
	PVP40	29.2 ± 0.9	90.2 ± 2.1	33.2 ± 5.2	36.3 ± 1.7
	TOAB	42.5 ± 1.3	99.5 ± 1.5	40.5 ± 2.8	88.6 ± 2.0
Ag	Citrate	35.7 ± 2.5	93.0 ± 1.5	31.2 ± 3.9	107.4 ± 4.0
	PVP10	37.9 ± 2.0	95.0 ± 0.9	38.7 ± 1.7	103.7 ± 1.8
	PVP40	30.1 ± 1.9	97.1 ± 0.8	32.8 ± 2.9	15.4 ± 2.5
	TOAB	38.6 ± 3.1	89.9 ± 1.3	40.2 ± 3.1	85.0 ± 1.6
Pd	Citrate	32.7 ± 2.1	87.1 ± 1.4	36.9 ± 0.8	106.6 ± 3.5
	PVP10	40.5 ± 2.9	86.6 ± 2.7	36.8 ± 3.0	92.4 ± 3.5
	PVP40	26.8 ± 5.7	89.1 ± 1.1	31.5 ± 4.1	15.3 ± 2.9
	TOAB	37.8 ± 2.4	90.3 ± 2.1	38.9 ± 2.9	88.6 ± 4.1

Table S4. Recovery of NPs in comparison to corresponding ions using the proposed method.

Element	Concentration (μg L^{-1})		Concentration (μg L^{-1})		Recovery (%)	
	Spiked NPs	Spiked ions	Extracted NPs	Extracted ions	NPs	Ions
Au	80	10	77.1 ± 1.8	< 1.0 [a]	96.4 ± 2.2	< 10
Ag	80	10	81.4 ± 1.0	< 0.5 [b]	101.8 ± 1.3	< 5
Pd	80	10	81.6 ± 2.0	< 0.5 [c]	102.0 ± 2.5	< 5

[a] The detection limit of Au is 1.0 μg L^{-1} using the GFAAS, and the concentration was below detection limit; [b] The detection limit of Ag is 0.5 μg L^{-1} using the GFAAS, and the concentration was below detection limit; [c] The detection limit of Pd is 0.5 μg L^{-1} using the GFAAS, and the concentration was below detection limit.

Table S5. Characteristics of real environmental water samples.

Sample [a]	pH	DOM mg L^{-1}	Ca (mg L^{-1})	Zn (mg L^{-1})	Cu (mg L^{-1})	Fe (mg L^{-1})
Danube river	8.00 ± 0.01	< 1	65.23 ± 0.03	n.d. [b]	n.d.	n.d.
Stanberger lake	8.05 ± 0.01	< 1	40.88 ± 0.32	n.d.	n.d.	n.d.
Brook water	8.22 ± 0.02	< 1	53.71 ± 1.86	n.d.	n.d.	0.003 ± 0.002

[a] The sample was filtrated by 0.45 μm syringe filter; [b] Concentration was below detection limit (< 1 μg/L).