Gold adsorption on the carbon surface of C/Co nanoparticles allows magnetic extraction from extremely diluted aqueous solutions

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Supporting Information

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1. Materials and Methods

Nanoparticle preparation. Carbon coated cobalt nanoparticles were produced by reducing flame spray synthesis [1]. The precursor is dispersed by an oxygen jet forming a spray, which is subsequently ignited by a premixed flame. In order to prepare metallic nanoparticles, the flame is operated in a nitrogen atmosphere (PanGas, 99.999%). The precursor is composed of 25 wt % Co(II)-2-ethylhexanoate (65 wt %. in mineral spirit, Aldrich) and 75 wt % tetrahydrofuran (THF) (ACS, Acros).

Preparation of the acid washed particles:. The as-prepared particles (Co/C) were treated in a solution of 20 ml water (deionized) and 0.2 ml HCl (puriss p.a. $\geq$ 36.5 %, Fluka) for 30 min in a ultrasonic bath (VWR, ultrasonic cleaner). The nanobeads were recovered from the reaction mixture with the aid of a neodymium based magnet (N42, Q-40-40-20-N, Webcraft GmbH) and washed 3x with water, 3x with DMF. Each washing step consisted of suspending the particles in the solvent for 5 minutes by ultrasonication or by stirring and retracting the particles from the solvent by the aid of the magnet. After this treatment, the particles are referred to as "washed". This procedure is necessary to remove the influence of surface alterations due to solvents and acids.

Gold extraction from water. The different solutions were prepared with a gold standard for atomic adsorption spectroscopy (AAS) (1002 mg / l $\pm$ 4 mg / l, Fluka).This solution is made of 1 l ultrapure, filtrated water (Millipore, S185, resistance >18.2 MΩ), 300 μl HCl (fuming 37%, TraceSelect, Fluka) and 100 μl HNO$_3$ (> 69.0%, TraceSelect, Fluka). The particles were placed in the solution (10 mg particles in 5 ml solution for gold

concentrations between 100 and 1000 ppm (measured with AAS) and 20 mg particles in

10 ml solution for gold concentrations between 10 ppm and 1 ppb). The particles were

dispersed in the solution by sonication for 10 sec and then by shaking 4 min 50 sec with

Heidolph REAX Top at room temperature. The nanobeads were retracted with the aid of

a magnet and the solution collected. 0.25 ml of a 60 % wt HCl/ HNO_3 were mixed to 4.75

ml of the collected solution to obtain a 3 % HCl/ HNO_3 solution, for measuring AAS or

ICP-MS. The Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) measurements

were done on two different instruments (ELAN and Agilent 7500 cs) with iridium as

internal standard (10 ppb and 100 ppb respectively). The Atomic Adsorption

Spectroscopy (AAS) measures were conducted on Varian Spectra AA 220FS at a

wavelength of 242.8 nm and a flame composition of 13.50 l / min air and 2.00 l/min

acetylene.

Particles characterization. The specific surface area of the as-prepared particles was

determined by BET measurement (Brunauer-Emmett-Teller, Micromeritics Tristar 3000).

The transmission electron microscopy (TEM) images were done on CM30 ST (Philips,

LaB_6 cathode, operated at 300kV, point resolution ~4Å). and the X-ray diffraction

spectroscopy on X'Pert PRO-MPD (CuKα radiation, X'Celerator linear detector system,

step size of 0.033°, ambient conditions). For transmission electron microscopy (TEM)

investigation, the material was deposited onto a holey carbon foil supported on a copper

grid. TEM investigations were performed with a CM30ST microscope (FEI; LaB_6

cathode, operated at 300 kV, point resolution ~2Å).

Scanning transmission electron microscopy (STEM) images were recorded with a high-angle annular dark field (HAADF) detector at a Tecnai F30 microscope (FEI; field emission gun, operated at 300 kV, point resolution ~2Å). HAADF-STEM images reveal the metal particles with bright contrast (Z contrast). Energy dispersive X-ray spectroscopy (EDS) has been done using an EDAX system which is attached to the Tecnai F30 microscope. The thermal stability was quantitatively followed by thermoanalysis (Linseis TG/STA-PT1600, 25–700 8C, 10 8C min^{-1}) under air. The saturation magnetization was measured by a vibrating sample magnetometer (Princeton measurements corporation, **MODEL 3900 VSM SYSTEM).**

Cobalt concentration in water. The cobalt concentration in the water after gold adsorption by the particles was measured by AAS (Varian Spectra AA 220FS at a wavelength of 240.7 nm and a flame composition of 13.50 l / min air and 2.00 l / min acetylene).

2. Supplementary Results and Discussion

Acid long term stability and recycling. Above earlier observations on metal migration across graphene offer a starting point for explaining why some cobalt slowly leaches out of otherwise perfectly coated particles when exposed to acidic solutions over several weeks. We exposed the carbon coated nanomagnets to concentrated hydrochloric acid (24 % HCl) to simulate application in highly acidic conditions as during hundreds of extraction runs with recycle. Figure S1 shows that a few mass percent of the cobalt was dissolved in the first week of contact with strong acids. Prolonged contact of the as-prepared nanomagnets with highly acidic solutions resulted in up to 21 wt% loss after 8 weeks. The remaining particles, however, are of exceptional stability and virtually no cobalt is lost anymore during processing, i.e. the particles appear stabilized. Most cobalt loss immediately occurs during the first few hours of acid immersion which allows preconditioning (i.e. removal of unstable parts of the reagent prior to use) as can be seen on Figure S2 where the cobalt concentration present in the solution was analyzed everyday during a month.
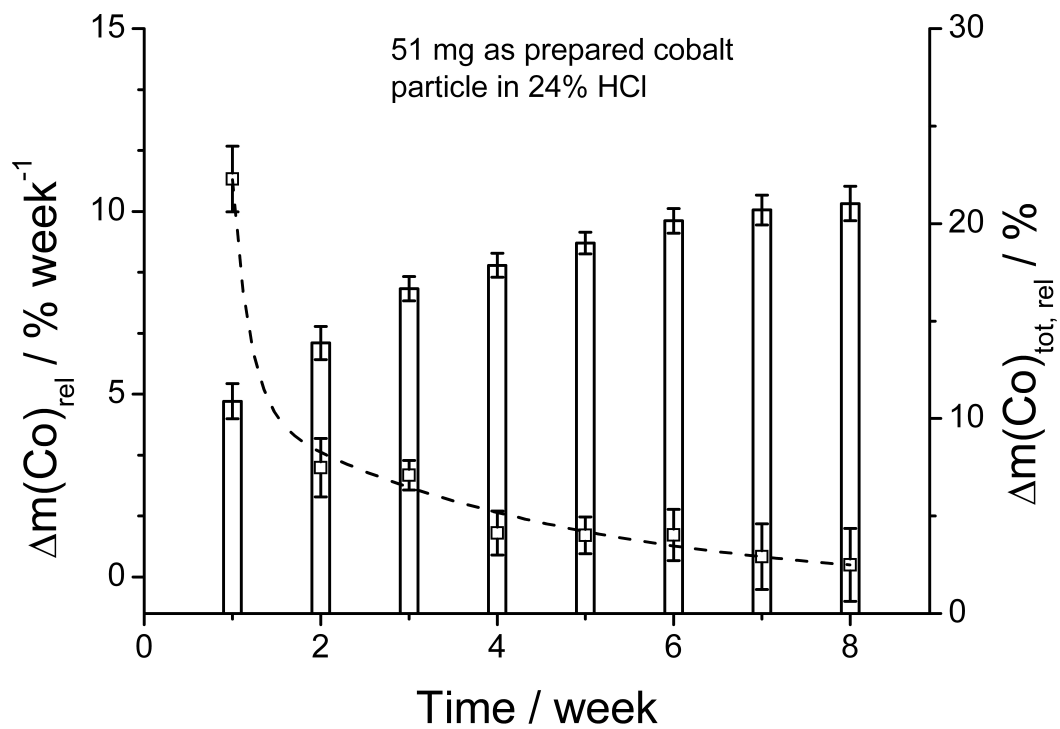
Figure S1: Cobalt ions release in highly acidic media. Solution change and analyzed every week.
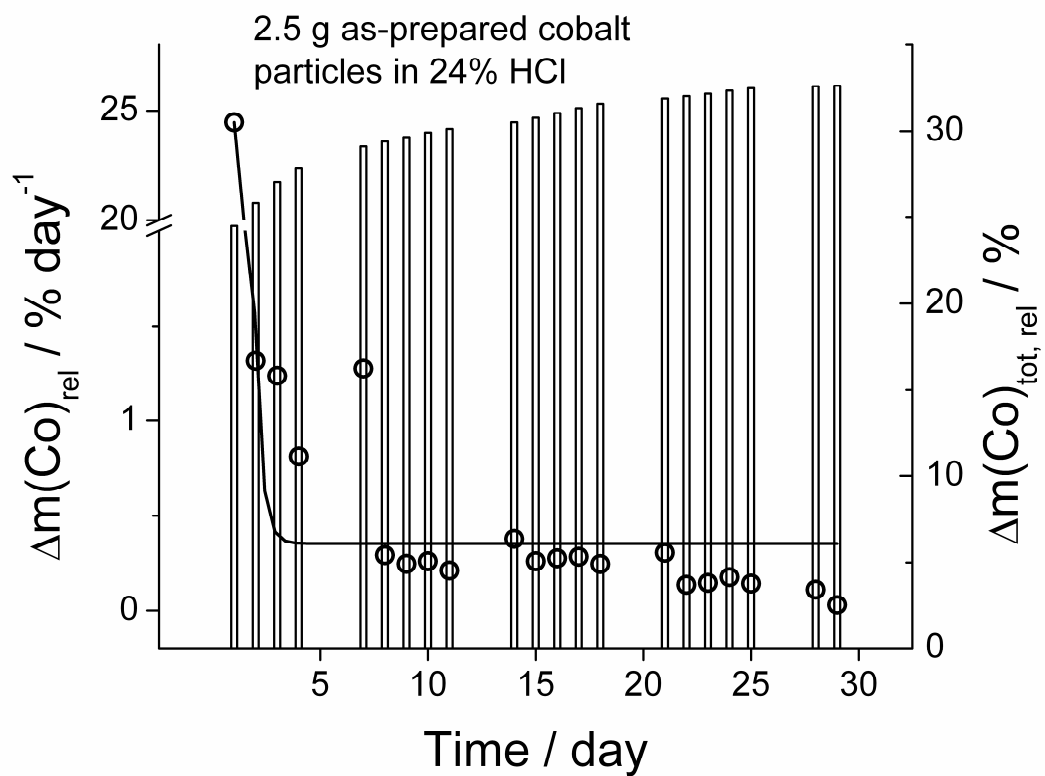
Figure S2: Cobalt ion release in highly acidic media (24 % HCl). The solutions were changed and analyzed every day to determine an accurate Co-ion release profile.

Thermal stability. On Figure S3, it can be seen that the carbon coated magnetic

nanoparticles are stable until 213 °C. They are afterward oxidized and gain 24 %

relatively to their mass.
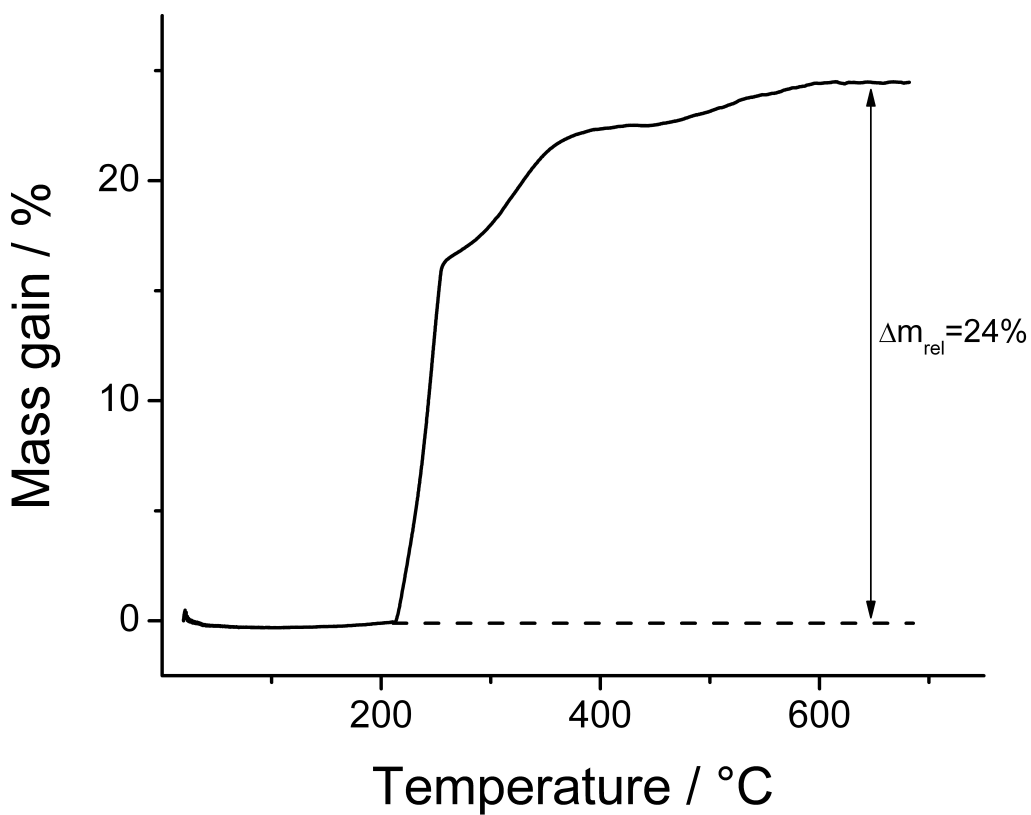
Figure S3: Thermal stability of the carbon coated cobalt nanoparticles under air

conditions.

Loading capacity. The comparison of the gold loading capacity of different separation methods shows that the carbon coated nanomagnets have a comparable performance regarding the gold adsorption capacity.
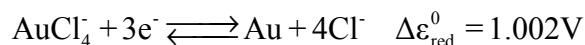
$C(Au)_0{}^a$ (ppm)	$C(Au)_{final}{}^a$ (ppm)	Loading gold mg per unit adsorbent [b]	Ref.
50	2.5	48 [d]	[2]
250	136	114 [d]	[3]
3000	1748	60 [e]	[4]
104	0.3	72 [e]	This work

Table S1. Comparison of the loading capacity (in mg gold) per gram adsorbent of different separation processes. a: concentration of gold present in the solution in ppm (mg metal per kg solution); b: quantity gold in mg adsorbed on a unit (ml [d] or g [e,f]) adsorbent; c: temperature at which the adsorption was done; d: per g polymer; e: per g magnetic particles; TW: this work.

Oxydation potential of gold. The calculations of the oxidation potential of gold were done as following.
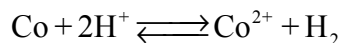
Reduction potential:

$$Co^{2+} + 2e^- \rightleftharpoons Co \qquad \Delta\varepsilon^0_{red} = -0.28V$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad \Delta\varepsilon^0_{red} = 0.000V$$

$$AuCl_4^- + 3e^- \rightleftharpoons Au + 4Cl^- \quad \Delta\varepsilon^0_{red} = 1.002V$$

Equation and constants:

$$\Delta\varepsilon_{reaction} = \Delta\varepsilon^0_{reaction} - \frac{RT}{zF} \ln \frac{c_{red}}{c_{ox}}$$

$R = 8.31 J \bullet mol^{-1} \bullet K^{-1}$
$T = 295K$
$F = 96485 s \bullet A \bullet mol^{-1}$

Reactions involved during the adsorption process:

$$Co + 2H^+ \rightleftharpoons Co^{2+} + H_2$$

$c_{red} = [Co^{2+}][H_2]$ $\qquad$ $c_{ox} = [H^+]^2$
$[Co^{2+}] = 8 \bullet 10^{-6} mol \bullet l^{-1}$ $\qquad$ $[H^+] = 10^{-2} mol \bullet l^{-1}$
$[H_2] = 1.5 \bullet 10^{-3} mol \bullet l^{-1}$ $\qquad$ $z = 2$
$\qquad \Delta\varepsilon_{reaction} = 0.366V$

$$2Au^{3+} + 3Co \rightleftharpoons 2Au + 3Co^{2+}$$
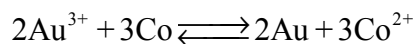
$c_{red} = [Co^{2+}]^3$ $\qquad$ $c_{ox} = [Au^{3+}]^2$
$[Co^{2+}] = 8 \bullet 10^{-6} mol \bullet l^{-1}$ $\qquad$ $[Au^{3+}] = 5.08 \bullet 10^{-5} mol \bullet l^{-1}$
$\qquad\qquad\qquad\qquad z = 6$
$\qquad \Delta\varepsilon_{reaction} = 1.348V$

Cobalt released during gold adsorption. On Figure S4, it can be seen that the amount of cobalt released during the adsorption increase with the initial gold concentration present in the solution.
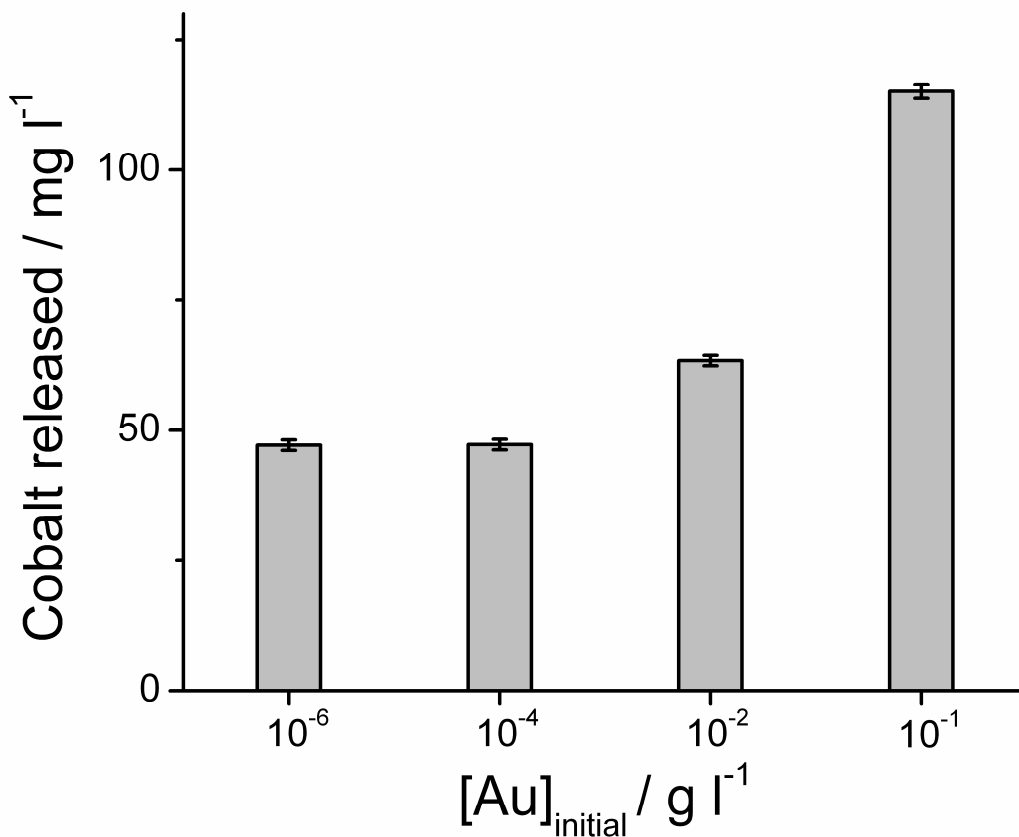
Figure S4: Cobalt released during the gold adsorption. Adsorption experiments were carried out using 20 mg particles in 10 ml gold solution during 5 minutes. Concentrations were measured by atomic absorption spectroscopy (AAS).

Supporting Literature

1.   R. N. Grass and W. J. Stark, *J. Mater. Chem.*, 2006, **16**, 1825-1830.
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