

Supporting Information

Effect of phosphate, sulfate, arsenate and pyrite on surface transformations and chemical retention of gold nanoparticles (Au-NPs) in partially saturated soil columns

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X-ray Photoelectron Spectroscopy (XPS)

Experimental

XPS measurements were performed on a Kratos AXIS-Ultra DLD spectrometer, using a monochromatic Al $K\alpha$ source at 15-75 W and detection pass energies of 20-80 eV. Dissolved materials were deposited on Si substrates for the XPS analysis and, as a reference, powder of the pyrite source material was also measured. Sample instabilities under the probing beam were treated by following the evolution of spectral lines through repeated scans. This accounted for both irreversible chemical changes, which were minor in all cases, and independently, the charging effects with which we could gain useful information, as discussed below. No calibration of the energy scale was applied, because of use of the evolution of raw binding energies (as a function of time and source power), encountering differential (positive) charging up to 0.7 eV (see Results below).

Results

Traces of elements found in these samples should be noted, including mainly Na, Cl, C and O. To first approximation, their presence did not interfere with the analysis of the gold nanoparticles. Of greater concern were the traces of oxidized Fe and oxidized S, which were found in the reference sample as well. They are believed to originate in pyrite domains that were oxidized and therefore became inactive during the treatment. The amount of residual FeS_2 after treatment was proven to be extremely small, if at all, and its possible presence was taken into account in the analysis of gold S-passivation. It should also be noted that Cu was detected, presumably an impurity in the gold nanoparticles that segregated to the surface and, therefore, might play a role in the binding of sulfur.

A qualitative inspection of elemental proximities was gained from the differential charging effects encountered under our experimental conditions. While Au, Cu and reduced-S did not undergo any observable peak shift (also the Si-wafer signal), all other elements, including the oxidized-S, exhibited a consistent shift toward higher binding energies. This result provides indirect evidence that the reduced sulfur signal relates indeed to gold passivation, perhaps also involving Cu.

Two components of reduced-S were resolved at comparable amounts, with their S $2p_{3/2}$ binding energy appearing around 161.5 eV and 162.5 eV. We associate these signals with different binding states, such as a single bond and a two-bond passivation of the gold. It is possible that binding to Cu (we found $\text{Au/Cu}=4.5$) indicates the more reduced S state.

The amount of reduced S is weighted with respect to the gold, yielding $\text{S}^{\text{red}}/(\text{Au}+\text{Cu}) \leq 0.11$ (with experimental relative error of about 10%); this translates for spherical particles, at the upper limit, into *monolayer coverage*. In this estimation, the possibility of having residual non-

reacted pyrite is not taken into account and, therefore, based on the analysis of the Fe 2p line, the relevant amount of S bonded to gold may be only ~50% of the value given above.

Table S1: XPS-derived atomic concentrations (%) and recorded charging shifts (meV) of the dominant elements found in the reacted sample. The Si substrate and its native oxide are included. Note the clear contrast between elements that exhibited charging peak-shifts and those that are practically at fixed energy. L denotes positive charging, namely a shift to a higher binding energy. R denotes a shift to a lower binding energy, which may be relevant, within the experimental error, for the Cu and the Au lines.

	S red.	S ox	Au	Cu	Fe	C	O	Na	Si waf.	Si ox
atomic %	0.26 *	1.69	1.68	0.39	3.59	48.02	34.27	6.24	2.15	0.71
shift (meV)	< 45 L	230 L	0 R	< 20 R	100-240 L **	220 L	190 L	110 L	0	~120 L

* The two states of reduced sulfur are summed here (see Discussion above).

** Intensity increase and line shape changes were encountered at the Fe 2p signal as a function of time under the x-ray beam.

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