**SUPPLEMENTARY INFORMATION**

# SYNTHESIS OF VARIOUS CRYSTALLINE GOLD NANOSTRUCTURES IN WATER: THE POLYOXOMETALATE β-$[H_4PMo_{12}O_{40}]^{3-}$ AS THE REDUCING AND STABILIZING AGENT

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**Contents**

**General mother solution work-up**

Gold nanostructures are recovered from the mother solution in the following manner. The mother solution is centrifuged at 13,000 rpm for 30 min, the solid collected and dispersed in water. The washing process, followed each time by a 30 min centrifugation at 6,000 rpm, was repeated until a clear and colorless supernatant solution was obtained. Generally, this result is already achieved after the first centrifugation even though at least one washing step is applied. Finally, the collected solid was re-dispersed in water for various analyses. UV-visible spectra were also run for the supernatant solutions and found to contain little, if any, gold nanostructures.

**XPS analysis of the various Au nanostructures**

The samples for XPS (X-ray Photoelectron Spectroscopy) analysis were deposited on glassy carbon wafers as supports. The XPS spectrometer was a Thermo Electron ESCALAB 220i XL. A non-monochromatic X-ray Al Kα source was used for excitation, with an incident energy of 1486.6 eV. The X-ray power was 300 W (20 mA x 15 kV). The pass energy was 20 eV for detail spectra. The beam diameter was roughly (6 x 7) $mm^2$. The non monochromatic source was selected because it delivers a higher energy compared to the monochromatic one and is thus more suitable in case elements in low concentrations are to be determined. Among the possibilities of the XPS technique, attention was focused on the extraction of oxidation states of elements from the treatment and recombining of complex photoelectric peaks. Au samples were centrifuged at 13,000 rpm for 30 min, re-dispersed in water, and then, centrifuged at 6,000 rpm for 30 min. The collected solid is finally deposited on a glassy carbon wafer and let to dry in a continuously argon-flushed box.

The analysis was carried out on Au nanoparticles ($C^0_{POM}$ = 1mM, γ = 1), on nanowires ($C^0_{POM}$ = 0.1 mM, γ = 4) and on nanoplates ($C^0_{POM}$ = 0.1 mM, γ = 0.2). The results show invariably the presence of $Au^0$ as the unique valence of gold present.

**Au nanoparticles ($C^0_{POM}$ = 1mM, γ = 1)**

- Only the metallic form of gold is present with the $4f_{7/2}$ and $4f_{5/2}$ levels located respectively at 84.0 ± 0.3 eV and 87.8 ± 0.3 eV. The absolutely clean $Au^0$ spectrum is worth pointing out.

- Two valence states were found for Mo: $Mo^{V}$ ($3d_{5/2}$ and $3d_{3/2}$ respectively at 231.7 ± 0.3 eV and 234.9 ± 0.3 eV) and $Mo^{VI}$ ($3d_{5/2}$ and $3d_{3/2}$ respectively at 232.9 ± 0.3 eV and 236.1 ± 0.3 eV). $Mo^{VI}$ is the more abundant of the two species.
- Phosphorus is detected at 133.7 ± 0.3 eV ($2p_{3/2}$) and at 134.8 ± 0.3 eV ($2p_{1/2}$) in a $PO_4^{3-}$ environment.
- Taking into account the Scofield sensitivity factors, the relative atomic composition of the analyzed deposit is 58% Mo and 42% Au even though such values must mainly be considered as indicative.

**Au nanowires and nanoplates**

Exactly the same XPS spectra were obtained for nanowire and nanoplate samples. They replicate the same spectra as found for nanoparticles. Very slight shifts in peak locations are due to the fact that the new values were collected several months after the first ones and the detectors had been re-calibrated. In any case, the shifts do not exceed the usual errors in our experimental set-up.

- Only the metallic form of gold is present with the $4f_{7/2}$ and $4f_{5/2}$ levels located respectively at 83.8 ± 0.3 eV and 87.5 ± 0.3 eV. The absolutely clean $Au^{0}$ spectrum is worth pointing out.
- Two valence states were found for Mo: $Mo^{V}$ ($3d_{5/2}$ and $3d_{3/2}$ respectively at 231.5 ± 0.3 eV and 234.6 ± 0.3 eV) and $Mo^{VI}$ ($3d_{5/2}$ and $3d_{3/2}$ respectively at 232.7 ± 0.3 eV and 235.8 ± 0.3 eV). $Mo^{VI}$ is the more abundant of the two species.
- Phosphorus is detected at 133.4 ± 0.3 eV ($2p_{3/2}$) and at 134.8 ± 0.3 eV ($2p_{1/2}$) in a $PO_4^{3-}$ environment.
- Taking into account the Scofield sensitivity factors, the relative atomic composition of the analyzed deposit is 35.2% Mo and 64.8% Au for nanoplates, and 55.7% Mo and 44.3% Au for nanowires. Here again, such values must mainly be considered as indicative.

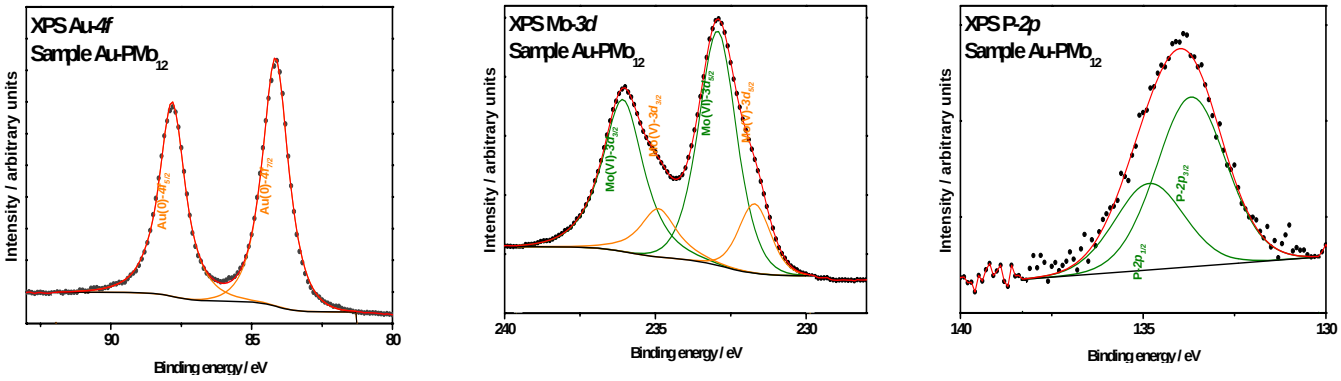


**Figure S1a.** Deconvolution of the core levels for gold (*4f*), Mo (*3d*) and P (*2p*) XPS spectrum in the synthesis with $\mathbf{C^0_{POM}}$ **= 1mM, γ = 1.**

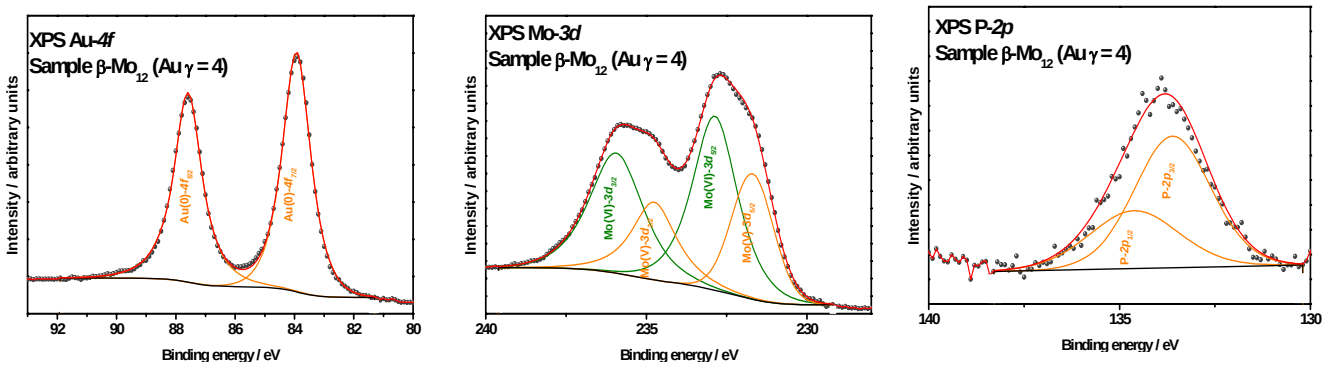


**Figure S1b.** Deconvolution of the core levels for gold (*4f*), Mo (*3d*) and P (*2p*) XPS spectrum in the synthesis with $\mathbf{C^0_{POM}}$ **= 0.1mM, γ = 4.**

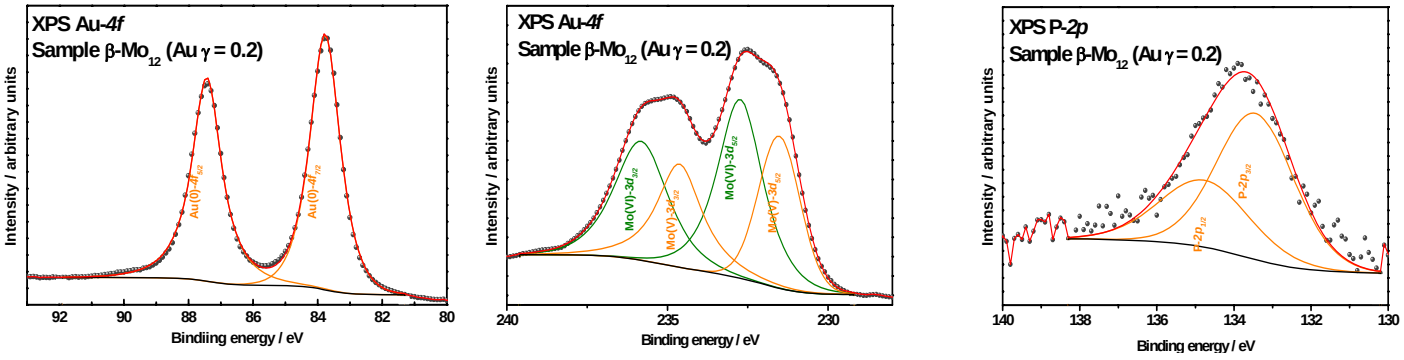


**Figure S1c.** Deconvolution of the core levels for gold (*4f*), Mo (*3d*) and P (*2p*) XPS spectrum in the synthesis with $\mathbf{C^0_{POM}}$ **= 0.1mM, γ = 0.2.**

**Electrochemical characterization of the $Au^0$ NPs**

**Electrode preparation**. A glassy carbon electrode is thoroughly polished (see Experimental Section) and then is modified as follows: a few μl of the centrifuged and washed $Au^0$ nanoparticle suspension in water are deposited on the polished glassy carbon surface (GC), and let to dry in the air at room temperature. The surface is then covered with 3 μl of 5 wt % Nafion solution and again let to dry in the air at room temperature. The cyclic voltammogram run in pure pH = 2 medium shows simultaneously the characteristic features of bulk gold electrodes and redox systems which correspond to those of the POM.

**Figure S2.** Cyclic voltammogram run in pure 0.5 M $H_2SO_4$ (pH = 0.3) medium with a glassy carbon electrode modified with $Au^0$ NPs as explained in the text. The nanoparticles were prepared using $C^0_{POM}$ = 0.5 mM, $\gamma$ = 1. Scan rate: 50 mV $s^{-1}$.

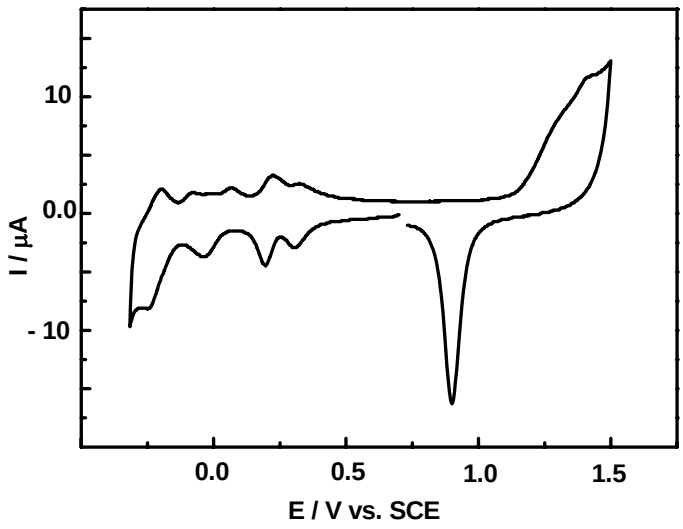

**Figure S3.** Cyclic voltammogram with the glassy carbon electrode modified with $Au^0$ nanoparticles as described previously and showing a typical two-wave reduction of dioxygen. The nanoparticles were prepared using $C^0_{POM}$ = 0.1 mM, $\gamma$ = 1. The background current in the absence of dioxygen is also shown. The electrolyte was 0.4 M PBS buffer (pH = 7). The scan rate was 50 mV $s^{-1}$.

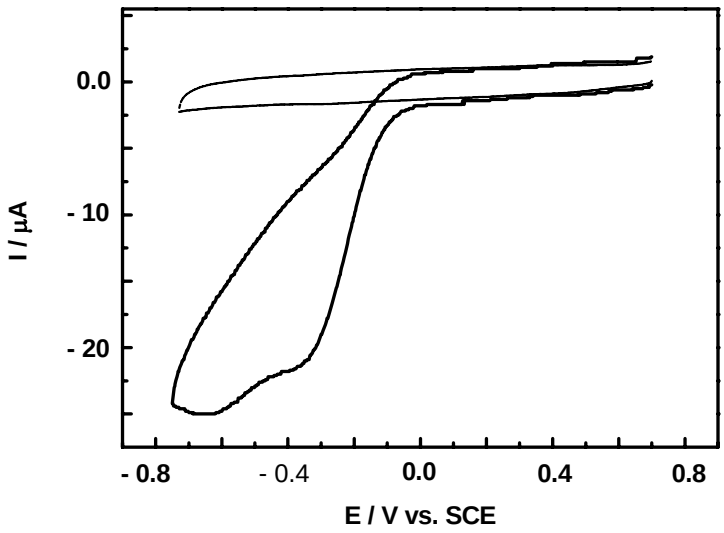

**Figure S4**. Cyclic voltammogram showing the reduction of hydrogen peroxide on the glassy carbon electrode modified with $Au^0$ nanoparticles as described previously. The nanoparticles were prepared using $C^0_{POM}$ = 0.1 mM, $\gamma$ = 1. The electrolyte was 0.4 M PBS buffer (pH = 7). The inset shows the linearity of the peak current as a function of the concentration of $H_2O_2$. The scan rate was 50 mV $s^{-1}$.