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SUPPLEMENTARY INFORMATION

One-Step Synthesis and Stabilization of Gold Nanoparticles in Water with the Simple Oxothiometalate $Na_2[Mo_3(\mu_3S)(\mu S)_3(Hnta)_3]$

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Experimental Section

Chemicals.

$Na_2[Mo_3(\mu_3S)(\mu_2S)_3(Hnta)_3]$ was synthesised according to literature procedures[17] and checked by routine methods (UV-visible, FT-IR, NMR).

UV-visible spectroscopy

UV-visible spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer or a diode array Hewlett Packard (HP 8453) spectrophotometer.

Experimental conditions for XPS Characterization of Au nanoparticles

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. The monochromatic X-ray Al Kα source was used for excitation, with incident energy of 1486.6 eV. The X-ray power was 200 W (20 mA x 10 kV). The pass energy was 20 eV for detail spectra. The analysis zone was roughly (1 x 1) cm^2. The monochromatic source was selected because it is better resolved in energy compared to the non-monochromatic one and is thus more suitable in case elements in large 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 photoelectronic peaks. Gold nanoparticle samples were centrifugated at 13,000 cpm for 30 min, redispersed in water, and then washed two more times with water, centrifugated after each water addition and finally redispersed in water. A drop of such solution is then deposited on a glassy carbon wafer and let to dry in a continuously argon-flushed box.

XRD performed with a Panalytical PW 3040/60 X'Pert Pro powder diffractometer and Cu Kα_1 radiation, showed that the samples were single phase.

TEM observations were performed with a PHILIPS EM 208 transmission electron microscope at an accelerating voltage of 80 kV. The sample drops were deposited and dried on carbon-coated copper grids.

DLS (Dynamic Light Scattering) analysis of the solutions was performed with a Malvern Zetasizer Nano ZS equipped with a He-Ne laser operating at 632.8 nm.

Electrochemistry equipment, apparatus and procedures

For electrochemical studies, the source, mounting and polishing of the glassy carbon (GC, Tokai, Japan) electrodes has been described previously.[1] The glassy carbon samples had a diameter of 3 mm. The electrochemical set-up was an EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area.

Pure water was used throughout. It was obtained by passing through a RiOs 8 unit followed by a Millipore-Q Academic purification set. The solutions were deaerated thoroughly for at least 30 minutes with pure argon and kept under a positive pressure of this gas during the experiments.

(1) B. Keita, L. Nadjo *J. Electroanal. Chem.* 1988, **243**, 87.

Table S1. pH values for synthesis mother solutions

Mixtures in water	pH
0.5 mM Mo_3S_4	3.30
0.5 mM Mo_3S_4 _ Au^{3+} / $\gamma = 0.5$	2.72
0.5 mM Mo_3S_4 _ Au^{3+} / $\gamma = 1.0$	2.53
0.5 mM Mo_3S_4 _ Au^{3+} / $\gamma = 2.0$	2.38
0.5 mM Mo_3S_4 _ Au^{3+} / $\gamma = 3.0$	2.09
0.5 mM Mo_3S_4 _ Au^{3+} / $\gamma = 4.0$	1.90

Figure S1. Evolution, as a function of time, of the UV-visible spectrum of a mixture of $Na_2[Mo_3(\mu_3S)(\mu S)_3(Hnta)_3]$ (C° = 0.5 mM) and $HAuCl_4$ 0.5 mM ($\gamma = 1$). The spectra of the individual species are superimposed for comparison. The quartz cell has 2 mm optical path.

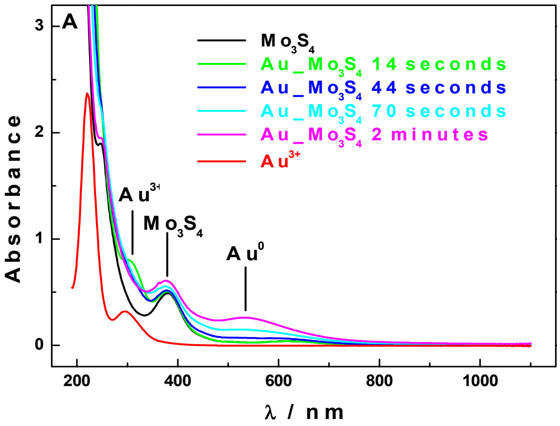
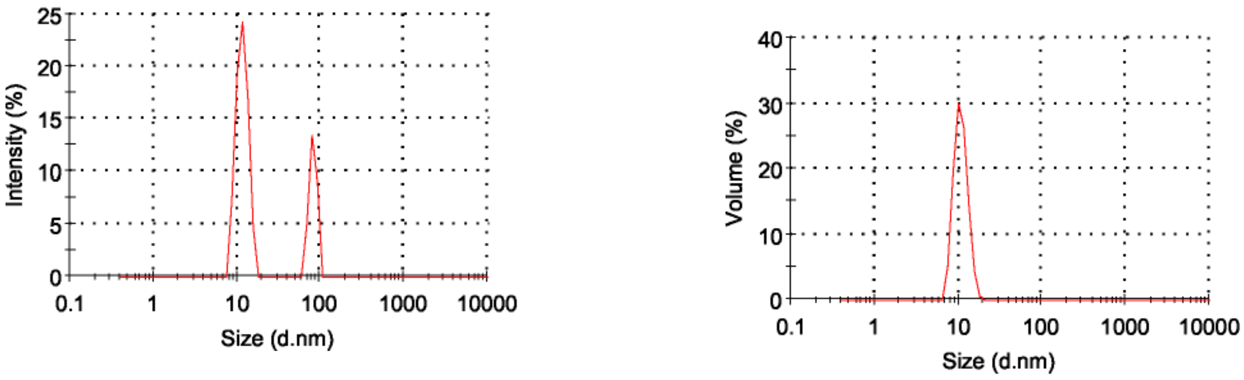


Figure S2. DLS measurement of Au nanoparticles synthesized in water from 0.5 mM of $HAuCl_4$ and 0.5 mM of $Na_2[Mo_3(\mu_3S)(\mu_2S)_3(Hnta)_3]$ (γ = [$HAuCl_4$] / [Oxothiometalate] is equal to 1).


Size distribution by Intensity

Size distribution by Volume

Size Peak (d.nm): 11.70
Size Peak (%): 72.6

Size Peak 2 (d.nm): 78.82
Size Peak 2 Area (%): 27.4

Size Peak 1 Volume (d.nm): 10.10
Size Peak 1 Area Volume (%): 99.9

Size Peak 2 Volume (d.nm): 78.82
Size Peak 23 Volume Area (%): 0.1

Figure S3. UV-visible spectra of the following species in water : black : 0.5 mM $Na_2[Mo_3(\mu_3S)(\mu S)_3(Hnta)_3]$ (Mo_3S_4); red: mother mixture of $HAuCl_4$ and Mo_3S_4 $\gamma = 0.5$ after reaction completion (Au_Mo_3S_4) ; pink: Au_Mo_3S_4 after centrifugation and washing.

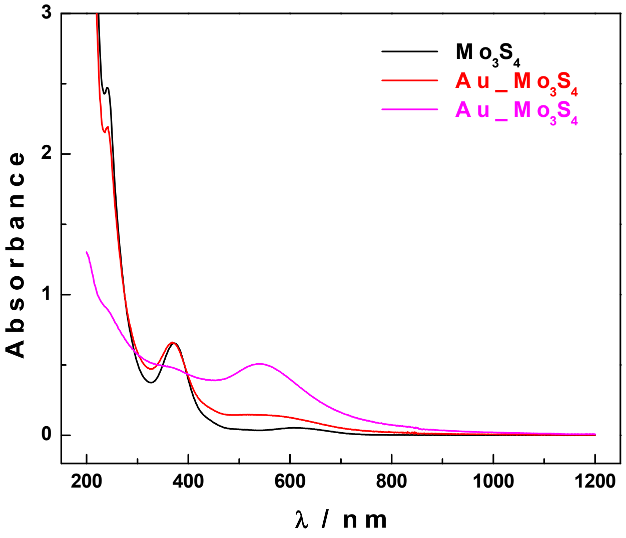
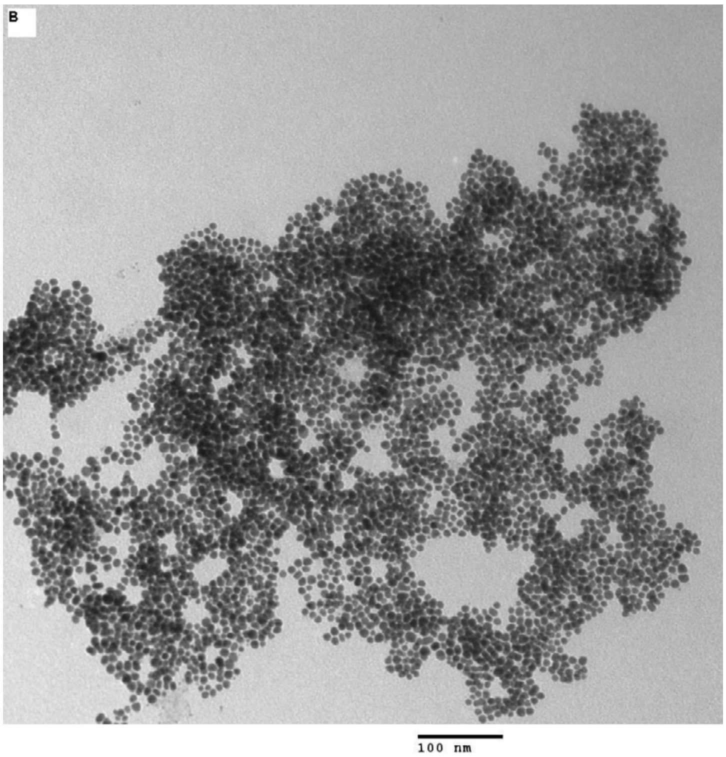


Figure S4. TEM images of Au^0 nanoparticles synthesized by the reduction of $HAuCl_4$ with $Na_2[Mo_3(\mu_3S)(\mu S)_3(Hnta)_3]$. The concentration ratio γ = $[HAuCl_4]$ / [Oxothiometalate] was 0.5. The initial concentration of the oxothiometalate was 0.5 mM.



Electrochemical Characterization of Au^0 NPs

Typical results are described for an electrode fabricated by depositing a few µl of centrifugated and washed Au^0 nanoparticles suspension in water ($\gamma = 1$ and $C_0 = 0.5$ mM) on a polished glassy carbon surface, covering with 6 µl of 5 wt % Nafion solution and leaving to dry in the air at room temperature. In the potential domain explored in the following, an electrode modified with Nafion alone shows no specific wave, as expected. Figure S4A shows the cyclic voltammetry response for such an electrode in 0.5 M H_2SO_4 solution (pH 0.30). A broad composite oxidation peak at 1.338 V vs SCE associated with a sharp reduction located at 0.882 V indicate the presence of Au^0 NPs on the electrode surface. A complementary feature is the proton reduction at the negative potential limit of this cyclic voltammogram. We wondered whether the oxothiometalate used for NPs synthesis could be detected, at least partly, on this electrode. In this issue, it must be reminded that XPS analysis has indicated molybdenum to be present under the IV, V, and VI valence states. As a consequence, the potential domain where such observation is expected on gold (between - 0.1 V and + 1.1 V vs SCE) was focused on and current intensities expanded. Figure S4B shows in superposition the CV patterns recorded with the modified electrode in pure 0.5 M H_2SO_4 electrolyte and with a polished glassy carbon electrode soaking in a solution of the oxothiometalate freely diffusing in the same medium. The slight difference in oxidation peak potentials between these two systems is most probably related to the adsorption on gold on the one hand and diffusion in solution on the other hand. In any case, the similarity of the voltammetric patterns induces to conclude that the Au^0 NPs are indeed capped with a thin layer of oxothiometalate. This observation is supported by the conclusions of both UV-visible spetra and XPS analysis of centrifugated and washed Au NPs obtained in the present experiments.

Figure S5. A) Cyclic voltammogram (CV) obtained with the Au^0-modified glassy carbon (GC) electrode in 0.5 M H_2SO_4 (Au_Mo_3S_4). The scan rate was 100 mV s^{-1}; the reference electrode was a SCE.

B) Expansion of the potential domain (-0.100 V to + 1.100 V vs SCE) (Au_Mo_3S_4, red curve) in the CV shown in Figure 4A and superposition with the CV of $Na_2[Mo_3(\mu_3S)(\mu S)_3(Hnta)_3]$ (Mo_3S_4, black curve) dissolved in 0.5 M H_2SO_4 and run on a polished glassy carbon electrode. The diffusion current was scaled up for easier comparison.