

## Supporting information for

# Enhanced catalytic electrochemical reduction of dissolved oxygen with ultraclean Cucurbituril[7]-capped gold nanoparticles

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**General.** Tetrachloroauric(III) acid hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ; 99.9% trace metal basis), hydrogen peroxide (50%), cucurbituril[7] and methylene blue hydrate (97%) were purchased from Sigma-Aldrich and used as received.

**Synthesis and Characterization of AuNPs.** An aqueous solution of 0.5 mM  $\text{HAuCl}_4$  was mixed with 0.75 mM  $\text{H}_2\text{O}_2$  in the dark and immediately irradiated in a glass tube for *ca.* 240 min using a Brilliant Q-switched Nd/YAG laser. Laser excitation was performed at 532 nm with a frequency of 10 Hz and an 18-23 mJ laser pulse. Thus, once AuNPs were synthesized, a careful 3-fold dilution (3 mL of AuNPs were added slowly to 9 mL of water) was immediately carried out to avoid agglomeration of the AuNPs and samples were kept in 15 mL plastic centrifuge tubes. Then, the remaining hydrogen peroxide was evaluated by using a Merck peroxide test strip (Merckoquant®), which can detect quantities up to 0.5 mg/mL. To get rid of the excess of hydrogen peroxide, the diluted AuNP solution was placed in a 24-well plate and irradiated in an LZC-4 Luzchem photoreactor (Luzchem Research, Inc.) with 10 UVA lamps (8-W HITACHI FL8BL-B;  $\lambda = (350 \pm 50)$  nm) for less than an hour until peroxide test was negative.<sup>1</sup> This can be also followed by absorption spectroscopy since there is an absorbance decrease in the UV (followed at 240 nm) that corresponds to the hydrogen peroxide absorption. In all cases, aqueous solutions were prepared using Milli-Q water at room temperature obtained from a Millipore system. Water was pretreated with Chelex at least for one day to eliminate ion traces.

**Instrumentation.** All absorbance spectra were measured using an Agilent G1103A UV-visible spectrophotometer in UV PLASTIBRAND Cuvettes from Aldrich. The UV-Visible spectra measurements were performed taking aliquots of the reaction mixtures at certain time intervals after excitation with a 532 nm laser.

$\zeta$ -potential measurements were carried out on a Zetasizer nano ZS (Malvern Instrument) following manufacturer instructions. Each value reported is the average of three consecutive measurements.

Nanoparticle sizes were determined using transmission electronic microscope (TEM) with a JEM-1010 from Jeol Ltd operated at 100 kV. TEM samples were prepared by depositing 10  $\mu\text{L}$  of the AuNPs suspension onto a carbon-coated copper grid (300 mesh), which was subsequently dried at room temperature. Nanoparticle sizes were calculated by using ImageJ software.<sup>2</sup> The concentration of nanoparticles was estimated from TEM experiments as described by A.K. Rao *et al.*<sup>3</sup>

Voltammetric measurements were carried out in a conventional three-electrode cell using CH 660C equipment. Glassy carbon (GCE) working electrode (BAS MF 2012, geometrical area 0.071  $\text{cm}^2$ ), carbon fiber (BAS MF) and Pt (BAS MF) microelectrodes (diam. 20  $\mu\text{m}$ ) were used as working electrodes.

The three-electrode arrangement was completed with a Pt-wire auxiliary electrode and a Ag/AgCl (3 M NaCl) reference electrode. Voltammetric measurements were performed in freshly prepared solutions with no supporting electrolyte to avoid nanoparticle aggregation and in 0.067 M NaClO<sub>4</sub> solutions in nanopure water. Solutions were optionally deaerated by bubbling Ar during 15 min. Under our experimental conditions, solution conductivity was high enough to yield well-defined voltammetric responses slightly distorted by uncompensated ohmic drops in the cell. Electrochemical measurements were performed at least 30 min after addition of CB to the NP.

In view of the high resistive background due to the low electrolyte (and low analyte) concentration, deconvolution procedures were applied to the voltammograms in order to increase the signal/background ratio. Deconvolution of voltammograms was performed using the CH Instruments algorithm which is based on the Savitzky and Golay algorithm.<sup>4</sup>

### Calculation of AuNP concentration

The concentration of these nanoparticles was estimated from TEM experiments.<sup>3</sup>

For large ‘spherical’ clusters it can be assumed that the volume of the cluster ( $V_{NP}$ ) is  $N$  times the volume of the individual atom ( $V_A$ ),

$$V_{NP} = N \times V_A$$

that can also be expressed as

$$V_{NP} = \frac{4}{3} \pi R_{NP}^3 = N \times \frac{4}{3} \pi r_A^3$$

where  $N$  is the number of atoms in the cluster,  $R_{NP}$  is the radius of the cluster (Note: we used for all calculations the average radius determined by TEM of 8.3 nm) and  $r_A$  is the atomic radius (0.144 nm for fcc Au). From these values,  $N$  was estimated as

$$N = \left( \frac{R_{NP}}{r_A} \right)^3 = \left( \frac{8.3 \times 10^{-9}}{0.144 \times 10^{-9}} \right)^3$$

$$N = 191490 \text{ gold atoms per nanoparticle}$$

The concentration of nanoparticles ( $C_{NP}$ ) can be estimated assuming that all Au<sup>3+</sup> ions are reduced to Au<sup>0</sup> atoms and the following equation:

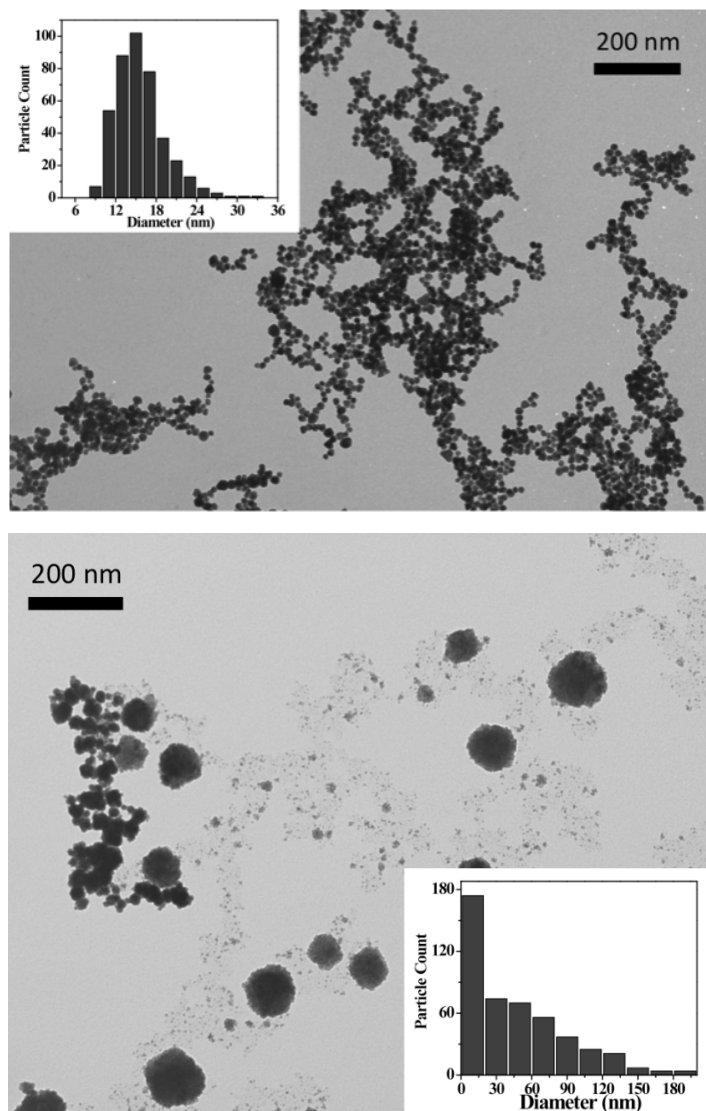
$$C_{NP} = \frac{N_{NP}}{N_A} = \frac{N_{atoms}}{N \times N_A} = \frac{\text{moles Au}^{3+} \text{ per liter} \times N_A}{N \times N_A}$$

$$C_{NP} = \frac{0.5 \times 10^{-3}}{191490}$$

$$C_{NP} = 2.6 \text{ nM}$$

where  $N_{NP}$  and  $N_{atoms}$  are the number of nanoparticles and gold atoms obtained in one liter, respectively and  $N_A$  is the Avogadro number.

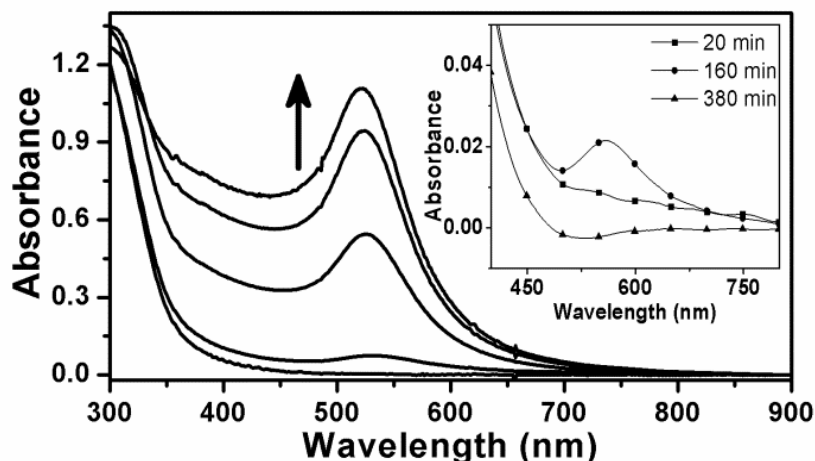
This was used as stock solution.



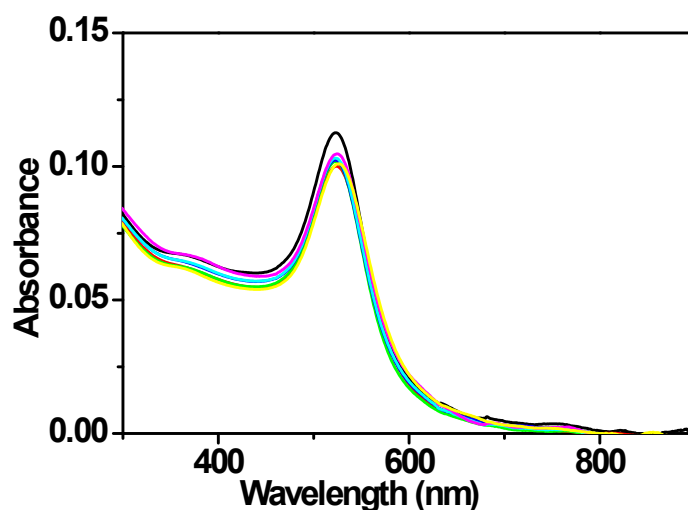
**Figure S1.** Representative TEM micrograph and histogram with AuNP' size distribution obtained after 532 nm laser irradiation (left) or in the dark (right).

A lag in time in the one-pot generation of AuNPs with a narrow plasmon band centred at 532 nm was detected by UV-visible spectroscopy (Figure S2). This is in accordance with the in situ thermal generation of the AuNPs.

Figure S2 shows the generation of AuNPs by reacting  $\text{HAuCl}_4$  with  $\text{H}_2\text{O}_2$  i) in the dark (inset) and ii) under laser irradiation at 532 nm. The gold salt was quickly transformed in the presence of  $\text{H}_2\text{O}_2$  (no band was detected at 350 nm in the absorption spectra even in those of the dark experiments). Laser irradiation at 532 nm ablated the thermally generated nanoparticles in situ. The pH of the colloidal samples was ca. 3.3 and their zeta potential was negative (ca. -45 mV).



**Figure S2.** UV-visible spectra of AuNPs synthesised from  $\text{HAuCl}_4$  and  $\text{H}_2\text{O}_2$  by using a 532 nm laser irradiation at different times (30, 60, 90, 120, and 240 min in the arrow direction). Inset: UV-visible spectra of AuNPs synthesised by reacting  $\text{HAuCl}_4$  with  $\text{H}_2\text{O}_2$  in the dark.



**Figure S3.** UV-visible spectra NP@CB 0.18 nM (black) and AuNPs with increasing CB concentrations: 0.044  $\mu\text{M}$  (red), 0.131  $\mu\text{M}$  (green), 0.240  $\mu\text{M}$  (blue), 0.720  $\mu\text{M}$  (cyan), 2.052  $\mu\text{M}$  (magenta) and 3.930  $\mu\text{M}$  (yellow).

**Table S1.** Molar concentrations of CB added to the [NP]=0.18 nM and CB/NP molar ratios.

run <sup>a</sup>	[CB] ( $\mu$ M)	CB/NP <sup>b</sup>
1	0.044	244
2	0.131	728
3	0.240	1333
4	0.720	4000
5	2.052	11400
6	3.930	21833

#### References

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4. A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 1964, **36**, 1627-1639.