

### Supporting information for the article

#### Matter of age: Growing anisotropic gold nanocrystals in organic media

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#### Experimental section

**Materials and instrumentation.** In situ UV-visible measurements were performed using a Hewlett Packard 8453 spectrophotometer with a diode array detector. The quartz cuvette (Hellma Benelux, approximately 3.5 ml, path length 1 cm) was mounted on a sample holder with controlled heating (Neslab constant temperature bath) and stirring (compressed air was used to rotate the stirrer at the bottom of the cuvette). The recorded wavelength range was 190–1100 nm, at 1 nm resolution. TEM images were obtained with a JEOL model JEM-1200 EXII instrument, operated at an accelerating voltage of 120 kV. Unless stated otherwise, chemicals were purchased from commercial firms (>98% pure) and used as received. All solvents were degassed for 10 min with dry N<sub>2</sub> prior to use. GC-MS measurements were done using Agilent 6890/5793 instrument (with HP-5 MS crosslink phase column, 30 m length, internal diameter 0.25 mm, film thickness 0.25 μm). IR spectra were measured using Bruker Vortex 70 instrument using CaCl<sub>2</sub> cell. Karl-fisher titrations were performed using a Mettler Toledo DL 36 KF coulometer instrument. 250 ml of Hydraneal water standard (0.1% H<sub>2</sub>O) was used as internal standard. Cyclic voltammograms were recorded with a PAR EG&G model 283 potentiostat, using an airtight single-compartment cell placed in a Faraday cage. The working electrode was a Pt microdisk (0.42 mm<sup>2</sup> apparent surface area), polished with a 0.25 μm diamond paste between the scans. Coiled Pt and Ag wires served as an auxiliary and pseudoreference electrode, respectively. The concentration of the analyte was 1 mM. Ferrocene (Fc) was used as the internal standard. The supporting electrolyte,

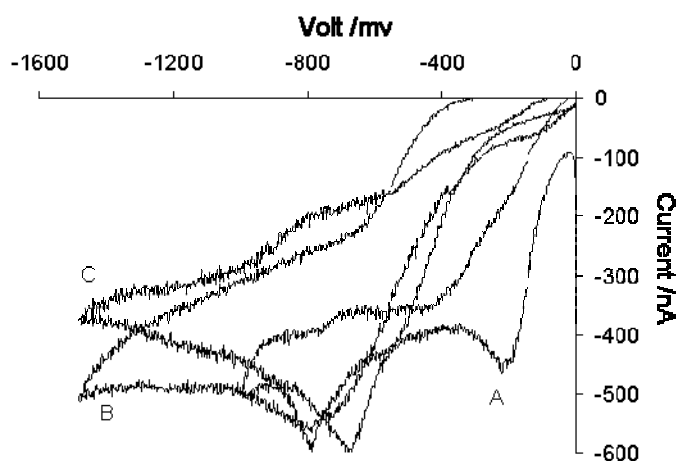
[Bu<sub>4</sub>N][PF<sub>6</sub>], was recrystallized twice from absolute EtOH and dried overnight under vacuum at 80 °C before use.

**Procedure for *in situ* monitoring of Au nanoparticles and anisotropic particles.**

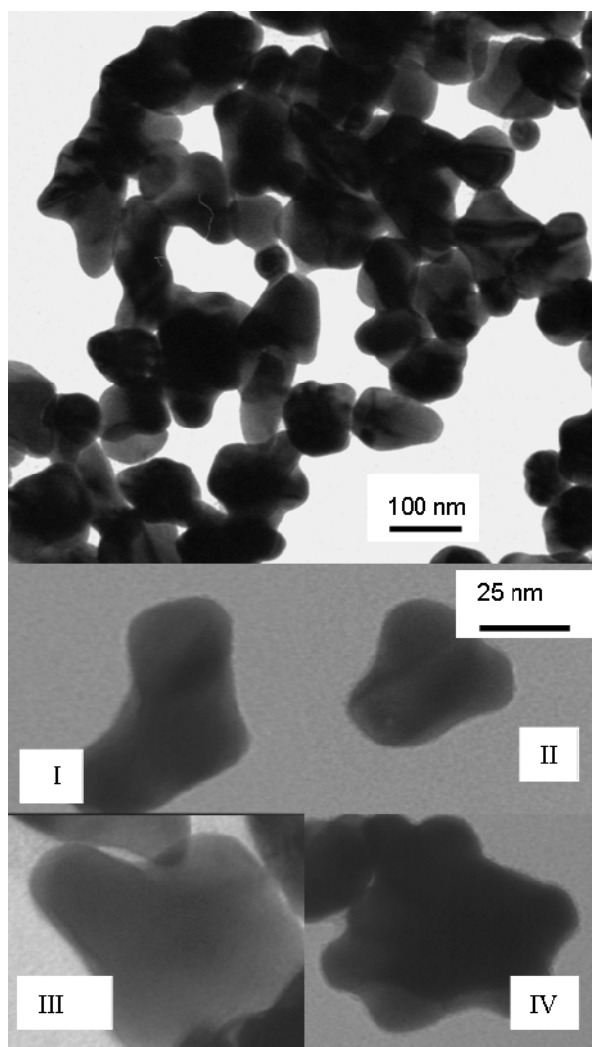
**Sample A.** A quartz cuvette equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N<sub>2</sub>. It was charged with 2 ml of a 0.5 mM AuCl<sub>3</sub>/DMF aged solution. Then, 75 μl of 100 mM of TOAF in DMF was added in one portion into the cuvette and stirred and heated at 65 °C for 1 h. UV-vis spectra were recorded every 1.1 min for 60 min.

**Sample B** was prepared using the same method, but using 2 ml of a fresh 0.5 mM AuCl<sub>3</sub>/DMF solution and 60 μl of 100 mM of TOAF/DMF was added. **Sample C** was prepared using 2 ml of a fresh 0.5 mM AuCl solution in DMF and 60 μl of 100 mM of TOAF/DMF. **Sample D** was prepared using the same Au<sup>3+</sup> solution but a higher amount of TOAF/DMF (60 μl of 200 mM).

**Cyclic Voltammetric studies.** Cyclic voltmetric studies were performed with fresh AuCl<sub>3</sub>, fresh AuCl and aged AuCl<sub>3</sub> solutions in DMF as shown in the figure S1.



**Figure S1.** Cyclic voltammograms of fresh AuCl<sub>3</sub> (A), fresh AuCl (B), and aged AuCl<sub>3</sub> (C) solution in DMF. The different value for  $E_v$  for Au<sup>+</sup> in the fresh and aged solution may arise from the presence of Au<sup>0</sup> seeds in latter solution.



**Figure S2.** (top) TEM images of branched particles prepared using an aged  $\text{AuCl}_3$  precursor solution in DMF – sample **A**; (bottom) Close ups of TEM images of different shaped particles that can be distinguished: (I) bipod, (II) tripod, (III) tetrapod, and (IV) branched gold nanocrystals.