Gold nanowires growth through stacking fault mechanism by oleylamine-mediated synthesis

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Additional experimental data about Au-TPNW samples with different reaction conditions, XRD code simulation and results for stacking fault Au nanorods and crude data for the temperature dependence XRD, and UV-Vis simulations for the LSPR spectrum with different dielectric mediums are included in this ESI.

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Results and Discussion

*Modifications in the gold tadpole-like nanowires synthesis*

Different parameters were used according to the experimental procedure to evaluate its influence on the gold nanoparticles formation, and the main ones are described in Table S1. The influence of a solvent mixture, and the synthesis parameters (Table S1) have been evaluated to advance in the knowledge of a possible formation mechanism of gold tadpole-like nanowires (Au-TPNW). When pure OAm was used under a gentle stirring and intermediate temperature (65 °C), a mixture consisting of nanowires (large amount) and nanospheres were obtained, and the nanowires was easily separated by standard size-selective approach (sample Au3, Fig. 1b and 1c) as described in the Methods section for Au-TPNW synthesis. This initial result is in good agreement with the reported works showing that vigorous stirring and high temperature lead to spherical nanoparticles growth. In small amounts of oleylamine and using the best conditions to synthesize the Au-TPNW (sample Au2) did not was possible to observe the formation of the nanowires. Fig. S1d shows that sample Au2 is composed majority for spherical nanoparticles and just a little portion of elongated nanomaterials, inferring that the formation of the nanowires strongly depends on oleylamine presence, besides more gently conditions of temperature and stirring.

The main synthesis procedure described in the Methods section using a mixture of 1-octadecene and oleylamine as solvents, results in the monodisperse spherical gold nanoparticles (sample Au1, Fig. 1a and S1a) with coefficient of variation (average diameter/standard deviation, \(\sigma/\mu\)) lower than 0.1, as observed in the histogram presented in the Fig. S1b. The nucleation and growth processes control result in the spherical nanoparticles as predicted by the theories already discussed in the literature for well-known spherical nanoparticles formation. Low temperatures, slightly above room temperature, is enough to synthesize gold nanoparticles since the gold has a positive reduction potential, meaning the reduction of Au\(^{3+}\) to metallic gold is favorable at this condition. At temperatures around 70 °C, it is possible to visualize the reduction of Au\(^{3+}\) to Au\(^+\) as the yellow gold solution becomes colorless while the reduction process takes place. The metallic gold by the reduction of Au\(^+\) to Au and the formation of metallic nanoparticles can be readily observed by the appearance of the red color related to the LSPR (Localized Surface Plasmon Resonance) absorption band centered around 520 nm, Fig. S1c.
Table S1. Experimental parameters used in the syntheses of gold nanomaterials.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Samples</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>Au1[^a]</td>
<td>Au2</td>
<td>Au3[^b]</td>
</tr>
<tr>
<td>HAuCl4/mmol</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>ODE/mL</td>
<td>8</td>
<td>11.5</td>
<td>0</td>
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<tr>
<td>OAm/mL</td>
<td>4</td>
<td>0.5</td>
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</tr>
<tr>
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<td>2</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Stirring</td>
<td>Strong</td>
<td>Gentle</td>
<td>Gentle</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>80</td>
<td>65</td>
<td>65</td>
</tr>
</tbody>
</table>

[^a] Spherical gold nanoparticles, and [^b] tadpole-like gold nanowires both discussed in the main text.
Fig. S1. Samples at different experimental conditions described in Table S1. Sample Au1: (a) TEM image of the spherical gold nanoparticles synthesized using a mixture of HAuCl₄·3H₂O, octadecene and oleylamine at 80 °C and its (b) histogram concerning the particle size distribution. In (c), the UV-Vis spectrum shows the LSPR band centered at 520 nm. The TEM image of the (d) Au2 sample synthesized at low OAm concentrations in similar conditions for the Au-TPNW formation.
Figures and XRD Simulation Code

**Fig. S2.** Face-centered cubic (fcc) unit cell observed for Au materials showing the three principal crystallographic facets {111}, {110}, and {100}. The Truncated cuboctahedron shows the three different facets within the unit cell.
**XRD simulation of stacking fault gold nanoparticles using DiFaX**

The code hereafter was used to generate the simulated XRD pattern (Fig. S3) for gold nanorods with a length of 100 nm (425 layers of the close-packed planes (111)) and a diameter of 10 nm. The values of PFCC (probability of fcc stacking) and PHCC (probability of hcp stacking) was changed accordingly keeping PFCC + PHCC = 1.

```plaintext
{data file for gold with random hexagonal intergrowths}
{probability of cubic stacking was variable by changing layers transitions}
{cubic stacking sequence = 111111111.... or 222222222...}
{Hexagonal staking sequence = 1212121212121212....}

INSTRUMENTAL
{Header for instrumental section}
X-RAY
{Simulate X-ray diffraction}
1.5418
{X-ray wavelength}
Lorentzian 0.1 trim
{Instrumental broadening (much faster)}

STRUCTURAL
{Header for structural section}
2.8667 2.8667 2.3550 120.0
{unit cell coordinates, a, b, c, gamma}
6/MMM
{hexagonal, c = cubic [111]}
2
{111 sheet, plus its mirror}
100 100
{Layers wide in the a-b plane Angstrom, 10 nm}

LAYER 1
CENTROSYMMETRIC
Au   1  0.0  0.0  0.0  0.0  1.0
{Atom, Number id, x, y, z, B_iso - Debye-Waller, Occ}

LAYER 2 = 1

STACKING
recursive
{Statistical ensemble permutation all possibilities}
425
{425 layers near 100 nm, aspect ratio of 10}

TRANSITIONS
{Header for stacking transition data}

{Transitions from layer 1}
PFCC  1/3  2/3  1.0
{layer 1 to layer 1, PFCC probabilities of FCC phase between 0-1}
PHCP  2/3  1/3  1.0
{layer 1 to layer 2, PHCP probabilities of HCO phase between 0-1}

{Transitions from layer 2}
PHCP  1/3  2/3  1.0
{layer 2 to layer 1}
PFCC  2/3  1/3  1.0
{layer 2 to layer 2}
```
Fig. S3. Close-packed planes and XRD simulations of the fcc and hcp structures. (a) Illustration of the stacking sequence of the closed-packed planes that leads to hcp (ABABAB...) and fcc (ABCABC...) along with their in-plane ($ab$-plane) dislocation vectors for axes $a$ and $b$ showing that transitions 1 to 2 or 2 to 1 leads to hcp packing and transitions 1 to 1 or 2 to 2 leads to fcc packing. For each transition, a 2.35 Å dislocation that is normal to the $ab$-plane occurs (parallel to the $c$-axis and to the $[111]$$_{fcc}$ direction). (b) XRD simulations for gold nanorods with an aspect ratio of 10 (width 10 nm and length 100 nm) using different amounts of stacking sequences of the closed packed plane that leads to hcp (ABABAB...) or fcc (ABCABC...) phase performed using DiFFaX software.
Fig. S4. Temperature dependence of XRD data of gold nanowires showing (a) the typical Rietveld refinement realized for sample at room temperature that was used to excluded the Pt peaks (XRD heating foil) and background; different graphical plots to highlight (b) the diffraction halos vanishing and (c) 3D plot showing the (111) peaks intensities.
HTEM images

**Fig. S5.** HRTEM images showing the stacking faulted tail growth from the \([111]_{fcc}\) direction of the \(fcc\) head. Insets correspond to the FFT images obtained from the \(fcc\) head regions.
Optical and Magnetic properties

**Fig. S6.** UV-Vis spectroscopy for (a) experimental Au-TPNW sample in hexane and (b) simulated LSPR spectrum for gold nanorods with a different aspect ratio (R) for the z-polarized band position (parallel to the rod lengths). Nanorods simulation was achieved by keeping the width 10 nm and changing the length for the different R values. The multiplication factor is shown to keep the maximum absorption aligned and give the correct scattering cross-section. Magnetic characterization of the Au-TPNW: (c) the hysteresis loop measured at 5 K shows the ferromagnetic behavior. The zoom (inset) highlighted the MREM and HC values assigned to the ferromagnetic behavior; (d) field-cooled (FC) and zero field-cooled (ZFC) measured with a maximum applied field of 100 Oe show a blocking temperature (TB) value of 301.15 K and inferring that ferromagnetic behavior remains slightly above the room temperature.
**Fig. S6** shows the optical and magnetic properties of the Au-TPNW. The UV-Vis spectrum of Au-TPNW sample featuring a broad absorption band from 800 nm to the near-IR region of the electromagnetic spectrum. The sharp band about 500 nm was assigned to the presence of both the LSPR from spherical gold nanoparticles and the y-polarized absorption of the gold nanowire. The two LSPR modes for gold nanorods or nanowires, longitudinal and transverse plasmon bands, can be visualized in **Fig. S7**. The simulated local electric field enhancement ($|E|^2/|E_0|^2$) from the LSPR is displayed in **Fig. S7** showing both y-polarized (transverse) and z-polarized (longitudinal) plane-wave, whereby the light propagates along the x-axis, and the nanorods are oriented with its long axis oriented parallel to the z-axis. Whereas the y-polarized spectra for nanorods with a different aspect ratio (length by width, $R$) keep their maximum absorption around 515 nm (**Fig. S8**) the z-polarized absorption band is highly dependent upon $R$, **Fig. S6b** and **Fig. S9**. The longitudinal LSPR dependence with $R$ arises from the depolarization field associated with the particle’s geometry, the depolarization form factor. A red-shift of the longitudinal plasmon band is observed increasing $R$ and the longitudinal absorption band ranges from ~600 nm ($R = 3$) to ~1700 nm ($R = 20$) when simulated using vacuum permittivity constant (dielectric constant) as surrounding medium (**Fig. S9**) for water and hexane medium. The broad plasmon band observed in **Fig. S6a** for the longitudinal mode, ranging from UV-Vis to near-IR region, is originated by the presence of nanowires having a large size distribution in lengths, *i.e.*, it has a statistical contribution of nanorods having different $R$ values, as visualized by simulated spectra in the **Fig. S6b**. The spectrum in **Fig. S6a** was limited at 1600 nm, but the longitudinal band continues into the near-IR region, and it was not included due to the signal noise originated by molecular absorptions. The longitudinal maximum band absorption position also depends upon the surrounding media besides $R$ values (**Fig. S10**), and size-controlled nanorods can also be used as in dielectric constant sensor devices.

Magnetic phenomena in gold nanoparticles have been reported in the literature.$^{1-7}$ The magnetic behavior was initially observed in organic molecules-capped Au nanoparticles with just a few nanometers in size. The ferromagnetic-like behavior was attributed to the covalent bonds between the organic capping molecules and the nanoparticle surface gold atoms that, which induces modifications in its electronic structure. Ligands covalent bonds induce the formation of a 5d hole, and localized magnetic moments remain frozen due to the strong spin-orbit coupling, and consequently, the magnetic behavior.$^{1,6,7}$ After that, the magnetism has also been observed in other Au materials such as gold clusters (small nanocrystals), films, and nanocrystalline films with or without the organic molecules capping. Besides the presence of the covalent bond effects, the magnetic behavior in bare Au nanocrystals was recently associated with the spin-glass-like behavior,$^{1,4}$ but the
no is a complete comprehension concerning the magnetic phenomenon observed in gold nanostructure until now. Here, the magnetic properties of the Au-TPNW were evaluated by the typical magnetic hysteresis loop measured at 5 K (Fig. S6c) and also by the field-cooled (FC) and zero-field cooled (ZFC) curves, as shown in Fig. S6d. The magnetic hysteresis curve of sample indicates an unusual ferromagnetic behavior at 5 K exhibiting the typical profile corresponding to the ferromagnetic behavior with remanent magnetization ($M_{REM}$), saturation magnetization ($M_{SAT}$), and coercive field ($H_C$) of $2.8 \times 10^{-2}$ emu $g^{-1}$, $9.1 \times 10^{-2}$ emu $g^{-1}$, and 230 Oe, respectively. The temperature-dependence magnetization curves inferred that the Au tadpoles have ferromagnetic behavior up to room temperature, with the blocking temperature ($T_B$) value around 301 K (Fig. S6d). The $T_B$ value, where the curves split, it corresponds to the onset of the change in the magnetic behavior, since that the magnetic moments orientation is frozen below $T_B$ (ferromagnetic) and becomes randomly oriented above this value (paramagnetic). The ferromagnetic behavior at room temperature was previously reported in Au nanorods less than 80 nm in length, becomes paramagnetic if the size of the nanorods increases above this limit. Our results indicate that the ferromagnetism holds on for tadpoles with size as large as 500 nm.
Fig. S7. Simulated local electric field enhancement ($|E|^2/|E_0|^2$) from the localized surface plasmon resonance (LSPR) showing both $y$-polarized (transverse) and $z$-polarized (longitudinal) plane-wave excitations direction, being light propagation direction ($k$) along the $x$-axis and the nanorods is oriented with its long axis parallel to the $z$-axis. The $z$-polarized has the electric field $E$ from the light aligned with the $z$-axis as shown on the bottom of the figure and the $y$-polarized has the $E$ vector aligned horizontally. The images were obtained for the position’s maximums of their respective plasmon bans, being the wavelength 740 nm for the $z$-polarized and 520 nm for the $y$-polarized. The refractive index of the medium was vacuum ($\varepsilon$ of 1.0).
**Fig. S8.** Simulated LSPR spectrum for gold nanowires with a different aspect ratio ($R$) for the $y$-polarized band position as shown in Fig. S5. Nanorods simulation was achieved by keeping the width 10 nm and changing the length for the different $R$ values. The multiplication factor is shown to keep the maximum absorption aligned and give the correct scattering cross-section. It is possible to observe that the maximum of the $y$-polarized band is almost invariable with $R$, keeping the maximum scattering around 515 nm for the transverse plasmon band. This value is close to the observed for spherical nanoparticles as shown in Fig. S1c.
Fig. 59. Simulated scattering cross sections for gold nanowires with fixed aspect ratio (R) but different width (W) and length (L) showing the small changing in peak position.
**Fig. S10.** Simulated scattering cross sections for gold nanowires using the refractive index of the embedding medium ($\varepsilon$) for vacuum (0.0), water (1.33), and hexane (1.37).

**References**