

# Unraveling the causes of the instability of $\text{Au}_n(\text{SR})_x$ nanoclusters on Au(111)

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DOI:

[10.1021/acs.chemmater.1c00816](https://doi.org/10.1021/acs.chemmater.1c00816)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Carro, P, Azofra, LM, Albrecht, T, Salvarezza, RC & Pensa, E 2021, 'Unraveling the causes of the instability of  $\text{Au}(\text{SR})$  nanoclusters on Au(111)', *Chemistry of Materials*, vol. 33, no. 9, pp. 3428-3435.  
<https://doi.org/10.1021/acs.chemmater.1c00816>

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## Unravelling the causes of the instability of $\text{Au}_n(\text{SR})_x$ nanoclusters on metal substrates

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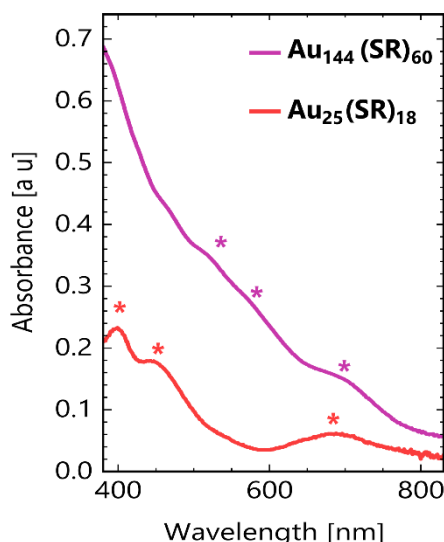
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## UV-Vis spectra of the AuNCs used in this work



**Figure S1.** UV-Vis spectrum of the AuNCs used in this work. Characteristic peaks are indicated with asterisks.

Figure S1 shows the UV-Vis spectra of both nanoclusters used in this work. The spectra show some distinctive absorption peaks of the  $\text{Au}_{144}(\text{SR})_{60}$  and  $\text{Au}_{25}(\text{SR})_{18}$  nanoclusters.<sup>[1-2]</sup> For  $\text{Au}_{144}(\text{SR})_{60}$  spectrum, typical bands are observed at  $\sim 525$  nm,  $\sim 565$  nm, and  $\sim 700$  nm, while for  $\text{Au}_{25}(\text{SR})_{18}$ , bands at 397 nm, 446 nm, and 685 nm are observed. Importantly, for  $\text{Au}_{25}(\text{RS})_{18}$  nanoclusters, three charged states have been identified previously: -1, 0, and +1.<sup>[2]</sup> This charge state can be easily identified from the AuNCs UV-Vis spectroscopic features, namely, the relative intensities of the 400 and 450 nm peaks and the presence or absence of the 800 nm shoulder peak. The spectrum of  $\text{Au}_{25}$  anion shows a shoulder at ca. 800 nm, and the absorption peak at ca. 400 nm is less prominent than the one at ca. 450 nm. For the cationic and neutral forms, the shoulder is not present. In the cationic form, the intensity of peaks at ca. 400, and 450 nm are sizeable, while for the neutral form, the intensity peak at 400 nm is more prominent than the one at ca. 450 nm.<sup>[2]</sup>

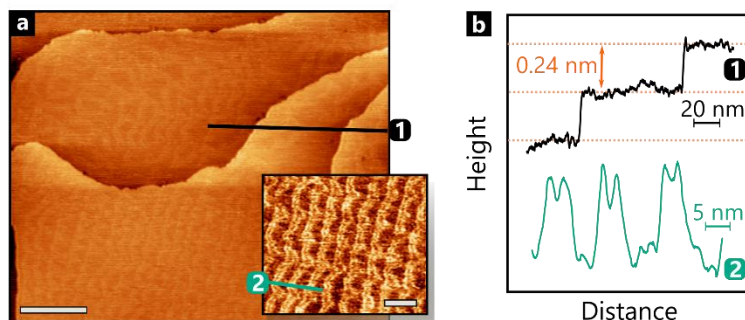
All the spectral features agree with the expected nanoclusters in their uncharged state.<sup>[1-2]</sup>

## Scanning Tunneling Microscopy (STM). Additional images and imaging acquisition parameters

**Table S1.** STM imaging conditions.

Figure	$i_{\text{sp}}$ [nA]	$E_{\text{bias}}$ [V]	Scan rate [lines·s <sup>-1</sup> ]
<b>1a</b>	0.10	0.20	4.039
<b>1d</b>	0.30	-0.10	12.12
<b>1e</b>	0.10	0.20	12.12
<b>3a</b>	0.30	0.20	12.12
<b>3b</b>	0.10	0.10	12.12
<b>S2a</b>	0.01	-0.08	6.06
<b>S2a-inset</b>	0.50	-0.03	12.12

The Au(111) substrate were measured before immersing in the AuNC dispersion to assure that the observed features resulting only from the AuNC/Au(111) interaction. A typical STM image of the substrate is shown in Figure S2. The quality of the surface and the cleaning process is evidenced by the presence of large and flat terraces, that are monoatomic in height and present the typical herringbone structure ascribed to the Au(111) reconstruction.



**Figure S2.** STM images of Au(111) before immersion in AuNC dispersions. (a) Image of the substrate after flame annealing with H<sub>2</sub>, showing the large and atomically flat terrace. The slightly pattern observed on the surface corresponds to the herringbone structure, typical for clean Au(111). Inset: Zoom of images a, showing the herringbone reconstruction. (b) Height profiles along lines 1 and 2. Orange dotted lines are included to highlight that the distance between Au steps agrees with the one between monoatomic layers of Au(111) -i. e. 0.24 nm. Scale bars correspond to 60 nm (image a) and 20 nm (image in the inset).

#### Determination of Au island coverage ( $\theta_{\text{Au\_island}}$ )

The Au island coverage was determined as the area of STM images covered by the Au islands. STM imaging analysis was performed by employing The “flooding” tool provided the WSxM software<sup>[3]</sup>, on images where Au islands are in the top large terraces and far apart to the step edges. The height-threshold was adjusted in order to only account the Au islands and remove the rest of the surface. Then, the software tool automatically calculates the area of the remaining islands relative to the total area of the image, which is indeed the coverage of Au islands ( $\theta_{\text{Au\_islands}}$ ).

#### Determination of the SR coverage from electroreduction curves ( $\theta_{\text{SR}}$ )

The SR coverage,  $\theta_{\text{SR}}$ , is obtained from by the SR reduction charge ( $q_{\text{SR}}$ ) by using the following relation:

$$\theta_{\text{SR}} = \frac{q_{\text{SR}}}{e} n_{\text{Au}(111)} \quad [\text{S1}]$$

where  $n_{\text{Au}(111)}$  is the number of Au atoms per cm<sup>2</sup> at the (111) surface and,  $e$  is the elemental charge.

The thiolate reduction charge,  $q_{\text{SR}}$ , was determined according to

$$q_{\text{SR}} = B \frac{A_{\text{SR}} v_{\text{Au}}}{v_{\text{SR}} A_{\text{Au}}} \quad [\text{S2}]$$

where  $A_{\text{SR}}$  is the area of the thiolate electroreduction peak,  $A_{\text{Au}}$  is area of the electroreduction peak of Au oxide layer,  $v_{\text{SR}}$  and  $v_{\text{Au}}$  are the scan rates at which the CVs were recorded and,  $B$  is a proportional constant that accounts for the charge provided by the oxidation of 1 cm<sup>2</sup> of Au(111) surface i.e.  $B = 444 \mu\text{C cm}^{-2}$ .<sup>[4]</sup>

The areas  $A_{\text{SR}}$  and  $A_{\text{Au}}$  were determined from the cyclic voltammograms recorded as stated below.

- $A_{SR}$  was obtained by integration of the a sharp peak observed at  $-0.97 \pm 0.02$  V, ascribed to the electroreduction of thiolate-Au bonds accordingly to  $Au-SR + e^- \rightarrow SR^- + Au^0$ .<sup>[5]</sup> The electroreduction of thiolate-Au bond was performed by scanning the potential between -0.2 to -1.3 V at  $0.1 \text{ V s}^{-1}$ , starting at -0.2V and in the cathodic direction.
- $A_{Au}$  was obtained by integration of the reduction peak centred at ca. 0.05V, assigned to the reduction of Au oxide monolayer generated during the anodic scan. The voltammogram was recorded by cycling the potential between to -1.35 V and 0.6 V at  $0.1 \text{ V s}^{-1}$ , starting at the open circuit potential (OCP) and in the anodic direction.

### Estimation of the expected Au island coverage $\theta_{Au\_island}$

**Table 2** Au island coverage for different decomposition degree of a single AuNC, yielding to LD phases that contain (1) RS-Au-SR staples or (2) SR thiyl radicals.

Decomposition Mechanism	Reaction	$n_{Au}$	$\theta_{Au\_island}$
1	$Au_{114}(RS-Au-SR)_{30} \xrightarrow{Au(111)} 30(RS-Au-SR)_{Au(111)} + 114 Au_{Au(111)}$	114	0.25
2	$Au_{114}(RS-Au-SR)_{30} \xrightarrow{Au(111)} 60(SR)_{Au(111)} + 144 Au_{Au(111)}$	144	0.31

As discussed in the main manuscript, due to the stoichiometry of the AuNC,  $n_{SR}$  is equal to 60, independently of the decomposition mechanism. Contrarily, the number of Au atoms available to form Au islands ( $n_{Au}$ ) depends on the degree of decomposition of the capping layer (RS-Au-SR).

A single AuNC is formed by  $n_{SR} = 60$  hexanethiolates and 144 Au atoms. After the AuNC disintegration the SR and Au island coverages can be expressed through the AuNC surface density,  $n_{AuNC}$  as:

$$\theta_{SR} = 60 n_{AuNC} \quad [S3]$$

$$\theta_{Au\_island}^{NC} = n_{AuNC} n_{Au} \quad [S4]$$

$\theta_{SR}$  can be obtained from electrochemistry data as already shown in equation S1. Hence, combining [S3] and [S9],

$\theta_{Au\_island}^{NC}$  can be determined from experimental data as

$$\theta_{Au\_island}^{NC} = \frac{\theta_{SR} n_{Au}}{60} \quad [S5]$$

Finally, as stated in the main text, to obtain the total Au coverage ( $\theta_{Au\_island}$ ) the Au atoms provided by the lifting of the herringbone reconstruction ( $\theta_{Au\_island}^h \approx 0.043$ ) must be added to the  $\theta_{Au\_island}^{NC}$  resulting

$$\theta_{Au\_island} = \theta_{Au\_island}^{NC} + \theta_{Au\_island}^h = \frac{\theta_{SR} n_{Au}}{60} + 0.043 \quad [S6]$$

Table 2 shows the Au island coverage obtained by using equation S6 depends on  $n_{Au}$  considering the different decomposition mechanism: single AuNC yielding to LD phases that contain (1) staples or (2) thiyl radicals.

### Determination of the number of particles that have been reached the surface

The number of nanoclusters that have been reached the surface ( $x_{AuNC}$ ) is given by:

$$x_{AuNC} = \frac{\theta_{SR}}{n_{SR}} n_{Au(111)} \quad [S7]$$

where  $\theta_{SR}$  and  $n_{SR}$  and  $n_{Au(111)}$  are the thiolate coverage, the number of thiolates per AuNC and number of Au atoms per  $cm^2$  on the (111) surface, respectively. As  $n_{Au(111)}$  is the same for both systems, the ratio of AuNCs that have been reached the surface for both systems is

$$\frac{x_{Au_{25}(SR)_{18}}}{x_{Au_{144}(SR)_{60}}} = \left( \frac{\theta_{SR}}{n_{SR}} \right)_{Au_{25}(SR)_{18}} \left( \frac{n_{SR}}{\theta_{SR}} \right)_{Au_{144}(SR)_{60}} = \left( \frac{0.25}{18} \right) \left( \frac{60}{0.11} \right) = 8 \quad [S8]$$

### Influence of AuNC size-dependent factors in the AuNC adsorption and disintegration

If AuNC size determines the adsorption and further decomposition, the process can be limited by the diffusion of the AuNC to the surface or by the steric effect that they impart to other upon adsorption.

If diffusion is limiting the process, the ratio of AuNCs that reach the surface can be determined by using the Fick's law, that is

$$\frac{x_{Au_{25}(SR)_{18}}}{x_{Au_{144}(SR)_{60}}} = \sqrt{\frac{D_{Au_{25}(SR)_{18}}}{D_{Au_{144}(SR)_{60}}}} e^{\frac{D_{Au_{144}(SR)_{60}}}{D_{Au_{25}(SR)_{18}}}} \quad [S9]$$

where D is the AuNC diffusion coefficient. D was estimated by using the Stock Einstein equation and considering that: (1) viscosity of DCM and mesitylene are  $0.000406 \text{ Kg m}^{-1} \text{ s}^{-1}$  [6] and  $0.00066 \text{ Kg m}^{-1} \text{ s}^{-1}$  [7], respectively; (2) the AuNC diameter is the one obtained from the DFT optimized structure, i.e. is 3.2 nm and 2.6 nm for  $Au_{144}(SR)_{60}$  and  $Au_{25}(SR)_{18}$ , respectively.

By applying equation S9, it was found that the ratio of AuNCs that reach the surface, if the process is diffusion-limited would be 2.4.

On the other hand, if steric effect regulates the AuNC adsorption, the ratio of AuNCs that reach the surface, should be

$$\frac{x_{Au_{25}(SR)_{18}}}{x_{Au_{144}(SR)_{60}}} = \left( \frac{A_{Au_{144}(SR)_{60}}}{A_{Au_{25}(SR)_{18}}} \right) = 1.5 \quad [S10]$$

None of the two factors mentioned above can explain the experimental value found for  $\frac{x_{Au_{25}(SR)_{18}}}{x_{Au_{144}(SR)_{60}}} = 8$ .

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