Supporting Information New Insights into the Chemistry of Thiolate-Protected Palladium Nanoparticles

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I. SYNTHESIS OF DODECANETHIOL-PROTECTED Pd NPS (Pd@SC12)

These NPs were synthesized by a modified two-phase Brust-Schiffrin method [1, 2]. Briefly, PdCl₂ (Aldrich, purum) was dissolved in water with a four-fold molar excess of HCl to form $[PdCl_4]^{2-}$, which was transferred to toluene with vigorous stirring using tetraoctylammonium bromide (ToABr, Aldrich) as a phase-transfer catalyst (ToABr:Pd = 1.5 : 1 molar ratio). The toluene phase turned deep red as the $[PdCl_4]^{2-}$ was completely transferred into it. After that, the water phase was discarded and dodecanethiol (SC12, Aldrich, 97%) was added (SC12:Pd = 0.5:1 molar ratio). The mixture was further stirred for 1 h and, then, $NaBH_4$ (Aldrich, 99%) was added in a 10-fold molar excess to reduce the Pd precursor and form the NPs, whereupon the solution quickly turned black. After further stirring for 3 h, the water phase from NaBH₄ was discarded, toluene was reduced by rotary evaporation at ambient temperature and the particles were rinsed four times with acetonitrile by a centrifugation/redispersion routine.

It is interesting to consider the expected products when the reduction is carried out at low temperature or, alternatively, the mixture is heated. It was already shown that when the temperature is raised, thiolate species adsorbed on Pd(0) are not stable anymore, and the decomposition of the ligand is produced, which results in the sulfidization of Pd(0) NPs [3]. As a result, in order to obtain Pd(0), at least in some extent, the preparation of Pd NPs must be carried out at room or lower temperatures [4].

In Fig. S1 it is shown the UV/vis spectra of the first steps of Brust-Schiffrin method, before adding sodium borohydride, to study the formation of Pd(II) thiolate complexes. Different thiol:Pd molar ratio were analyzed. [PdCl₄]²⁻ was transferred from the aqueous solution to the organic phase by the phase-transfer catalyst, tetraoctylammonium bromide and after discard-

ing the water phase, different amounts of dodecanethiol (SC12) were added to different aliquots. The spectrum corresponding to $[PdX_4]^{2-}$ without thiol (thiol:Pd = 0) presents a peak at ≈ 310 nm and a shoulder at ≈ 430 nm. When thiol is added, the spectra change until the thiol:Pd molar ratio is higher than 1 : 1. For the dodecanethiol:Pd molar ratio used in this paper (0.5 : 1), a mixture of Pd(II) thiolate complexes and $[PdX_4]^{2-}$ should be the responsible for the spectrum observed. In Fig. S1b, a photograph of each sample is shown.

The effect of adding sodium borohydride to each of the samples studied can be observed in Fig. S2. After the addition of the reducing agent, all samples immediately turned black. However, for thiol:Pd molar ratio higher than 2, after some hours, the solution returned to the original light orange color and the UV/vis spectra were similar to the ones obtained prior to the addition of sodium borohydride. For thiol:Pd < 1: the solutions remained black and the UV-vis spectra did not show any peak in the 300-500 nm range. However, for 1: 1 <thiol:Pd < 2:1 the UV/vis spectra showed the presence of peaks between 300 and 500 nm, denoting the existence of Pd(II) thiolate complexes. However for those molar ratios, the solutions remained black, with a weak orange color (Fig. S2b), indicating that a mixture of Pd NPs and Pd(II) thiolate complexes should be present in these solutions.

II. SYNTHESIS OF DODECYLAMINE-PROTECTED Pd NPS (Pd@NC12)

These particles were synthesized by the Leff method, originally described for Au NPs [5, 6]. $PdCl_2$ (Aldrich, purum) and dodecylamine (NC12, Aldrich, 98 %), were used as received. $[PdCl_4]^{2-}$ was produced as described above and transferred to toluene with vigorous stirring using ToABr. The ToABr:Pd molar ratio used was 2.3 : 1. Dodecylamine was added in 11 : 1 molar ratio with respect to Pd, without taking out the water phase. A milky white emulsion was formed, presumably due to the formation of a complex between the metallic species and the protonated amines. After 1 h, an aqueous solu-

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FIG. S1: **a)** UV/vis spectra of Pd(II) with different amounts of dodecanethiol (SC12), obtained 2 hours after the addition of SC12. The samples were diluted in toluene to achieve a Pd(II) concentration equals to 0.05 mM. Some sample were no included in the spectra for a better visualization. **b)** Photograph of the samples studied in **a**, before the dilution. The dodecanethiol:Pd (S:Pd) molar ratios of each sample are also shown.



FIG. S2: a) UV/vis of the samples showed in the previous figure 18 h after the addition of sodium borohydride. The samples were diluted 1/400. b) Photographs of the samples in **a**, before to the dilution. At the bottom of each vial, the water phase from sodium borohydride can be observed.

tion of NaBH₄ (Aldrich, 99%) was added while stirring (NaBH₄:Pd = 15 : 1). The suspension gradually became limpid and dark brown. It was further stirred for 18 h. After that, the aqueous phase was discarded and the toluene phase was reduced to half the original volume by rotary evaporation. The NPs were precipitated with ethanol, centrifuged, and rinsed three more times with ethanol. Finally, the dark brown powder was dried under ambient temperature.

III. SYNTHESIS OF DODECANETHIOL-PROTECTED Au NPS (Au@SC12)

Au@SC12 NPs were synthesized by the two-phase Brust-Schiffrin method [1]. HAuCl₄ was synthesized by dissolution of a Au wire (99.999%) in aqua regia, following the method described by Block [7]. A 50 mM HAuCl₄ aqueous solution was added to a ToABr toluene solution (ToABr:Au = 2.5 : 1 molar ratio). After transferring the [AuCl₄]⁻ to the organic layer, the water phase was discarded and dodecanethiol was added in a 2:1 SC12:Au molar ratio. The solution was stirred for 30 min and a 10fold molar excess of NaBH₄ was added as an aqueous solution. After further stirring for 3 h, the water phase was



FIG. S3: **a)** Representative TEM image of Au@SC12 NPs. The image was acquired with a Phillips CM 200 UT microscope, operating at 200 kV. **b)** Size distribution histogram and its log-normal fit.

discarded and the toluene was reduced by rotary evaporation at ambient temperature. Au NPs were rinsed four times with ethanol and dried at ambient temperature. The size of these particles was obtained by transmission electron microscopy (TEM) analysis, as shown in Fig. S3.

IV. PREPARATION OF ALKANETHIOLATE-COVERED Pd SURFACES

Dodecanethiol was adsorbed on Pd substrates prepared by electrodeposition, as described in ref [8]. The thiolate monolayers were prepared by immersing the Pd substrates in $50 \,\mu\text{M}$ dodecanethiol ethanolic solutions for 18 h. After the preparation, the samples were carefully cleaned in ethanol in order to remove physisorbed thiols.

V. SIZE DISTRIBUTION OF THE NANOPARTICLES

The size distribution of the NPs was performed using HAADF-STEM images and the particles analysis algorithm of Digital Micrograph software. The intensity threshold was adjusted for each image. Particles with diameters between 0 and 10 nm were considered and particles with an aspect ratio higher than 1.2 were discarded in order to avoid counting two particles joined together. A log-normal distribution function was fitted to the histogram obtained. The equation used was $1/[(2\pi)^{1/2}\sigma d] \exp \{-[\ln(d) - \mu)]^2/(2\sigma^2)\}$, where μ and σ are the mean and standard deviation of the logarithm of the diameter (d), respectively. The arithmetic mean diameter (<D>) and its standard deviation (s.d.) were calculated as $<D> = \exp(\mu + 1/2\sigma^2)$ and s.d. = $[\exp(\sigma^2) - 1]^{1/2} \exp(\mu + 1/2\sigma^2)$.

VI. FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra of these NPs can give clear evidence about the presence and structure of the thiol protecting layer. A typical spectrum collected over the range for Pd@SC12 particles is shown in Fig.S4. We observe the characteristic methylene symmetric (d⁺) and antisymmetric (d⁻) CH₂ stretching vibrations bands at 2850 and $2921 \,\mathrm{cm}^{-1}$, respectively, revealing that the alkyl chains are present and extended in a trans zigzag conformation. These bands have been used in previous infrared spectroscopic studies on two-dimensional SAMs to determine the orientation of the methylene chains [9]. The position of the d⁺ in Fig. S4 lies between the values reported for bulk Pd surfaces modified by hexadecanethiol $(2919 \,\mathrm{cm}^{-1})$ and decanethiol $(2922 \,\mathrm{cm}^{-1})$ [9]. Furthermore, the same wavenumber that we found for Pd@SC12 NPs was reported for similar Au@SC12 NPs [10], which means that the degree of organization of the alkyl chains is comparable for Pd and Au NPs. It should be noted that this degree of organization is also susceptible to the way the sample is prepared to acquire the spectra. The concentration of the NPs suspension used to drop cast the sample and the rate of solvent evaporation after drop casting the suspension can produce variations on the collective organization of the alkyl chains. Additionally, the band observed at $2954 \,\mathrm{cm}^{-1}$ and the shoulder at $2872 \,\mathrm{cm}^{-1}$ correspond to the asymmetric (r^{-}) and symmetric (r^{+}) stretching modes of the CH_3 group, respectively. These absorption bands are nearly invariant with respect to the 3D-SAM formation onto the particle surface [10]. A very weak S-H stretching vibration mode, ν (S–H), is usually observed in the spectral range $2550-2600 \,\mathrm{cm}^{-1}$. This vibration mode appears at $2575 \,\mathrm{cm}^{-1}$ for free dodecanethiol. Consequently, the absence of an absorption in the ν (S–H) region (inset of Fig. S4) indicates the breakage of the S-H bond of dodecanethiol [11].

In the $1300-1500 \,\mathrm{cm}^{-1}$ region, the strong band observed at $1463 \,\mathrm{cm}^{-1}$ is assigned to the methylene scissoring mode (δ) while the CH₃ symmetric bending vibration, also known as the umbrella mode (U), appears at $\sim 1376 \,\mathrm{cm}^{-1}$. This mode is essentially isolated to the motion of the methyl group and is thus relatively insensitive to the conformation of the rest of the chain. The series of peaks observed between 1000 and $1150 \,\mathrm{cm}^{-1}$ are assigned to the skeletal C–C–C vibrational modes (R_x) , while the progression bands in the region $700-980 \,\mathrm{cm}^$ are assigned to the rocking modes (\mathbf{P}_x) of the methylene chains. The main band at $720 \,\mathrm{cm}^{-1}$ (\mathbf{P}_1) is the head band of the rocking progression. Note that the intensity of this band is enough to partially obscure the conformational information about C-C bonds adjacent to the C–S bond, which might be obtained from the analysis of the C–S stretching bands. For alkanethiols of short alkyl chains, both in the gas and the liquid phase, the vibrational spectral region between 600 and $750 \,\mathrm{cm}^{-1}$ show two ν (C–S) bands. They correspond to different conformers, which have been labeled TT and GT, where the first letter describes the conformation (trans or gauche) around the C-C bond adjacent to the C-S bond and the second letter describes the conformation around the C—S bond. For propanethiol the GT conformer has a ν (C–S)G band at $655 \,\mathrm{cm}^{-1}$ whereas, for the TT conformer, this stretching mode, ν (C–S)_T, appears at 706 cm⁻¹ [12].

We found that the gauche band was undetectable (*i.e.*, the uncertainty associated with the background subtraction has a magnitude comparable to the intensity of the small peaks observed for wavenumbers smaller than $700\,{\rm cm^{-1}}.$ Nevertheless, a significantly intense shoulder at $700 \,\mathrm{cm}^{-1}$, which can be assigned to the C–S stretches to adjacent trans $\nu(C-S)_T$ methylene units was observed in our spectrum. Although the population of trans conformers has been estimated for hexanethiolate-protected AuNPs [13], the P_1 band is more intense in the case of moieties derived from dodecanethiol [10] which would make spectra deconvolution less trustable. Contrary to our results, a 100% gauche conformation, which was interpreted considering dioctyl-disulfide as capping species, was found in the infrared spectrum of ${}^{13}C_1$ labeled octanethiol-protected Pd NPs [14]. Although quantitative information cannot be extracted with regards to the relative abundance of the rotational isomers, our spectra resemble those obtained for Au NPs protected by alkanethiols [10], instead of the full gauche conformation reported by Zelakiewicz, et al. [14]. Thus, albeit almost the same recipe has been used, the nature of the capping species or their dominant conformation seems to be different. On the other hand, dialkyl disulfide cannot be disregarded as a plausible capping molecule based on the absence of signals due to S—S bond, usually found around $575 \,\mathrm{cm}^{-1}$, since these vibrations are too weak [15]. This point is discussed on the basis of XPS data.



FIG. S4: FTIR spectrum of Pd@SC12 NPs. The absorbance in the region between 1650 and 600 cm⁻¹ was multiplied by a factor of 4. In the inset, the region near 2575 cm⁻¹ is amplified to verify the absence of the peak corresponding to ν (S–H).

VII. C:S ATOMIC RATIO BY X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The analysis of the C:S atomic ratio also support the fact that the surface species in planar and nanoparticle surfaces are of the same nature. In the case of Pd@SC12 NPs, the C:S atomic ratio is approximately 11.5 : 1, while for Au@SC12 NPs it is over 14 : 1. The value obtained for Au is greater than the stoichiometric relation (12:1)for two reasons. The first one is that there is always carbon that comes from contamination of the sample (carbon from ToABr, adventitious carbon), which increases this ratio. The second is that C 1s electrons, from the thiol hydrocarbon chains are less attenuated than S 2p electrons, from the thiol group. Interestingly, the result obtained for Pd NPs is not consistent with dialkyldisulfides or simply alkanethiolates as capping species, but reasonably approaches the value expected for a mixed sulfide + thiolate interface. In this way, we answered the open questions remaining from FTIR data.

VIII. XPS S 2p SIGNAL OF Pd@SC12 NPS STUDIED USING SYNCHROTRON RADIATION

Fig. S5 shows the S 2p high resolution XPS signal taken with a source of 250 eV. Extensive data collection did not support an increase in signal to noise ratio because radiation damage might be significant. This can be seen in the need to fit the spectrum with a small peak at higher binding energies (5.5%). However, the deconvolution of this spectrum shows the same main species found with Mg K α source, but here they are better resolved. Table S1 shows the relative contribution of the different components of the S 2p signal.



FIG. S5: S 2p spectrum of Pd@SC12 NPS, obtained with a source of 250 eV.

TABLE S1: Relative contribution of the different components of the S 2p signal.

Position	\mathbf{FWHM}	(eV)	(%)
162.2	0.9		34.4
163.2	0.9		35.2
163.8	0.9		24.9
164.9	0.9		5.5

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