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Supporting Information

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Electrochemical Preparation and Delivery of Melanin- iron Covered Gold Nanoparticles

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In order to derive the radius of gyration of the nano-objects, a Guinier plot (ln(*I(q)*) versus q^2) is commonly used. In this plot, a straight line is expected to fit the data within a more or less wide *q* range at small *q* ($q\ R_g < 1$), depending on the size and shape of the object (see reference 15). From the slope of the straight line, a_G, the radius of gyration is obtained as $R_g = \sqrt{3\ _G}$. The radius of gyration of a homogeneous and spherical object is related to its geometrical radius *R* by $R_g = \sqrt{\frac{3}{5}}R$. In Table 1 we report the obtained values of a_G, and R_g for the NT-AuNP and melanin NT-AuNP.

Sample	a_G / nm^2	R_g / nm
NT – AuNP	0.1401(1)	0.6483(4)
Melanin NT – AuNP	0.861(3)	1.607(6)

Table 1: Guinier slope a_G obtained from the linear fit and the calculated radius of gyration R_g for melanin-iron modified and non modified NT-AuNP.

The small angle scattering intensity *I(q)* of an isotropic solution of polydisperse spherical NP can be written within the "decoupling approximation" as

$$I(q) = \tilde{P}(q) \cdot S(q) \quad (1).$$

S(q) is the effective structure factor and $\tilde{P}(q)$ is the average of the form factor *P(q,r)* over the NP radius distribution *f(r)*:

$$\tilde{P}(q) = \int_0^\infty P(q,r) \cdot f(r) \cdot dr \quad (2).$$

The form factor gives the shape of the aggregates and the structure factor takes into account the possible interaction between them. In order to obtain more quantitative information of the SAXS curves we made the

assumption that the particles have a spherical shape of radius *r* and that there is a soft "shell" covering the NP surface with a density profile that is a function of the radial distance r (Figure 1).

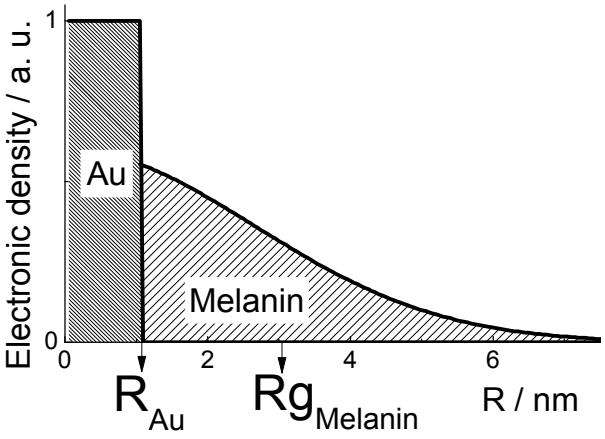

Figure 1: Schematic model for the electron densities used for melanin iron NT-AuNPs in hexane solution proposed for SAXS fitting.

Under these assumptions the form factor for this type of system is given by[a]:

$$P(q) = [\Delta_{Au} A(q) - A_{Melanin}(q)]^2 \quad (3),$$

where Δ_{Au} is the electronic density of Au NP core relative to solvent. *A(q)* is the amplitude function for a hard sphere of radius R given by

$$A(q) = \frac{4}{3} R^3 .3 \frac{\sin(q.R) - qR\cos(qR)}{(qR)^3} \quad (4).$$

To model the polymer shell we use a decaying electronic density profile described by Guinier [a] which is parameterized by $\Delta_{Melanin}$ to tune the electronic density of the polymer shell:

$$A_{Melanin} = \Delta_{Melanin} e^{-(\mathrm{Rg}_{\mathrm{Melanin}} \quad q)^2/6} \quad (5)$$

Assuming a LogNormal radius distribution function the average form factor $\tilde{P}(q)$ is expressed as:

$$\tilde{P}(q) = \int_0^{\infty} [A_{Au}(q) - \Delta_{r} . A_{Melanin}(q)]^2 \cdot \frac{e^{-\left[(\ln(r) -)^2/(2s^2)\right]}}{Rrs\,(2\ )^{1/2}} \cdot dr \quad (6),$$

This distribution is assumed for the NP core (fig. 1) where μ and s are the mean and standard deviation of the variable's natural logarithm that gives an expression for the mean value $R_{Au} = e^{+ \ ^2/2}$. Equation (6) introduces a new parameter, Δ_r which is defined only to facilitate the fitting routine as $\Delta_{Melanin} / \Delta_{Au}$.

To model the NT-AuNP we only considered a hard sphere model (Equation (4)) with a LogNormal size distribution. The parameters obtained in each fit are shown in Table 2.

Sample	NT-AuNP	Melanin iron NT-AuNP
μ	0.0124(4)	0.0124(4)
σ / nm^2	0.0673(3)	0.0673(3)
$Rg_{Melanin}$ /nm	-	2.89(7)
Δ_r	-	900(10)

Table 2: Parameters obtained from the fitting routine described above for Melanin Iron modified and non modified NT – AuNP

[a] A. Guinier, X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies (Freeman, San Francisco, 1963).