

Synthesis and characterization of amphiphilic fluorinated polymers for phase transfer solubilization of hydrophobic gold nanoparticles.

Juan Manuel Arango

Sónia Lopez-Fernandez, Jorge Blanco, Carolina Carrillo-Carrión, Mónica Carril.

Instituto Biofisika UPV/EHU, CSIC, Barrio Sarriena s/n, E-48940, Leioa, Bizkaia, Spain. Departamento de Bioquímica y Biología Molecular, UPV/EHU, 48940, Bilbao, Spain

jarango001@ikasle.ehu.eus

There are many synthetic protocols that produce nanoparticles (NPs) that are only dispersed in organic solvents [1]. Among the methods to transfer those NPs to water, the polymer coating strategy is one of the most popular ones. It is based on the use of an amphiphilic polymer that orients its hydrophobic side to the NPs and exposes a water-friendly side that allows water dispersibility [2]. In this context, herein we report a methodology for the encapsulation of hydrophobic NPs that takes advantage of the enhanced hydrophobicity of novel fluorinated amphiphilic polymers.

The synthesis of the fluorinated polymers was based on a ring opening reaction over poly (isobutylene-*alt*-maleic anhydride) polymer with a small fluorinated amino ending building block. The amount of fluorine present in such polymers was controlled by the reaction stoichiometry and confirmed by elemental analysis and ^{19}F NMR. Thus, a family of polymers with different degree of fluorination were synthesized to encapsulate hydrophobic Au NPs of gold core size of 4, 14 and 18 nm. The encapsulation process took place by a simple and straightforward phase transfer strategy and could be monitored by observing the transfer of colour from the organic phase to the aqueous phase, indicating that the red coloured Au NPs were eventually dispersed in water, as a result of the proper encapsulation with the amphiphilic fluorinated polymer (figure 1).

The colloidal stability of freshly encapsulated NPs was confirmed by ultraviolet-visible spectroscopy (UV-Vis) and the gold core size was analysed by transmission electronic microscopy (TEM). The colloidal stability over time was controlled by visual inspection of

the formation of precipitates, by UV-Vis and by Dynamic Light Scattering (DLS). We observed that the highest colloidal stability was achieved with the polymer having the highest fluorination degree. Nonetheless, similar colloidal stability could be achieved with the rest of the polymers by increasing the amount of polymer around the NPs.

Furthermore, the so-obtained Au NPs were exposed to different pH conditions (pH =5, 6 and 7.4) and to the presence of different cations of biological interest such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} at two ranges of concentration (20 and 100 mM). Accordingly, Dynamic Light Scattering (DLS) experiments allowed to determine how the hydrodynamic radii changed over these parameters. A raise in the pH value generated a slight increase in the radii of the Au NPs for every single sample. Also, divalent cations generated a dramatic increase in the radii observed compared to the monovalent ones leading to aggregation in some cases. These observations indicate that these amphiphilic polymers may be potentially used in the future to deliver hydrophobic cargoes.

References

- [1]. S. Ashraf, B. Pelaz, P. del Pino, M. Carril, A. Escudero, W. J. Parak, M. G. Soliman, Q. Zhang, C. Carrillo-Carrion, *Chem. Mater.* 1 (2017), 411.
- [2]. C.J. Lin, R.A. Sperling, J. K. Li, T. Yang, P. Li, M. Zanella, W. H. Chang, W. J. Parak. *Small*, 3 (2008), 335.

Figures

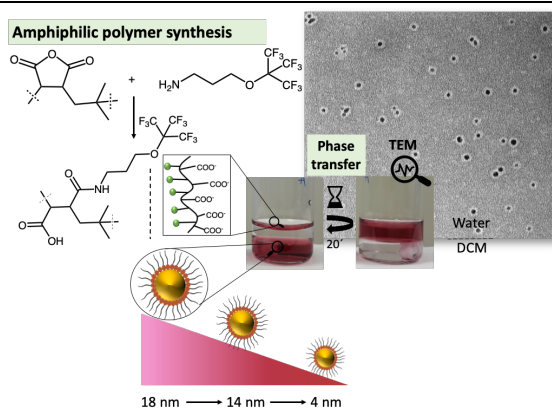


Figure 1: Encapsulation process of Au NPs with amphiphilic fluorinated polymers