One-step synthesis of Janus Nanoparticles by self-assembly monolayers.

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Described first by De Gennes[1] Janus Nanoparticles (Janus NPs) are called like the Roman God custodian of universe, God of gates and doors, beginnings and endings and hence represented with a double-faced head. Janus Nanoparticles are therefore particles with two distinct sides. The term Janus has been used to describe different particles such as dendritic macromolecules, block-copolymers micelles, or inorganic materials. The asymmetry generated in these particles is useful in wide range of applications. The most known is probably the one that uses the so-called Pickering effect, [2] that is, particles can be used to stabilize oil-in-water and water-in-oil emulsions. It has been demonstrated theoretically and experimentally that this stabilization is much higher when it is done by amphiphilic Janus nanoparticles instead of homogeneous particles, due to the higher adsorption energy of the particles at the liquid-liquid interface. These stabilized droplets could be used for diverse applications from water-based paints to heterogeneous nanocatalysis. The Janus nanoparticles can also be used in other important fields like electronic displays, nanomotors, drug or gene delivery or as building blocks for assembly of suprastructures. [3]

Up to now a few different strategies to obtain Janus nanoparticles have been described in the literature that can be included in one of these groups: toposelective surface modification that includes: 1. selective masking, use of reactive directional fluxes, microcontact printing or arrangement of the particle along an interface and partial contact with a reactive medium; 2. template-directed self-assembly; controlled phase separation phenomena; 3. and controlled surface nucleation.[3] There are several problems related to these strategies like the difficulty to obtain small nanoparticles (<10nm); the complexity of the synthesis methods that involves first the synthesis of symmetric particles (homogenous or core-shell) and them a posterior modification; and the low yield of this strategies due to the fact that most of them require the use of a surface where the particles are placed to avoid the reaction of one of the sides. To the best of our knowledge none of these strategies has the ability of producing truly large nanoparticle quantities in an easy way, as a direct synthesis can do.[3]

In our group it has been reported previously that when a metallic nanoparticle is synthesized with mixture of dislike ligands, there is a self-assembly with the formation of stripes on the topology of the nanoparticle.[4-7] However this is not the only possible topological conformation, depending on the parameters of the particle (ligand lengths, ligands functionality or surface curvature) other self-assembly structures such as Janus or random domains are also possible.[6] Here we report the synthesis of Janus Nanoparticles with the use of self-assembly monolayers (SAMs) composed of two types of ligand molecules of different length. The particles have been synthesized using a modification of the method described by Zheng et al.[8] extended to mixtures of ligands. This synthesis is an easy one-step, one-phase synthesis for monodisperse metallic nanoparticles of small size (<10 nm) that can be scaled up to produce enough particles for useful applications and that can be extended to different functionalities. The two ligands used here were 1-hexanethiol (HT) and 1-dodecanethiol (DDT). TEM images were used to calculate the size and size distribution of the particle. ^{1}H NMR spectroscopy after particle decomposition was used to calculate the ligand ratio. Once synthesized the particles were deposited on

gold-on-mica substrates using Langmuir-Blodget deposition and then imaged using STM. The phase separation calculations were made using mesoscale simulations.

Figure 1 shows a representative STM image of a monolayer of nanoparticles made of 1:2 HT:DDT (ratio in solution). As we can see in the image the particles tend to order in a hexagonal lattice due to the monodispersity of the nanoparticles. The most interesting feature of these NPs is however the existence of two clear phases, a big one that corresponds to the DDT ligand and an small and circular one (on the left size of the particles) that correspond to the HT ligand. To be sure this was a real feature and not an artifact several images were taken in different areas and with different tips, in addition this features were seen with to different STM microscopes a Veeco Multimode in air and an Omicron in ultra high vacuum (UHV). We have also seen that the amount of Janus NPs depends on the ratio between ligands being bigger for mixtures far from the 1:1 ligands' ratio. Mesoscale simulations have shown the formation of Janus Nanoparticles for high values of the interaction parameter of the ligands. In our case the high difference in ligands length, and therefore high differences in the enthalpic component of the phase-separation makes this parameter to be high enough to make a complete phase-separation of the two ligands.

This new way to obtain Janus nanoparticles has a really high potential to be used I several applications due to its simplicity, scalability and variability of ligands ant therefore functionalities that can be used.

Figures

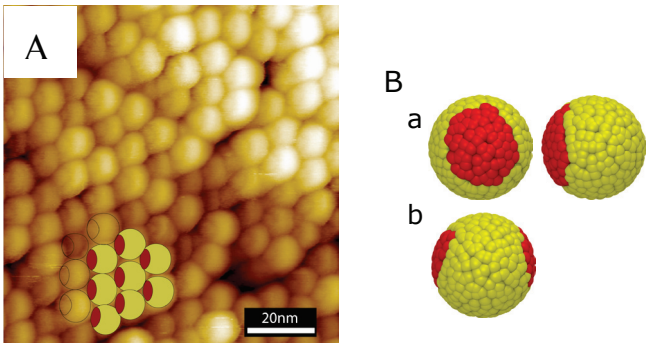

Figure 1. A) STM image of a monolayer of nanoparticles 1:2 HT:DDT Janus NPs (The cartoon has been drawn to help the reader to identify the Janus NPs). B) Mesoscale simulation of the same particles showing a phase-separation in equilibrium with distributions in 2 or 3 domains (a and b respectively).

References

[1] de Gennes, P. G. *Reviews of Modern Physics,* 64, (1992), 645.
[2] Pickering, S. U. *Journal of the Chemical Society,* 91, (1907), 2001-2021.
[3] Perro, A.; Reculusa, S.; Ravaine, S.; Bourgeat-Lami, E. B.; Duguet, E. *Journal of Materials Chemistry,* 15, (2005), 3745-3760.
[4] Jackson, A. M.; Myerson, J. W.; Stellacci, F. *Nature Materials,* 3, (2004), 330-336.
[5] DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. *Science,* 315, (2007), 358-361.
[6] Singh, C.; Ghorai, P. K.; Horsch, M. A.; Jackson, A. M.; Larson, R. G.; Stellacci, F.; Glotzer, S. C. *Physical Review Letters,* 99, (2007), 226106.
[7] Carney, R. P.; DeVries, G. A.; Dubois, C.; Kim, H.; Kim, J. Y.; Singh, C.; Ghorai, P. K.; Tracy, J. B.; Stiles, R. L.; Murray, R. W.; Glotzer, S. C.; Stellacci, F. *Journal of the American Chemical Society,* 130, (2008), 798-799.
[8] Zheng, N.; Fan, J.; Stucky, G. D. *Journal of the American Chemical Society,* 128, (2006), 6550-6551.