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Multi-responsive hybrid Janus nanoparticles: Surface functionalization through solvent physisorption

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ABSTRACT

In this work, we present a simple methodology to produce multi-responsive Janus nanoparticles using a Pickering emulsion-based approach. In order to use these nanoparticles (NPs) as emulsion stabilizers, tetrahydrofuran was physisorbed on the surface of freshly synthesized Fe_3O_4@SiO_2 NPs, which reduced their inherent hydrophilic character and permitted to create a close packed arrangement of particles at the emulsion interface. This situation allowed selective functionalization of the surface of the nanoparticles exposed to the water phase with a vinyl derivate molecule, which permitted to initiate the sequential polymerization of pNIPAM and poly(vinylimidazole). Thus, we obtained Janus nanoparticles that responded to changes in the temperature and the pH of the media as well as to external magnetic fields. The presented method does not require the surface modification of the original nanoparticles with surfactants or the use of fused silica and provides an easy way to create Janus particles in the nanoscale range.

1. Introduction

Anisotropy is a natural property of certain molecules and macromolecules that is used by living organisms to make complex processes such as structural assembling [1,2], information codification [3], or molecular identification [4]. This property has inspired scientists to create anisotropic materials with many industrial applications as surfactants, nanopatterns, smart inks, bifunctional coatings or auto-healing materials. Within this group of materials, Janus particles are an interesting type of particles which have two or more differentiated faces in terms of physical and/or chemical properties [5].

The outstanding properties derived from such marked surface character make possible to apply them in the fabrication of novel emulsion stabilizers, self-propelled particles, optical probes, self-assembling materials or electronic paper [6–10]. Since Janus particles have proved to be highly versatile materials, different synthetic approaches have been developed to control their properties and their number of differentiated sides, to boost their yield and to simplify their synthetic process.

For instance, one of the first reported procedures was based on the differentiation of the particles after their deposition on a planar 2D surface, which protected the face in contact with the solid substrate avoiding its modification during the process. This strategy is still used due to its simplicity and the different functionalization methods that can be carried out, such as metal deposition, UV photo-polymerization, or microcontact printing, among others [11–13].

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Another interesting methodology to produce Janus particles from silica spheres has been based on the production of Pickering emulsions. This process consists in stabilizing emulsions of melted paraffin in water with colloidal particles instead of surfactants. In these emulsions, the particles are located at the interface between the organic droplets and the water. This permits to protect the side of the particles that is buried in the paraffin and to modify the side that is exposed to the aqueous phase, which would provide the Janus character to the particles. In this step, silica surface provides a versatile platform that can be modified by many different chemical routes that would render surfaces with different functional groups that could be used in catalysis, biocatalysis, detection or as drug delivery systems [14–17]. The generation of 3D interfaces when stabilizing the emulsion permits to increase the specific surface of the system, compared with a 2D planar surface approach, and thus to boost the yield of the Janus NPs [18]. Once the solid particles locate between the two phases and the emulsion stabilization occurs, a surface energy well keeps the particles trapped at the interface. This is because the adsorption free energy of spherical solid particles is much larger than kT at 293 K. The desorption energy from the interface for a homogeneous particle has been calculated by Pieranski [19] and is given by,

$$E = \pi R^2 \gamma(\mathrm{OW})(1 - |\cos\beta|)^2$$

with

$$\cos\beta = \frac{|\gamma(\mathrm{PO}) - \gamma(\mathrm{PW})|}{\gamma(\mathrm{OW})}$$

where R is the radius of the particles, γ(PO), γ(PW), and γ(OW) are the interfacial tensions of the particle (P) with the oil (O) and the water (W) and the two phases (oil and water), respectively [20]. The maximum value of E occurs when $\gamma(\mathrm{PO}) - \gamma(\mathrm{PW}) \ll \gamma(\mathrm{OW})$ and reads

$$E_{\max} = \pi R^2 \gamma(\mathrm{OW})$$

This expression explains why the formation of Pickering emulsions is favored by increasing particle size and, on the contrary, presents a big challenge in case of using nanoparticles (NPs).

One challenge that pose this methodology is the difficulty to control the hydrophilic/hydrophobic character of the particles, which is critical to stabilize the emulsion. One possibility is to use fused silica particles as stabilizers, which present a hydrophobic/hydrophilic balance that makes them suitable as stabilizers of Pickering emulsions. Nevertheless, the dehydroxylation process carried out during the production of this material reduces its reactivity and hampers further chemical functionalizations. To overcome this problem, some authors modify the surface of hydrophilic silica particles with cationic surfactants like CTAB [21]. In this process the amount of surfactant needs to be adjusted depending on the specific surface of the particles in order to avoid the formation of micelles. For these reasons, it would be very interesting to develop an alternative route that could overcome the previous problems without adding further disadvantages. In this work we present a new methodology to produce Janus particles based on Fe_3O_4@SiO_2 core@shell NPs with diameters of 65 nm. These NPs were hydrophobized by a simple method based on the adsorption of THF on the surface of the NPs. The advantage of this method relays on the simplicity and the lack of tedious calculations that are required when molecules like surfactants are used for the same purpose. Subsequently, the THF adsorbed particles were used to stabilize a melted paraffin wax in water emulsion (O/W). After cooling down the paraffin wax droplets, the NPs were trapped on the solidified wax and their exposed surfaces were selectively modified with vinyl groups, which conferred them the Janus character. Then, the paraffin wax was dissolved and the particles were recovered to carry out two consecutive polymerization reactions onto the vinyl-functionalized side that permitted to obtain multi-responsive Janus particles, which could be applied as smart magnetic surfactants with a hydrophilic/lipophilic balance controlled by the temperature.

2. Experimental section

2.1. Materials

1-Octadecene (90%), Oleic acid (90%), Acetone (⩾99.5%), n-Hexane (95%), NIPAM (97%), AIBN (98%), Igepal CO-520 (⩾99.8%), Methanol (⩾99.8%), Tetrahydrofuran (THF 99.9%, inhibitor-free), Hydrochloric acid (37%) and 1-Vinylimidazol (⩾99%) were purchased from Sigma Aldrich. Sodium Hydroxide (97%) and Ammonium Hydroxide (30%), were purchased from Panreac. Iron(III) Chloride hexahydrate (97%) and Paraffin wax (melting point 58 °C) were purchased from Merck. Tetraethyl orthosilicate (TEOS, 97%) and o-Xilene (>98.0%) were purchased from Fluka. N-[3-(trimethoxylsilyl)propyl]-2-Propenamide was purchased from Angene Chemical. Ethanol (99.8%) was purchased from Alcoholes Aroca S.L. All chemicals were used as received without further purification.

2.2. Characterization

2.2.1. Transmission electron microscopy (TEM)

TEM pictures were taken using a JEOL JEM 1010 working at 80 kV. TEM samples were prepared putting a drop of NPs solution on a Formvar coated copper grid and letting it to dry at room temperature.