



Nanoscale hybrid silica/polymer Janus particles with a double-responsive hemicorona



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ABSTRACT

We report a versatile large-scale synthesis strategy for hybrid Janus nanoparticles with a silica core and a unilaterally attached polymer corona in a size range below 100 nm. The stimuli-responsive behavior of these nanoparticles with a poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) hemicorona is investigated. The synthesis is based on a modified version of the Pickering emulsion polymerization technique in combination with surface-initiated atom transfer radical polymerization (ATRP) in a “grafting from” approach. In a first step, poly(vinyl acetate) (PVAc) latex particles are prepared via Pickering emulsion polymerization. Colloidal stability is provided by 30 nm silica nanoparticles that adhere to the surface of the growing polymer particles. This results in polymer latexes which are armored with a layer of tightly immobilized nanoparticles, one side of which is immersed in the polymer particle and thus protected. After modification of the exposed side of the particles through chemisorption of an ATRP initiator, that is (2-bromo-2-methyl)propionyl-oxyhexyltriethoxysilane, and the removal of the particles from the interface, PDMAEMA chains are grown from this modified side of the silica particles, yielding well-defined Janus nanoparticles with a stimuli-responsive PDMAEMA hemicorona. Transmission and scanning electron microscopy, dynamic light scattering, thermogravimetric analysis and turbidity measurements were used to characterize the Janus particles. Most importantly, this synthetic approach is easily scalable and can be amended to furnish a wide range of nanoscale hybrid Janus particles. Furthermore, we demonstrate reversible switching behavior upon pH and temperature changes and find a peculiar self-assembly behavior of the Janus particles into linear strings at low pH and high concentration.

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1. Introduction

Hybrid nanoparticles combine relevant properties of organic and inorganic components, and will be important building blocks for in a modular concept of tailor-made multifunctional materials in future technologies [1–3]. As a unique type of building blocks, anisotropic particles, such as patchy, multicompartments, or Janus particles, have attracted much interest [4–6]. [7–9] The anisotropy in structure, shape, chemical and morphological patchiness can

generate defined self-assembly behavior and advanced functionalities and thus, has great potential in the scientific academic field as well as in industry. Besides being used as building blocks for the study of hierarchical self-assembly processes, Janus particles have in fact demonstrated a considerable potential in a number of fields such as drug carriers [10], stabilizers in emulsion polymerizations [11] and blends [12], surfactants [13–15], switchable devices [16] and optical probes [17,18]. Suitable Janus particles can be synthesized via several synthetic pathways including microfluidic techniques [10,19], lithography [20], controlled phase separation phenomena [21,22], template-directed self-assembly [23–25], controlled surface nucleation [26–28] and partial masking [29,30]. Despite advances in the synthesis routes mentioned above, major limitations prevail for the synthesis of nanoscale and highly

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functional Janus particles with facile and scalable procedures.

A promising route towards a large number of complex anisotropic Janus nanoparticles is based on the Pickering emulsion method [31–40]. Pickering emulsions are droplets dispersed in a liquid which are stabilized by particles instead of surfactant molecules. A kinetically stable oil-in-water emulsion is achieved when particles in the range of nanometers to micrometers are adhered to the surface of the droplets [41]. One part of a particle is located in the oil phase, whereas the other hemisphere is exposed to the continuous water phase, which renders it susceptible to chemical reactions. This template modification is easiest if the particles are locked preventing them from rotation (on the timescale of chemical reaction), and thus if the oil droplets are solid. After the chemical modification amphiphilic Janus particles can be obtained upon release from the intermediate template. This synthesis strategy was originally proposed by Granick and co-workers, who immobilized silica particles (>100 nm) at oil/wax interfaces [31–33]. The Pickering particles were frozen at the interface of water and wax upon cooling of the system. On the basis of this method, Stamm et al. prepared large stimuli-responsive bicomponent polymeric Janus particles with diameters larger than 800 nm [36]. Other groups used this method, too, to create a particularly interesting group of Janus colloidal particles which have asymmetric surface structures and specifically responding to external stimuli [36,38–40]. Research so far has focused on rather large Pickering particles (much larger than 100 nm), which are easier to immobilize at interfaces. When approaching nanoscale Pickering particles, their rotation needs to be arrested to furnish high-quality Janus nanoparticles [39]. This has been a major problem, so far.

In this work, we propose a versatile and simple synthetic route towards hybrid core-shell-corona Janus nanoparticles with a core size well below 100 nm. In comparison to other methods using Pickering emulsions we can work with particles, which are much smaller than those used in previous research and simultaneously reduce the experimental efforts. First, silica nanoparticles (30 nm in diameter) are immobilized at the interface of sub-micrometer sized droplets of poly(vinyl acetate) (PVAc) using a Pickering emulsion polymerization protocol developed by Bon et al. [42–48]. The nanoparticles are partially embedded in the resulting latex and thus protected on one side. Subsequently, after modification and removal of the particles from the latex we graft poly(2-dimethylamino)ethyl methacrylate (PDMAEMA) chains from the modified side of the silica particles using surface-initiated atom transfer radical polymerization (ATRP) [49]. Thus, we present the first detailed study on a synthesis route to obtain nanoscale amphiphilic Janus silica nanoparticles decorated with pH- and thermo-responsive PDMAEMA chains. We describe their double-stimuli responsive properties at high dilution and highlight their self-assembly behavior in more concentrated solutions, for which we find a pH-dependent aggregation into linear strings.

2. Experimental Section

2.1. Materials

AVS buffer solutions (Titrimorm, VWR), Ammonium hydroxide (NH₄OH; 28% in H₂O), potassium peroxydisulfate (KPS; >99%, Sigma Aldrich), Styrene (≥99%, Sigma Aldrich), AIBN (2,2'-Azobis(2-methylpropionitrile; 98%, Sigma Aldrich), 2-Bromo-2-methylpropionyl bromide (98%, Sigma-Aldrich), 2-(dimethylamino)-ethyl methacrylate (DMAEMA; 99%, Sigma-Aldrich), vinyl acetate (VAc; 99%, Sigma Aldrich), 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA; 97%, Sigma-Aldrich), Karstedt's catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution; platinum content ~3%, Sigma Aldrich),

Triethoxysilane (95%, Sigma Aldrich), Triethylamine (>99%, Sigma Aldrich), 5-Hexen-1-ol (98%, Sigma Aldrich), Ludox TM-40 sol (30 nm colloidal silica; 40 wt% in water) and HF (48 wt%, Sigma Aldrich) were used as received. Copper(I) chloride (99.99%, Sigma Aldrich) was purified according to the literature [50] and the monomer DMAEMA was destabilized by passing through a basic aluminum oxide column. For dialysis, a regenerated cellulose tube (ZelluTrans, Roth) with a MWCO of 6–8 kDa was used. All chemicals and solvents (ethanol; methanol, acetone) were used without further purification. Deionized water was generated by a MilliQ system (Millipore) and was used in all experiments.

2.2. Silica-armoured poly(vinyl acetate) latexes made using Pickering emulsion polymerization

The Pickering emulsion polymerization was carried out in round bottom flasks or in a double-walled cylindrical glass reactor (250 mL, Asynt Ltd.) equipped with an external circulating heating bath (Julabo F-25 unit), a condenser, and a four-bladed metal overhead turbine stirrer fitted at approximately 2 cm from the bottom of the reactor vessel (Cowie Ltd.) typically running at 300 rpm. The pH measurements were performed on a pH-Meter (765 calimatic, Knick).

A 40.0 wt% solution of Ludox TM-40 silica sol (33.0 g, 5.7 wt% overall, or 44.0 wt% based on monomer) was diluted and dispersed in 167.0 g of deionised water. The pH of the dispersion was adjusted with concentrated HCl (aq) to pH ~ 4.5 and was placed under a nitrogen atmosphere in a 250 mL double-walled glass reactor by purging. Monomer, 30.0 g, was added and the reaction mixture was heated to 65 °C, whilst stirring at 300 rpm. The emulsion polymerisation was started upon addition of 0.13 g KPS dissolved in 3.0 g of water. The reaction time was 6 h [42]. Contents and ratios of the experiment can be summarized as follows: The monomer content is 7.6 wt%, the silica content 4.3wt%, the ratio of silica to monomer (w:w) 0.56 and the ratio KPS to monomer is (w:w) 0.0055.

2.3. Synthesis of the ATRP initiator (2-bromo-2-methyl) propionyloxyhexyltriethoxysilane

The experimental procedure is illustrated in [Scheme S1 \(Supporting Information\)](#). The corresponding ¹H NMR spectra are shown in [Figure S1](#).

2.4. Pent-4'-enyl 2-bromo-2-methylpropionate

The synthesis follows a procedure mentioned in the literature [51]. 2-Bromo-2-methylpropionyl bromide (34.5 g, 150 mmol) was added in a dropwise fashion to a stirred solution of 5-hexen-1-ol (15.0 g, 150 mmol) and triethylamine (18.1 g, 179 mmol) in dry dichloromethane (80 mL). After stirring at 0 °C under argon for 1 h, the reaction mixture was allowed to warm to room temperature where it was stirred for an additional 2.5 h. The precipitated triethylamine hydrochloride was removed by filtration, and the solution was washed with aqueous ammonium chloride (saturated) and water. The dichloromethane was then removed, and the crude product was purified by vacuum distillation (85 °C/200 mbar) to give Pent-4'-enyl 2-bromo-2-methylpropionate as a colourless oily liquid.

¹H NMR (CDCl₃) δ 1.44 (quintet, 2H, CH₂), 1.65 (quartet, 2H, CH₂), 1.93 (s, 3H, CH₃), 2.08 (q, 2H, CH₂), 4.16 (t, 2H, CH₂), 4.91–5.04 (complex m, 2H, alkene = CH₂), and 5.70–5.85 (complex m, 1H, alkene = CH).

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