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One-pot facile synthesis of Janus particles with tailored shape and functionality†

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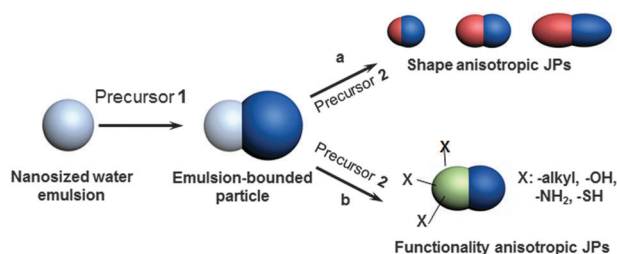
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This communication describes a novel strategy for the synthesis of silica Janus particles with controlled shape and functionality using a facile wet-chemical approach.

Janus particles (JPs) refer to a special class of colloidal particles having two compartments with different chemistry and/or polarity on their surface or interior. JPs have recently emerged as an exciting interdisciplinary field involving colloidal chemistry, materials science, medicine, and physics.¹ The structural non-centrosymmetry of JPs offers them fascinating properties such as dual-functionalities, magnetic or optical manipulation, and self-assembly behaviors.² JPs have shown applications as building blocks in self-assembly,³ as colloidal surfactants in stabilizing foams/emulsions,³ as dual-functional objects for catalysis, biological imaging, or drug delivery,⁴ and as functional components for optical, electronic, and sensor devices.⁵

To date, various synthetic techniques have been developed for the preparation of a variety of Janus objects (*e.g.*, Janus dendrimers, polymer micelles, and inorganic nanocrystals). These techniques include selective surface modification of particles by protecting one side of the particles,⁶ (electro)hydrodynamic techniques using ink-jetting⁷ or microfluidics,⁸ controlled surface nucleation,⁹ and phase separation method.¹⁰ However, these methods are either time consuming, uneconomic, or lack control over the geometry of the JPs. For example, a microfluidic-based hydrodynamic method can only produce JPs with dimensions above 5 μm .⁸ The selective surface modification approach requires multiple steps, and the quantity of produced JPs is limited by the surface area available for particles to form a monolayer.⁷

In this communication, we describe a simple general wet-chemical strategy for the preparation of colloidal JPs with controlled shape asymmetry or functionality anisotropy in each half. This novel method relies on the consecutive hydrolysis and condensation of two alkoxyisilanes in a mixture of pentanol, water, and ammonia. This synthetic approach does not require any additional steps such as surface protection (or modification), sample separation, and post-functionalization, which distinguishes our method from others. By controlling the relative amount of



Scheme 1 Schematic illustration of the wet-chemical approach to synthesize silica JPs with shape (a) and functionality (b) anisotropy via the consecutive hydrolysis and condensation of two alkoxyisilanes.

each precursor and according reaction condition, we synthesized a variety of JPs with various combinations of shapes and functionalities (*e.g.* amine and thiol). The design and synthesis of such JPs are illustrated in Scheme 1. Briefly, in the presence of polyvinylpyrrolidone (PVP) and sodium citrate, water forms nanosized emulsion droplets containing the catalyst ammonium for the hydrolysis and condensation of silica precursors in *n*-pentanol. The hydrolysis and condensation of precursor 1 are confined at the surface of nanosized water emulsions,¹¹ resulting in the nucleation and growth of hemispherical silica particles with one side bounded to the emulsions. Upon the addition of silica precursor 2, the hemispherical particles serve as seeds for further anisotropic growth of silica JPs.

We first demonstrated the synthesis of JPs with asymmetric shape including “moon-like”, “dumbbell-like”, and “rod-like” JPs using a single silica precursor, tetraethoxysilane (TEOS) for both two hydrolysis steps. The synthesized JPs are composed of two halves as indicated by a clear boundary between the two compartments due to the difference in the diameter of two silica hemispheres (Fig. 1). The control over the shape and the relative volume of each half of JPs were achieved by precisely tuning the water concentration in the reaction.^{11,12} With decreasing water concentration, the aspect ratio of each half of JPs increased, resulting in the morphology transition of JPs from “moon-like” (Fig. 1a), to “dumbbell-like” (Fig. 1b), eventually to “rod-like” shape (Fig. 1c). At a high water concentration ($\geq 34.0 \text{ mg mL}^{-1}$), each hydrolysis step of TEOS generated one half with approximately spherical shape. In this case, “moon-like” or “dumbbell-like” JPs were obtained. For example, in a reaction containing 35.0 mg mL^{-1} of water, two additions of 0.32 mmol of TEOS resulted in “moon-like” JPs with an average diameter of $662.2 \pm 96 \text{ nm}$ (see ESI†). By slightly decreasing the water

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† Electronic supplementary information (ESI) available: The synthesis details of JPs, self-assembly of JPs and more SEM/TEM images. See DOI: 10.1039/c1cc15603a

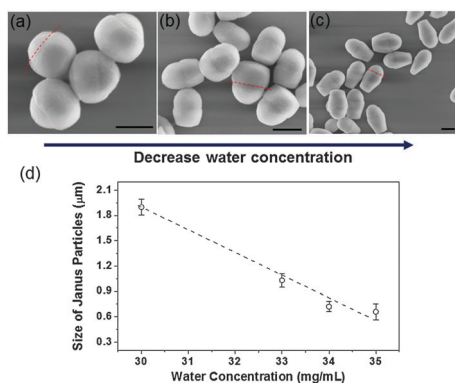


Fig. 1 SEM images of Janus particles with anisotropic shape: (a) “moon-like” JPs, (b) “dumbbell-like” JPs, and (c) “rod-like” JPs. Both halves of the JPs are synthesized from the TEOS precursor. The JPs show a clear boundary between the two halves, as indicated by a dashed red line. Scale bars are 500 nm. (d) Average diameter (along the longitudinal axis of particles if the particles are non-spherical) of JPs as a function of water concentration in the reaction.

content to 34.0 mg mL^{-1} , “dumbbell-like” JPs with an average diameter of $704.4 \pm 61 \text{ nm}$ along the longitudinal axis were formed (Fig. 1b). At a low water concentration ($<34.0 \text{ mg mL}^{-1}$), the constituent halves of JPs continuously grew along the longitudinal direction to form one-dimensional rod-like JPs under the assistance of structure-directing agent PVP. For example, at a water concentration of 33.0 mg mL^{-1} , rod-like JPs with a diameter of $625.7 \pm 73 \text{ nm}$ (close to the diameter of “moon-like” JPs) and a length up to $1.03 \pm 0.08 \mu\text{m}$ were obtained (Fig. 1c). We note that the diameter of JPs along the transverse axis was mainly determined by the size of the initial water emulsions.^{11b}

This synthetic strategy also allows us to readily control the functionality of each compartment of the JPs. We synthesized JPs with different functionalities on each half of the particles using a combination of two precursors with different functional groups, such as TEOS/hexadecyltrimethoxysilane (HDTMOS), TEOS/aminopropyltrimethoxysilane (APS) and TEOS/mercaptopropyltrimethoxysilane (MPTMOS).¹³ Fig. 2 shows the synthesized JPs with one half carrying different functional groups including alkyl chains, amine groups and thiol groups (see ESI† for more SEM/TEM images). The morphologies of JPs indicate a clear structural boundary between two halves, although it is difficult to distinguish the surface chemistry between two parts. When HDTMOS was used as precursor **2**, the hydrolysis of HDTMOS generated flexible thin films on one side of JPs with a surface coverage of $\sim 1/3$ (Fig. 2a and b). The average diameter of such JPs is $\sim 375.2 \pm 48 \text{ nm}$ by analyzing TEM images and $\sim 280.2 \text{ nm}$ obtained from dynamic light scattering (DLS) measurement in ethanol. The much smaller value of diameter by DLS could be due to not being perfectly spherical shape of the particles. When a silane coupling agent APS was used as precursor **2**, the reaction produced JPs with one half carrying amine groups on both the surface and the interior of the JPs (Fig. 2c and d). For MPTMOS as precursor **2**, JPs with one part containing thiol groups were synthesized (Fig. 2e and f). We are aware that the compartments made from MPTMOS had a hollow spherical morphology, as presented in TEM images (Fig. 2f). The formation

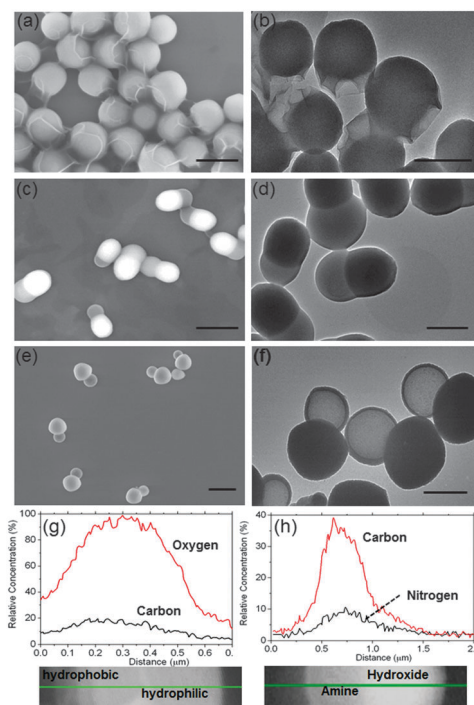


Fig. 2 Janus particles with anisotropic functionality. (a, b) SEM (a) and TEM (b) images of JPs having one half made from TEOS and the other made from HDTMOS. The flexible film side is made from HDTMOS. (c, d) SEM (c) and TEM (d) images of JPs having one half made from TEOS and the other made from APS. In (c), the white portion is TEOS and the grey portion is APS. In (d), the dark compartment is TEOS and the grey part is APS part. (e, f) SEM (e) and TEM (f) images of JPs having one half made from TEOS and the other made from MPTMOS. In (e), the darker halves are from MPTMOS, while lights side is TEOS. In (f), the hollow part is made from MPTMOS, while the dark part is TEOS. (g) SEM-EDX of JPs in (a, b) across the two halves. The difference in the relative concentration profile of carbon and oxygen in two halves indicates the formation of “moon-like” JPs. (h) SEM-EDX of JPs in (c, d) across the two halves. The difference in the relative concentration profile of carbon and nitrogen in two halves indicates the formation of “dumbbell-like” JPs. Scale bars are 500 nm.

of hollow structures is rarely observed in a Stöber synthesis of silica particles. A possible explanation is that the rapid hydrolysis and condensation of MPTMOS on the surface of water emulsions formed a membrane to fully cover the water/pentanol interface, preventing the further catalytic polymerization of silane monomers.^{13a}

We confirmed the chemical heterogeneity of the JPs, using SEM energy-dispersive X-ray analysis (SEM-EDX) (Fig. 2g and h). For example, due to the hexadecyl groups originated from HDTMOS, the half made from HDTMOS showed a relative carbon concentration of $\sim 20\%$, which is two times higher than that of the TEOS half (Fig. 2g). The compositional difference endowed the JPs with amphiphilic features (see below for a demonstration). For JPs made from TEOS/APS, the relative nitrogen concentration of the APS half is $\sim 8\%$, much higher than $\sim 2\%$ of the other half (Fig. 2h). The amine and thiol functionalities would facilitate the coupling of other desired molecules regioselectively onto the surface of particles. The relative volume of each half of the JPs can be fine-tuned by controlling the relative amount of the precursors. For example,

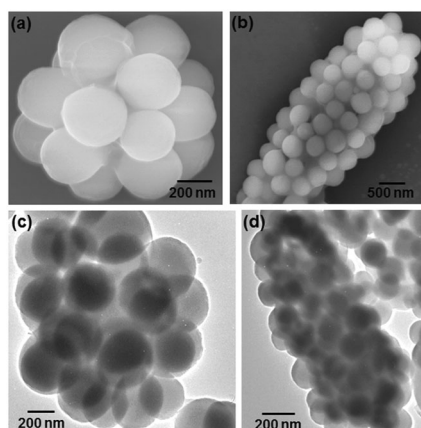


Fig. 3 Self-assembly of amphiphilic Janus particles in water–ethanol (1 : 1, vol) mixture. (a, c) SEM and TEM images of hollow clusters. (b, d) SEM and TEM images of tube-like self-assembled structures.

when [HDTMOS]/[TEOS] is 1/2, “rod-like” JPs with the tip of the particles made from HDTMOS can be obtained (see ESI†). Further tailoring of the functionality and morphology of JPs by this strategy is currently ongoing in the laboratory.

The control over the chemical compositions or surface functional groups of JPs allows fine-tuning of the properties of two halves of JPs. For example, the hydrolysis of HDTMOS introduced a large fraction of long alkyl chains to one half of the JPs, leading to the amphiphilic features of silica JPs. We demonstrated that such amphiphilic JPs could self-assemble in selective solvents or at the liquid–liquid or air–liquid interface.¹⁴ By slowly adding water into a solution of amphiphilic JPs dispersed in ethanol, the JPs spontaneously organized into various clusters with such as hollow spherical or tube-like morphology with hydrophilic portion facing the surrounding solvent media (Fig. 3a–d) (see ESI† for more images). The formation of clusters and tubes is largely driven by the favorable enthalpy gain in the selective solvent for the hydrophobic compartments.^{14a} The aggregation number of clusters ranges from about 5 to 20 of JPs, while the tubes normally have more than 50 particles. The self-assembly behaviour of JPs further confirmed the asymmetric surface chemistry of the two halves of JPs. It is noteworthy that the formed clusters and tubes are hollow, which might attribute to the film-like structures of the hydrophobic side of JPs and the large aggregation number.^{14c} The amphiphilic JP also showed superior performance in stabilizing water-in-oil emulsions and foams (see ESI†). The water emulsions/foams stabilized by amphiphilic JPs showed excellent durability and stability: they were stable in sealed glass vials for months. This is attributed to much higher adsorption energy of amphiphilic JPs at an oil–water or air–water interface than that of homogeneous particles or molecular surfactants.^{14a}

In summary, we have developed a wet-chemical approach to the synthesis of silica JPs with tailored shape and functionality. To the best of our knowledge, this is the first report of one-pot synthesis of silica JPs. This synthetic approach has three features: (i) it is a simple, fast, and general method; (ii) it is scalable for the production of large quantities of JPs; (iii) it allows us to readily tailor the surface chemistry of the JPs without the additional steps (e.g., surface protection). This method may open up a new route to the design and synthesis of colloidal particles with

complex functionality and morphology for a wide range of applications such as self-assembly, photonic crystals, and drug delivery.²

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