Janus Colloids

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Janus Colloids Formed by Biphasic Grafting at a Pickering Emulsion Interface**

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The term “Janus” is used to describe objects which have two parts with different compositions or properties.[1] The synthesis and self-assembly of Janus colloids have attracted increasing attention recently due to their potential applications in many fields, such as microrheological probes, optical biosensors, functional surfactants, building blocks of complex superstructures, and electronic paper.[2] Several methods have been developed to synthesize Janus colloids.[3–7] Amongst these, mask-protecting assisted site-selective modification[4] or template-directed self-assembly[5] on a two-dimensional plane have been proposed, although their efficiency is too low for large-scale production. Microfluidic methods have also been developed to prepare Janus particles with unconventional morphologies. However, a special design of the fluidic channels is required and it has proved difficult to synthesize nanosized colloids with a size of 10–100 nm.[6] Recently, particle-stabilized emulsion methods, for example the Pickering emulsion assisted synthesis of Janus colloids, have gained increasing interest as a range of particles with different sizes and compositions can be used as Pickering emulsifiers.[8] The two parts of the particles are separated by the oil/water interface and protected in the two phases, which often means that they can be further modified. It is still unclear whether rotation of the particles at the interface affects the formation of Janus colloids. In order to avoid such effects, however, a wax solidification method has been reported where the fumed silica particles are embedded in a frozen wax/water Pickering emulsion interface, where rotation is prohibited. The unprotected parts of the silica particles are then selectively modified with a silane to form Janus colloids.[7a] Janus colloids can be prepared at a liquid/liquid Pickering emulsion interface, where the particles are free to rotate, by a fast carbodiimidation onto one part of the microgel particles at one liquid phase.[7b] The composition of such Janus colloids is rather restricted however, and it remains to be seen whether the particles’ rotation can influence the formation of Janus colloids.

Calculations have shown that a Janus particle with amphiphilic character will be more strongly absorbed at a Pickering emulsion interface.[9] Accordingly, it is expected that once the two parts of a uniform colloid absorbed at a Pickering emulsion interface have been simultaneously grafted with different polymers, the colloid surface will be immediately divided into two structural parts. This means that colloid rotation will become more difficult and will facilitate further polymer growth and Janus colloid formation.

Herein we present the formation of Janus colloids by simultaneous biphasic grafting of different polymer brushes onto the two parts of a Pickering colloid at a liquid/liquid emulsion interface by atomic transfer radical polymerization (ATRP; Figure 1). ATRP has been widely used to grow a diversity of polymer brushes onto both planar substrates and spherical surfaces in either polar or apolar media.[10] The two parts of a colloid at a Pickering emulsion interface are separated into two phases, which can be synchronously modified by ATRP in the two phases. As a result, additional hydrophilic/lipophilic interactions with the original Pickering colloid will restrict colloid rotation and facilitate further formation of Janus colloids. As a demonstration of this concept, we have made Janus colloids with one lipophilic side and one hydrophilic side. These colloids can be further modified to give various new Janus composite colloids with different compositions.

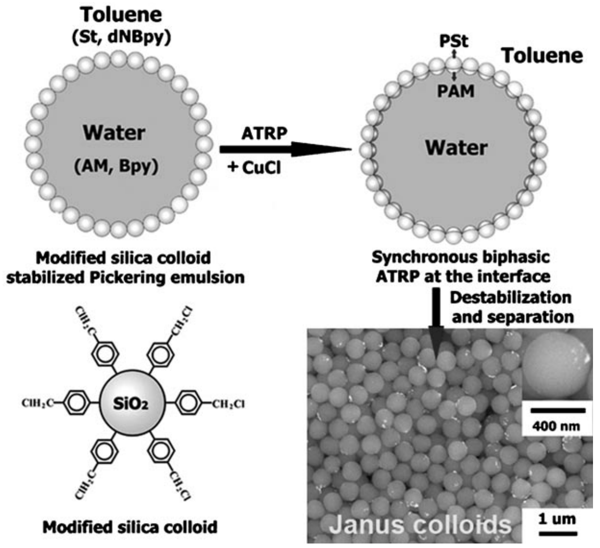

Figure 1. Synthesis of Janus colloids by biphasic grafting at a Pickering emulsion interface.

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A representative monodisperse silica (SiO_2) colloid with a diameter of about 450 nm was synthesized,[11] and (4-(chloromethyl)phenyl)trichlorosilane (CMPTS) was selected to modify this colloid as the lipophilically modified colloid can be used to stabilize water-in-oil (W/O) Pickering emulsions and the residual $-CH_2Cl$ group can be used as one component of the initiation system for ATRP (see the Supporting Information). The colloid remained well dispersed after modification (Figure S1 a in the Supporting Information) and its Cl content was determined to be 2.735 mol% by XPS measurements (Figure S1 b and Table S1 in the Supporting Information). A W/O Pickering emulsion was then formed (Figure 2 a) with a dispersed water phase containing acrylamide (AAm) monomer and the water soluble ligand 2,2′-bipyridine (Bpy) and a continuous oil phase containing styrene monomer, the oil-soluble ligand 4,4′-di-5-nonyl-2,2′-bipyridine (dNBpy), and toluene. This emulsion is polydispersed to a size of a few tens of micrometers. The SEM image of one emulsion drop after drying (Figure 2 b) shows that the CMPTS-modified SiO_2 colloids predominantly exist at the interface. CuCl was then added to activate the initiator by abstraction of Cl from CMPTS, and the alternating (redox) initiation and growth of polymers on the two parts of the colloids was allowed to occur at high temperature (60 °C) for about 2 h. The polymerized emulsion remained stable. The grafting of PAAm and PS brushes was confirmed by FT-IR spectroscopy (Figure S2 in the Supporting Information). The formation of PAAm was also verified by monitoring the N 1s band in the X-ray photoelectron spectrum (Figures S1 b,c in the Supporting Information). The Cl content decreased to 1.494 mol% after polymerization for 2 h (Figure S1 b and Table S1 in the Supporting Information), and the PAAm content increased while the Cl content decreased with increasing polymerization time.

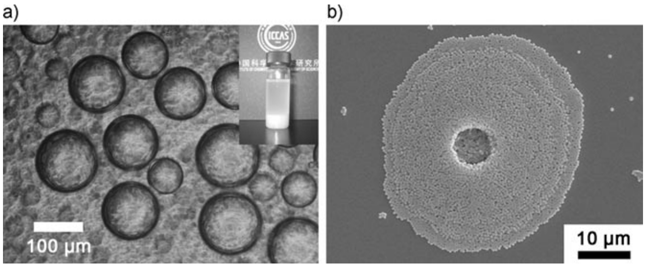

Figure 2. a) Optical microscope image of the W/O Pickering emulsion stabilized by CMPTS-modified SiO_2 colloids (inset: the emulsion appearance); b) SEM image of one emulsion drop after drying.

Various other experiments were performed to further confirm the formation of PAAm. For example, no different regions can be observed in the TEM images of the as-prepared Janus colloids (Figure 3 a). To clarify the location of PAAm, preformed Au nanoparticles (Au NPs) containing citrate groups were selectively adsorbed onto the PAAm region. Each Janus colloid shows a bright region corresponding to the Au-NPs/PAAm complex (Figure 3 b). The TEM image (Figure 3 c) further confirms that each Janus colloid has only one PAAm region. The selected area energy-dispersive X-ray (EDX) spectrum (Figure 3 e) also confirms the presence of Au; no Au is detected on the PS part.

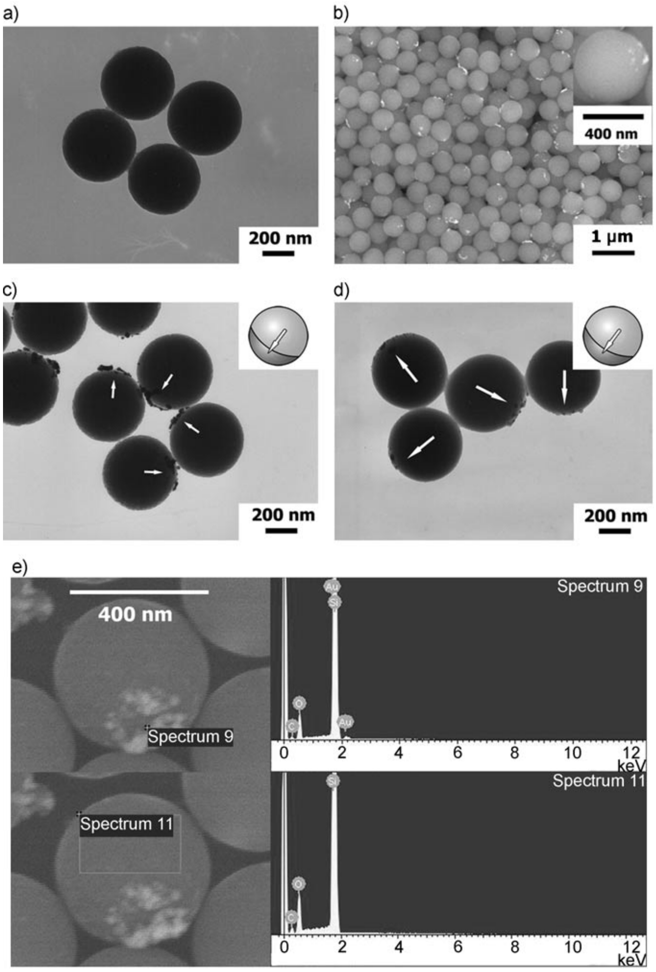

Figure 3. a) TEM image of the as-prepared Janus colloids; b) SEM and c) TEM images of Janus colloids with adsorbed Au NPs; d) TEM image of Janus colloids with adsorbed Ag NPs formed by in situ reduction; e) EDX spectra of Au NP-labeled SiO_2 Janus colloids: spectrum 9: PAAm region; spectrum 11: PS region. No Au peak is detected in the smooth PS region. The arrows in (c) and (d) indicate the boundary between the two faces.

In a similar approach, Fe_3O_4 NPs were also adsorbed onto the PAAm region of the Janus colloids (Figure S3 in the Supporting Information). For comparison, no Fe_3O_4 NPs were absorbed onto the CMPTS-modified silica particles even after treatment under the same conditions as for polymerization but in the absence of monomers (Figure S4 in the Supporting Information). This indicates that the NPs are indeed adsorbed onto the PAAm region.

Functional materials can also be synthesized in situ. For example, reduction of Ag^+ cations adsorbed onto the desired PAAm region resulted in the formation of Ag NPs (Figure 3 d). It is expected that the size of the PAAm region can be controlled by tuning the wettability of the Pickering colloids and thereby varying the surface area exposed in the two phases.[8b]

Two comparison experiments were conducted under the same conditions but in a single phase to determine the formation mechanism of these Janus structures. Both emulsions are stable during polymerization but the morphology of the colloids is clearly different. ATRP of styrene in the oil phase in the presence of the CMPTS-modified silica colloid (Figure 4a) leads to a PS-grafted silica core/shell structure (Figure 4b). The PS matrix around the silica core can clearly be distinguished in both the SEM and TEM images. This implies that the CMPTS-modified silica colloid rotates at the interface during the polymerization process. Since the formed PS brush is just as lipophilic as the original colloids, this rotation cannot be restricted. In comparison, when acrylamide was polymerized in the aqueous phase the PAAm brush formed makes the colloid amphiphilic. This means that the colloid's rotation is restricted and that the Janus colloids can therefore be further derivatized. These colloids do not have a core/shell structure (Figure 4c), and adsorption of Fe_3O_4 NPs onto the PAAm region clearly indicates that the colloids are of the Janus type (Figure 4d).

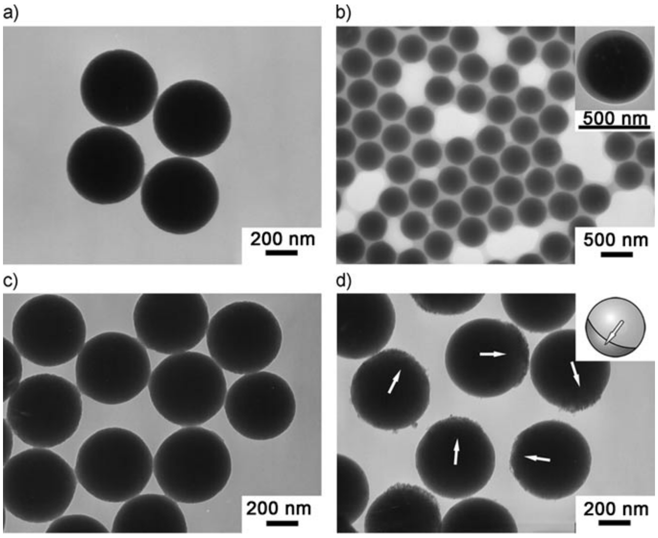

Figure 4. TEM images of a) CMPTS-modified SiO_2 colloids, b) the PS-grafted silica core/shell structure, c) PAAm-grafted silica Janus colloids, and d) Fe_3O_4 NP-labeled PAAm-grafted Janus colloids. The arrows in (d) indicate the boundary between the two faces.

In conclusion, we have developed a new, single-step approach for synthesizing novel Janus colloids by biphasic grafting at a liquid/liquid Pickering emulsion interface. The key to this approach lies in restricting the rotation of colloids by the in situ formation of Janus colloids with an amphiphilic character. Other Janus colloids, for example metal/SiO_2 composites, can be obtained by a preferred growth in the PAAm region of these colloids. This approach still needs further optimization in order to better control the polymerization[12] but could be extended to the synthesis of a huge family of Janus colloids.

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