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Supermicelles

One-Pot Synthesis of Amphiphilic Polymeric Janus Particles and Their Self-Assembly into Supermicelles with a Narrow Size Distribution**

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There is increasing interest in the preparation of Janus particles owing to their potential for application in a number of fields, such as the development of microrheological probes, optical biosensors, functional surfactants, and electronic devices.[1a–d] Janus particles can also be used to fabricate complex superstructures that would not be accessible from uniformly functionalized particles.[1e] Microfluidic methods and flow-lithography techniques can be used to produce Janus particles of various shapes with good control over size distribution, but at present the particle size is limited to a diameter of approximately 5–100 μm.[2] Müller and co-workers reported the preparation of Janus micelles from ABC triblock copolymers[3a] and their self-assembly into supermicelles.[3b] However, the supermicelles coexist with the Janus micelles and a small number of large aggregates.[3b] Promising approaches in which an interface is used as a desymmetrization tool to prepare Janus particles have also been reported.[4] As most interface-based techniques rely on the two-dimensional modification of a monolayer, the preparation efficiency is low.[5] It is expected that the industrial future of these routes will depend mainly on the development of processes in which very large surfaces or interfaces are involved.[5] Janus particles can be prepared in emulsion systems in potentially high yield.[6] However, to our knowledge, Janus particles have been produced in large quantities by only two interface-based emulsion methods.[7] The success of these methods lies in the restriction of the rotation of the precursor spheres at the interface of emulsion droplets. Nearly all interface-based approaches start with inorganic precursor spheres, which limits the structural variety of the Janus particles and their ability to form uniform superstructures. Clearly, efficient approaches to nanosized Janus particles capable of self-assembling into uniform superstructures need to be explored.

Herein we report an efficient one-pot approach to the preparation of amphiphilic polymeric Janus nanoparticles that can self-assemble into supermicelles with a narrow size distribution. Our strategy is to use water-dispersible hybrid nanotubes (HNs) composed of an inorganic nanotube surrounded by a hydrophobic polymer layer (HPL) with water-soluble polymer chains grafted on the outer surface of the HPL as a desymmetrization tool. In an aqueous suspension of HNs, a hydrophobic divinyl cross-linker and a hydrophobic free-radical initiator were solubilized in the HPL, and a hydrophilic monomer remained in the aqueous phase. During the polymerization of the hydrophobic cross-linker, hydrophobic spheres composed of the resulting polymer were formed and grew in the HPL. One side of a sphere was exposed to the water phase when the diameter was larger than the thickness of the HPL. Polymeric free radicals at the hydrophobic-sphere/water interface then initiated the polymerization of the water-soluble monomer; the other side of the hydrophobic sphere was embedded in and protected by the HPL. This process led to the formation of amphiphilic Janus particles in which water-soluble polymer chains are grafted on one side of a hydrophobic sphere. We found that the Janus particles can self-assemble in water into supermicelles with a narrow size distribution. Under suitable conditions, the supermicelles can dissociate into individual nanosized Janus particles (Figure 1). The preparation efficiency of this method is relatively high as a result of the large area of the curved water/HPL interface. We believe that the rotation of the hydrophobic spheres at the interface is highly restricted, as the spheres are partially embedded in the semisolid HPL.

Poly(ethylene oxide)-*b*-poly(4-vinylpyridine) (PEO_{113}-*b*-$P4VP_{93}$) and yttrium hydroxide nanotubes (YNTs) with a diameter of approximately 200 nm and a length of 3–4 μm (see the Supporting Information) were used to form the HNs. PEO-*b*-P4VP and the YNTs were synthesized according to procedures reported previously.[8] When the block copolymer and the YNTs were mixed in chloroform, the P4VP block chains were adsorbed onto the surface of the YNTs because of favorable hydrogen bonding between the pyridine units and the surface hydroxy groups of the YNTs, as determined by FTIR spectroscopy (see the Supporting Information). We thus obtained HNs in the form of YNTs coated with a layer of the diblock copolymer. When the chloroform solvent was exchanged for neutral water, we obtained HNs in which the P4VP HPL[9a] surrounds the YNTs and the PEO block chains are grafted on the outer surface of the HPL. With gentle stirring, HNs can be dispersed individually in water for weeks owing to the solubilization of the PEO block chains. However, without stirring, HNs will start to sediment after a few hours. This characteristic facilitates the convenient purification or removal of HNs. The polymer weight fraction in the purified

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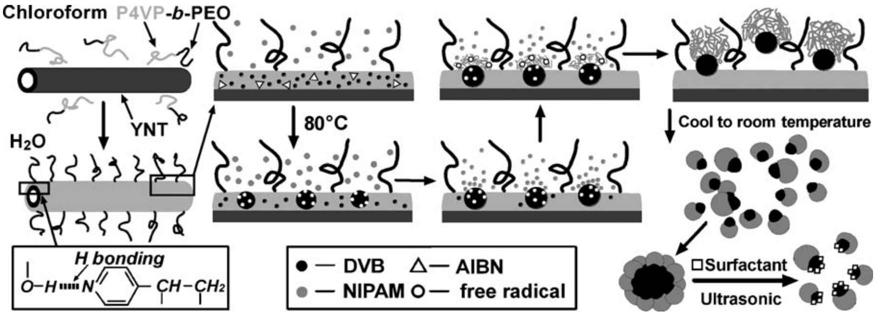

Figure 1. Diagram illustrating the formation of a water-dispersible hybrid nanotube (HN, lower left-hand diagram), the synthesis of Janus particles (shown top right still associated with the HN) by using the HN as a desymmetrization tool, the self-assembly of Janus particles into a supermicelle (flowerlike structure shown bottom right), and the dissociation of a supermicelle.

HNs was determined by thermograph analysis (TGA) to be 21% (see the Supporting Information). Further evidence for the adsorption of a layer of the diblock copolymer on the surface of the YNTs was obtained by transmission electron microscopy (TEM; Figure 2a).

2,2′-Azobis(isobutyronitrile) (AIBN; 2.6 mg) solubilized in divinylbenzene (DVB; 57.5 mg) and *N*-isopropylacrylamide (NIPAM; 80 mg) were added successively to a gently stirred aqueous suspension at room temperature of purified HNs (50.6 mg in 100 mL; this quantity of HNs contains 10.6 mg of the block copolymer on the basis of TGA). The mixture was stirred for a further 3 h to fully solubilize the DVB and AIBN in the HPL. Under a nitrogen atmosphere, the temperature was increased to 80°C to start the polymerization. After 6 h, the reaction mixture was cooled to room temperature. The standing of the suspension at room temperature for 3 days led to complete sedimentation of the HNs. The opalescent supernatant suspension was collected for further characterization.

The supernatant suspension was found to be quite stable: No apparent change was detected after 3 months. Dynamic light scattering (DLS) revealed the presence of particles with an average hydrodynamic diameter ($\langle D_h \rangle$) of 645 nm and a narrow size distribution (the polydispersity index is approximately 0.1; curve A, Figure 2f). TEM images showed that all particles in the suspensions obtained in our repeated experiments possessed a flowerlike morphology (Figure 2b,c; see the Supporting Information), and that the size of the particles ranged from 300 to 400 nm. These values are considerably smaller than the $\langle D_h \rangle$ value determined by DLS, as the TEM results correspond to the size of the dried particles. Spheres with a similar morphology were reported by Liu and co-workers.[9b] From the TEM image at greater magnification (Figure 2c), it is clear from the "petal" region that the flowerlike aggregates actually consist of smaller particles. Upon casting the supernatant suspension onto mica, atom force microscopy (AFM; Figure 2d) revealed only the presence of petal-shaped small particles (ca. 160 nm), the size and shape of which are comparable to those of the small component particles visible in Figure 2c. The hydrophilic mica surface possibly facilitates the dissociation of the large flowerlike aggregates. We added excess sodium dodecyl sulfate (5 mg mL^{-1}) to the supernatant suspension under ultrasonic vibration and found that the

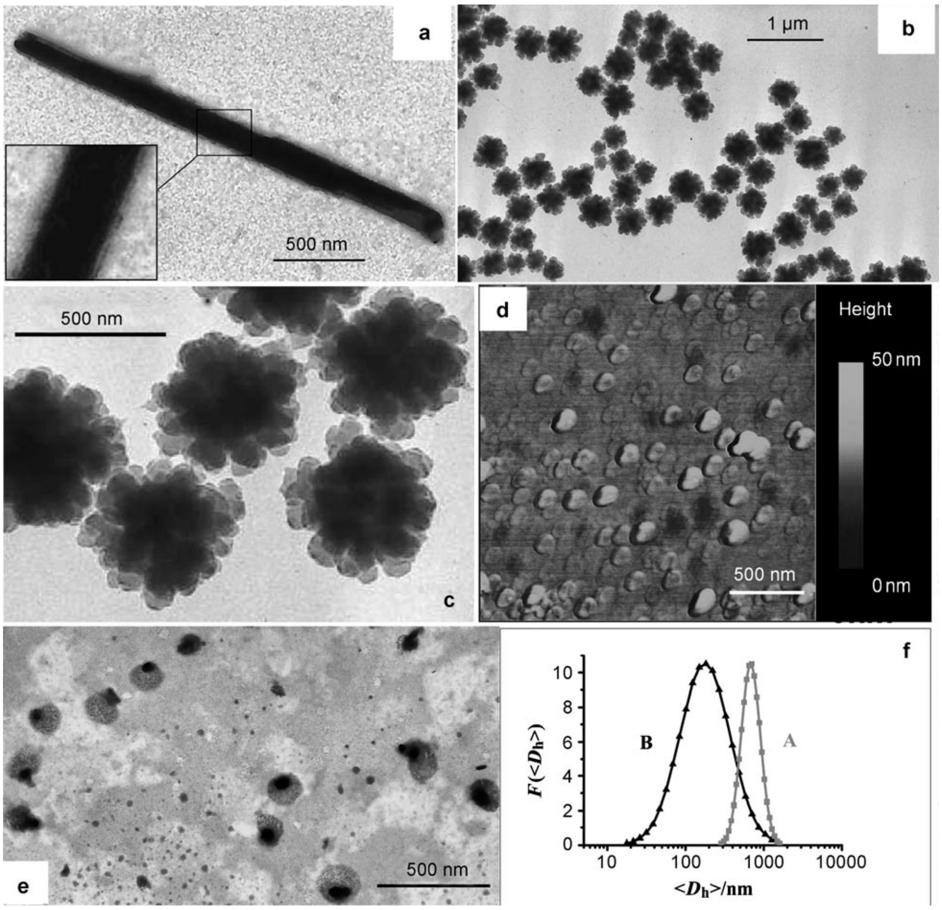

Figure 2. a) TEM image of a hybrid nanotube, and the same HN at a larger magnification to show the polymer layer surrounding the YNT; b) TEM image of the supermicelles; c) TEM image of the supermicelles at a larger magnification; d) AFM image of "petal-like" (Janus) particles that result from the dissociation of the supermicelles on mica; e) TEM image of the Janus particles stained with RuO_4; f) distribution of the hydrodynamic diameter ($\langle D_h \rangle$) of the supermicelles (A) and the Janus particles (B).

$\langle D_h \rangle$ value of the aggregates decreased to approximately 170 nm, as measured by DLS (curve B, Figure 2 f). One drop of the supernatant suspension was dried in the presence of the surfactant on copper grids and stained with RuO_4. TEM images revealed the presence of individual smaller particles (ca. 160 nm in diameter) rather than flowerlike aggregates (Figure 2 e), in agreement with the AFM results. Scattered small dots were observed in the TEM image in Figure 2 e. As no such irregular dots were observed in the TEM and AFM images of the samples in the absence of the surfactant (Figure 2 b–d), we believe that they result from the excess surfactant. The supermicelles also dissociated into Janus particles in *N*,*N*-dimethylformamide (DMF) without ultrasonic vibration and the surfactant (see the Supporting Information).

The FTIR spectrum of the flowerlike aggregates contained absorption bands due to the DVB polymer (PDVB) and poly(*N*-isopropylacrylamide) (PNIPAM). The TEM image in Figure 2 e shows through a contrast in color that each particle has two parts. The darker part is PDVB, which is sensitive to staining by RuO_4; the other part can be ascribed to PNIPAM. The particles in Figure 2 e are placed in such a manner that we can see the Janus-like morphology. Apparently, the amphiphilic nature of these Janus particles, the hydrophobic part of which is formed by PDVB and the hydrophilic part by PNIPAM, enables their self-assembly into the water-soluble flowerlike supermicelles (Figure 2 b).

The height of the Janus particles in the AFM images is between 25 and 30 nm. We believe that the collapse and spread of the PNIPAM graft chains on the substrates, which are also discernable in the TEM image (Figure 2 e), are responsible for the discrepancy between the height and the diameter. Besides, the size of the Janus particles deduced by TEM and AFM is close to the $\langle D_h \rangle$ value. This similarity also implicates the collapse and spread of the Janus particles on the substrates: If this process did not occur, the size of the Janus particles in a dried state as observed by TEM and AFM should be much less than the $\langle D_h \rangle$ value measured in the suspension.

As described earlier, DVB (57.5 mg) was mixed with HNs (50.6 mg) that contained 10.6 mg of the block copolymer. However, we observed that only a part of the DVB was solubilized in the HPL (see the Supporting Information). Under gentle stirring, without a surfactant, the remaining DVB outside of the HPL exists in the bulk aqueous phase as DVB droplets visible to the naked eye. After polymerization, PDVB is observed instead as particles visible to the naked eye that stick to the wall of the reaction flask and are thus separated from the supernatant suspension. In fact, following the polymerization and precipitation of HNs, only supermicelles were observed in the supernatant suspension. We conclude that the DVB that exists outside of the HPL has no effect on the preparation and characterization of the Janus particles and the supermicelles, whereas the DVB solubilized in the HPL leads to the hydrophobic part of the Janus particles. Experimental proof for the formation of PDVB spheres in the HPL and a brief discussion on the mechanism are presented in the Supporting Information. Characterization by FTIR spectroscopy showed that the particles that were stuck to the wall of the reaction flask and visible to the naked eye were composed of pure PDVB, although, in principle, PNIPAM chains should be grafted on the surface of these huge particles. It is understandable that these PNIPAM chains are not detected, as the size of the particles is of the order of hundreds of micrometers, whereas the thickness of a single-molecular layer of PNIPAM grafted on the surface must be much less than 1 μm. (That is, the weight fraction of PNIPAM chains grafted on the surface of the huge PDVB particles should be much less than 10^{-6}). The solubilization of NIPAM in the DVB phase is negligible: The concentration of NIPAM in DVB should be lower than 0.08 % (*w*/*v*) as a result of the good water solubility of NIPAM and the low concentration of NIPAM in the aqueous phase (80 mg in 100 mL of water). These considerations are consistent with the observation that the FTIR spectrum of the particles visible to the naked eye shows only absorption bands due to PDVB. Furthermore, we separated supermicelles from the aqueous suspension by ultrafiltration and then characterized the aqueous solution by gel-permeation chromatography (GPC). Only a small amount of the PNIPAM homopolymer, with a molecular weight of about 2×10^5, was detected in the aqueous solution.

A first control experiment demonstrated that the Janus particles do not escape from the HPL during polymerization at 80 °C. The suspension was cooled to room temperature, and the Janus particles were desorbed from the HPL and self-assembled in the water phase (see the Supporting Information). PNIPAM grafts are hydrophobic at 80 °C and become hydrophilic at room temperature. The embedding of the PDVB spheres in the HPL during polymerization at 80 °C assures that the PNIPAM chains are grafted on only one side of the PDVB spheres. Second, in the absence of NIPAM, polymerization under identical conditions led to the formation of PDVB spheres attached to HNs (see the Supporting Information); similar results were reported previously.[10] In a third control experiment without HNs, the polymerization of NIPAM and DVB in the presence of AIBN only resulted in the formation of large PDVB particles, which stuck to the wall of the reaction flask; no water-soluble aggregates were detected in the aqueous phase (see the Supporting Information). Finally, we added HNs ($5.6\ mg\,mL^{-1}$) to an aqueous solution of NIPAM ($0.8\ mg\,mL^{-1}$, 10 mL) and stirred the mixture for 24 h. We then separated the HNs from the suspension by centrifugation and characterized them by FTIR spectroscopy. No absorption bands due to NIPAM were detected. This result indicates that NIPAM does not dissolve in the HPL.

In conclusion, we have developed a straightforward one-pot approach to the fabrication of amphiphilic Janus particles in water. The particles are formed by the free-radical polymerization of a hydrophobic divinyl monomer and a hydrophilic monomer in the presence of a hydrophobic initiator with HNs employed as a desymmetrization tool. The semisolid state of the HPL greatly restricts the rotation of particles at the interface during polymerization. The Janus particles self-assemble in water into supermicelles with a narrow size distribution. These supermicelles undergo dissociation under certain conditions. The Janus particles can be prepared in relatively large quantities because of the large interfacial area of the water/HPL interface. In the present case, a quantity of about 15 mg of flowerlike aggregates was produced from a suspension in 100 mL of water. Although PNIPAM, which shows LCST (lower critical solution temperature) behavior, was used in the present study, our approach is not limited to this kind of hydrophilic monomer. In principle, hydrophilic monomers such as 4-vinylpyridine and 2-vinylpyridine, whose polymers are insoluble in water, are also applicable. It would also be possible to prevent the escape of the Janus particles from the HPL by controlling the thickness of the HPL or the length of the hydrophilic polymer grafts. We believe that this approach can be used to prepare a variety of amphiphilic Janus particles capable of forming higher-order supermicelles.

Experimental Section

Materials and instruments: AIBN (Aldrich), NIPAM (Aldrich), and DVB (Fluka) were purified by standard methods prior to use. THF and chloroform of analytical purity (Shanghai Chem.) were purified by desiccation and distillation. PEO_{113}-*b*-$P4VP_{93}$ was synthesized and purified according to procedures reported previously[8a] by using modified monomethoxy-terminated PEO (Aldrich; $M_n = 5000$, $M_w/M_n = 1.02$) as a macroinitiator. The degree of polymerization of the P4VP block was determined to be 93 by ^1H NMR spectroscopy. The polydispersity (M_w/M_n) of PEO_{113}-b-$P4VP_{93}$ was 1.15, as determined by GPC with a Perkin Elmer Series 200 instrument (eluent: DMF; flow rate: 1.0 mL min^{-1}).

Preparation of PEO-*b*-P4VP/YNT hybrid nanotubes: The block copolymer can be dissolved molecularly in chloroform, whereas pure YNTs can not be dispersed in chloroform even with stirring. The YNTs were mixed with PEO-*b*-P4VP in chloroform in a polymer/YNT weight ratio of 4:1 and at a YNT concentration in chloroform of 1 mg mL^{-1} with gentle stirring. Upon mixing, the P4VP blocks of the diblock-copolymer chains were adsorbed on the surface of the YNTs as a result of a hydrogen-bonding interaction between the pyridine units and the surface hydroxy groups of the YNTs (see the Supporting Information). The resulting individually dispersed hybrid nanotubes were separated from the uncomplexed block-copolymer chains in chloroform by centrifuging the mixture at 1000 rpm for 10 min and discarding the supernatant solution. An additional two cycles of dispersing the sediments in chloroform and subsequent centrifugation were carried out to guarantee the purity of HNs. The as-purified HNs were dried at 50 °C for 24 h in a vacuum oven. The polymer content in the purified HNs was determined by TGA to be approximately 21 wt % (see the Supporting Information).

Dissociation of the supermicelles: For the dissociation of the supermicelles in water, excess sodium dodecyl sulfate (5 mg mL^{-1}) was added to the aqueous suspension under ultrasonic vibration. For the dissociation of the supermicelles in DMF, the aqueous suspension of the supermicelles was freeze-dried to give a white powder. The white powder was dispersed in DMF and observed by DLS and TEM.

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