

Polymer/Metal Segmental Janus Nanoparticles*

Lin Tang^{a, b}, Fu-xin Liang^a, Qian Wang^a, Xiao-zhong Qu^b,
Bing-yin Jiang^a and Zhen-zhong Yang^{a, b**}

^a State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100190, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

Abstract Polymer/metal composite segmental Janus nanoparticles (NPs) are synthesized by sequential growth against poly(4-vinylpyridine) (P4VP) crosslinked cP4VP-PS Janus NPs. A Janus cluster of poly(4-vinylpyridine)-block-polystyrene (P4VP-*b*-PS) diblock copolymer is self-organized after absorption onto a silica patchy sphere *via* hydrogen bonding. Selective crosslinking of P4VP leads to the formation of robust cP4VP-PS Janus NPs. Within the cP4VP domain, functional species such as metals are preferentially grown by *in situ* reduction. Other thiol-capped polymers, for example, thiol-capped poly(*N*-isopropylacrylamide) (PNIPAM-SH), can be conjugated onto the opposite side to form polymer/metal triple segmental Janus NPs. The hyperthermia effect of Au NP of PNIPAM-Au@cP4VP-PS by near infrared (NIR) irradiation can trigger a fast transition from amphiphilic to hydrophobic of the Janus NPs at low surrounding temperature. De-stabilization of the emulsion is NIR triggered although the system temperature is below LCST (~32 °C).

Keywords Janus; Polymer; Composite; Nanoparticle; Interactive performance

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1946-1>.

INTRODUCTION

Janus materials can integrate two different compositions thus properties onto the same entity, which have gained growing academic and industrial interests^[1–4]. Janus nanoparticles (NP) have experienced a fast development due to their tunable composition and diversified functions^[5–8]. Especially, those Janus NPs with polymers conjugated onto one side or the opposite sides of a functional NP are more attractive^[9–13]. Additional interactive performances are expected besides a simple mixed one. It is important to develop new methods to precisely tune composition of the NPs and polymers. In the case of properly small NPs, two polymer chains of a triblock copolymer can be segregated onto the opposite sides owing to a steric constraint while the individual NP is wrapped by the middle block *via* complexation. However, this method is highly size and chemistry selective^[14, 15]. If the NPs are extremely small, several NPs are wrapped together by the individual middle block to form aggregates. In the case of larger NPs, more than two polymers or ligands are randomly grafted onto the NP surface. Janus feature can be achieved by re-arrangement of the polymers or ligands at the interface^[16–18]. The ligand exchange and re-arrangement are dynamic. So the Janus NPs are usually metastable^[19, 20]. Alternatively, substrate protection assisted synthesis of Janus NPs is straightforward. While one side of a NP is protected upon anchoring onto a substrate, polymers can be selectively grown onto the other side^[21, 22]. Strong

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51233007 and 51622308).

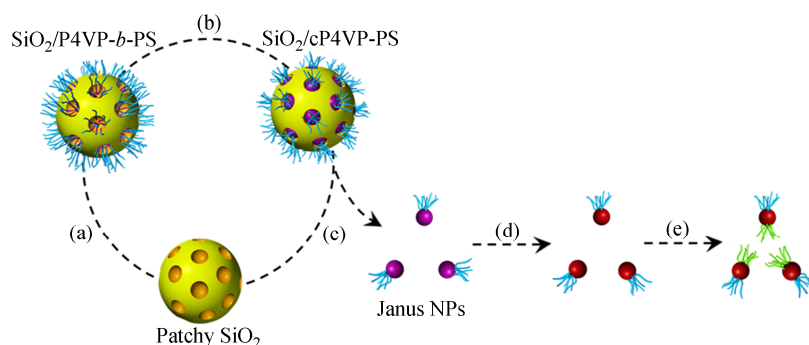
** Corresponding author: Zhen-zhong Yang (杨振忠), E-mail: Yangzz@iccas.ac.cn

Received January 26, 2017; Revised February 24, 2017; Accepted March 1, 2017

doi: 10.1007/s10118-017-1946-1

interaction between NP and the substrate is required for anchoring. As an example, when Au NPs are tethered onto a thiol-terminated poly(ethylene oxide) (PEO) single crystal surface, poly(methylmethacrylate) (PMMA) can be grafted onto the exposed side *via* atom transfer radical polymerization (ATRP)^[21]. After dissolution of PEO crystal, PMMA-Au-PEO triple segmental Janus NPs are obtained. It is difficult to precisely control the contact surface area for adjusting protection degree of a spherical NP onto a rigid substrate. Grafting polymer chains onto a nanoparticle surface is effective to form polymer/inorganic nanocomposites. For example, carboxyl group ended poly(styrene) can be easily grafted onto an oleic acid stabilized Fe₃O₄ NP surface through a ligand exchange reaction. The grafting density is decreased with increasing molecular weight. When the PS chain is enough long, the grafting number reaches a minimum of 2. This implies that two chains are grafted onto the NP opposite sides^[23]. We have recently reported the synthesis of single polymer chain functionalized Janus Fe₃O₄ NPs by a fast elimination method from the modified Fe₃O₄ NP with the anionic living polymer chain. It is the requisite that the polymer chain should be sufficiently large over the NP diameter for grafting a single polymer chain^[24]. On the other hand, copolymers with different blocks are inherently Janus at molecular scale, which are highly potential to derive Janus nanomaterials by proper processing. Selective intramolecular crosslinking of copolymers can easily achieve a polymeric NP with a single polymer chain onto one side or two chains onto the opposite sides^[25]. In order to avoid chain entanglement to cause intermolecular crosslinking, polymer concentration should be extremely low. Disassembly of copolymer supramolecular structures is effective to achieve polymeric Janus NPs with tunable shapes. However, sufficiently enough distribution of molecular weight of copolymers and strict processing conditions are required for the purpose of ensuring shape uniformity of the Janus NPs^[26, 27]. Recently, we have proposed a simple way to prepare poly(acrylic acid) (PAA) crosslinked cPAA-PS Janus NPs by selectively crosslinking PAA of a Janus PS-PAA cluster confined in a mesoporous silica channel although the synthetic efficiency is low^[28]. For releasing the Janus cPAA-PS from the channel, the mesoporous silica layer should be sacrificed after etching.

Herein, we propose a method to effectively synthesize polymeric Janus NPs against a recyclable SiO₂ mold sphere as illustrated in Scheme 1. The mold sphere is patchy with isolated hydrophilic domains at the hydrophobic surface. In the first step (a), for example, P4VP-*b*-PS copolymer is preferentially absorbed onto the patchy domains *via* hydrogen bonding between P4VP of the copolymer and Si—OH of the patchy domain. Secondly (b), the P4VP side is selectively crosslinked and becomes a robust NP (cP4VP). cP4VP-PS di-segment Janus NPs are released from the sphere surface by simply adding acid to break the hydrogen bonding in the third step (c), whilst the SiO₂ mold spheres are recycled. In the forth step (d), Janus composite NPs are obtained by the growth of functional species such as Au within the cP4VP segment. Finally (e), tri-segment Janus NPs are achieved by further grafting another polymer chains onto the opposite side of the Au@cP4VP composite



Scheme 1 Illustrative synthesis of cP4VP-PS and the composite segmental Janus NPs

(a) P4VP-*b*-PS is favourably absorbed onto the C8-SiO₂ patchy sphere to form a SiO₂/P4VP-*b*-PS composite sphere; (b) A copolymer Janus cluster forms at the patch in a PS selective solvent, following by selective crosslinking of the P4VP side; (c) A cP4VP-PS di-segment Janus NP is released from the sphere by adding acid, and the C8-SiO₂ patchy sphere is recycled; (d) A composite di-segment Janus NP after the growth of functional species within the cP4VP segment; (e) A composite tri-segment Janus NP after growing another polymer onto the opposite side of the composite cP4VP segment.

segment. The polymers and functional NPs as different segments are distinctly compartmentalized. The corresponding interactive performances are expected.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS) and silver nitrate (AgNO_3) were purchased from Sinopharm Chemical Reagent Beijing. Octyltrimethoxysilane (C8-TMS), *n*-butylamine, ammonium fluoride (NH_4F) and 1,5-diiodopentane were purchased from Acros Organics. *N*-isopropylacrylamide (NIPAM), 2,2'-azobisisobutyronitrile (AIBN), and 4-cyano-4-thiobenzoylthiopentanoic acid were purchased from J&K Scientific. $\text{P4VP}_{10\text{k}}\text{-}b\text{-PS}_{9.8\text{k}}$ ($\text{PDI} = 1.08$), $\text{P4VP}_{35\text{k}}\text{-}b\text{-PS}_{93\text{k}}$ ($\text{PDI} = 1.15$), and thiol-capped poly(ethylene glycol) ($\text{PEG}_{16\text{k}}\text{-SH}$) were purchased from Polymer Source. Ethanol, cyclohexane, chloroform (CHCl_3), tetrahydrofuran (THF), nitric acid (HNO_3), hydrochloric acid (HCl), 1,4-dioxane, and aqueous ammonia (25 wt%) were purchased from Beijing Chemical Works. All the materials were used as received.

Synthesis of $\text{SiO}_2\text{@Ag}$ Composite Spheres

The representative monodisperse silica spheres (SiO_2) with a diameter of 200 nm were prepared. 15.0 g of TEOS was added into a mixture of ethanol (195.0 mL), de-ionized water (16.0 mL), and 25 wt% aqueous ammonia (9.2 mL). The mixture was stirred for 12 h at 35 °C. The SiO_2 spheres were dried after centrifugation and washed with water and ethanol. After 50.0 mg of the SiO_2 spheres and 45.0 mg of AgNO_3 were dispersed in 35.0 mL of ethanol under stirring at 50 °C, 18.0 mg of *n*-butylamine was added. After reaction for desired time to *in situ* grow Ag NPs onto the SiO_2 sphere surface, the $\text{SiO}_2\text{@Ag}$ composite spheres were achieved after centrifugation and washing with ethanol.

Synthesis of C8- SiO_2 Patchy Spheres

After 50.0 mg of the $\text{SiO}_2\text{@Ag}$ composite spheres were dispersed in 12.0 mL of CHCl_3 , 25.0 mg of C8-TMS was added and stirred at 30 °C for 24 h. The product was centrifuged and washed with ethanol. The C8- $\text{SiO}_2\text{@Ag}$ composite spheres were obtained after modification of the exposed silica surface. The C8- $\text{SiO}_2\text{@Ag}$ composite spheres were immersed in 8 mol/L HNO_3 to dissolve Ag NPs from the sphere surface. The C8- SiO_2 spheres were obtained after centrifugation and washing with ethanol until the solution was neutral. 50.0 mg of the C8- SiO_2 spheres were immersed in 25.0 mL of NH_4F aqueous solution (5 wt%) for etching after 20 min; concave dents formed on the SiO_2 spheres. The C8- SiO_2 patchy spheres were thus achieved.

Synthesis of cP4VP-PS Di-segment Janus NPs

After 1.0 mg of $\text{P4VP-}b\text{-PS}$ was dissolved in 4.0 mL of THF, 40.0 mg of the C8- SiO_2 patchy spheres were added and stirred overnight at room temperature. After the copolymer was absorbed onto the concave dents, the spheres were centrifuged and washed with THF to remove the residual copolymer. After the $\text{SiO}_2/\text{P4VP-}b\text{-PS}$ composite spheres were dried at 30 °C for 12 h, the spheres were dispersed in 4.0 mL of cyclohexane containing 5.0 mg of 1,5-diiodopentane. After stirring at 60 °C for 6 h, the P4VP side was selectively crosslinked. The $\text{SiO}_2/\text{cP4VP-PS}$ composite spheres were collected by centrifugation and washed with THF. 2.0 mL of aqueous HCl solution (4 mol/L) was added into 2.0 mL of the composite dispersion in THF, and the cP4VP-PS di-segment Janus NPs were detached. The cP4VP-PS di-segment Janus NPs and C8- SiO_2 patchy spheres were separated by centrifugation. The Janus NPs were dried. The SiO_2 patchy spheres were recycled.

Synthesis of PEG-Au@cP4VP-PS Composite Tri-segment Janus NPs

0.5 mg of the cP4VP-PS Janus NPs and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.1 mL, 5 mg/mL) were mixed in 4.0 mL of THF. After stirring overnight at room temperature for the preferential absorption, residual HAuCl_4 was removed by centrifugation. After the sediment was dispersed in 4.0 mL of THF, 5.0 μL of NaBH_4 solution (1 mmol/L) was dropped under stirring. Au formed by *in situ* reduction within the cP4VP domain. The Au@cP4VP-PS composite di-segment Janus NPs were centrifuged. Au@cP4VP-PS Janus NPs and PEG-SH polymer at a desired ratio were mixed in 4.0 mL of THF and stirred overnight at room temperature. The PEG-Au@cP4VP-PS composite tri-segment Janus NPs were collected by centrifugation.

Synthesis of PNIPAM-SH

NIPAM (1.2 g, 10.6 mmol), RAFT agent (20.0 mg, 0.072 mmol) and AIBN (4.0 mg, 0.024 mmol) were dissolved in 1,4-dioxane (12.0 mL) in a 50 mL Schlenk flask with a magnetic stir bar. After the mixture was degassed by three cycles of freeze-pump-thaw, the tube was sealed under vacuum. The polymerization was carried out at 60 °C for 24 h. Poly(*N*-isopropylacrylamide) chain transfer agent (PNIPAM-CTA) precipitated after adding anhydrous ether. After three cycles of dissolution and precipitation, the product was dried in a vacuum oven. PNIPAM-CTA (80.0 mg) and NaBH₄ (180.0 μ L, 1 mol/L) were dissolved in 10.0 mL of deionized water. After reaction at 30 °C for 24 h, the aqueous solution was dialyzed and freeze-dried to obtain PNIPAM-SH.

Synthesis of PNIPAM-Au@cP4VP-PS Composite Tri-segment Janus NPs

1.0 mL of water containing 3.0 mg of Au@cP4VP-PS and 50.0 μ L of cyclohexane were stirred for 30 min to obtain an oil/water emulsion. 2.0 mg of PNIPAM-SH was dissolved in 0.2 mL of water and added into the emulsion under stirring for 12 h. The PNIPAM-Au@cP4VP-PS composite tri-segment Janus NPs were obtained by centrifugation.

Photo Thermal Effect of PNIPAM-Au@cP4VP-PS Janus NPs

2.0 mL of the aqueous dispersion containing 4.0 mg of PNIPAM-Au@cP4VP-PS and 100.0 μ L of cyclohexane was stirred for 30 min to obtain an oil/water emulsion. The emulsion was irradiated by near infrared (NIR) laser (808 nm, 3 W/cm²) vertically from the top of vessel for varied time.

Characterization

Morphology of the samples was characterized using transmission electron microscopy (TEM, JEOL 1011 operating at 100 kV). The samples for TEM observation were prepared by spreading very dilute dispersions onto carbon-coated copper grids. 0.1% Phosphotungstic acid (PTA) solution and ruthenium oxide (RuO₄) vapor were used to stain the samples. Size distribution was measured using Zetasizer (Nano Series, Malvern Instruments) at 25 °C. Fourier transform infrared (FTIR) spectra were recorded after scanning the samples for 32 times with Bruker EQUINOX 55 spectrometer. Ultraviolet visible near infrared (UV-Vis-NIR) absorption spectra were recorded on Perkin Elmer Lambda 950 spectrophotometer. Gel permeation chromatography (GPC) was conducted on the system comprised of a Waters 515 HPLC pump and a Waters 2414 RI detector equipped with three Agilent mixed columns (PLgel 20 μ m MIXED-A and PLgel 10 μ m MIXED-B $\times$ 2). DMF containing 0.01 mol/L LiBr was used as the eluent at 1 mL/min. Polystyrene standards were used for the calibration. Temperature was recorded by infrared (IR) thermal imaging camera (FLIR Systems) during irradiation with NIR laser (808 nm, Connet Fiber Optics Co.) vertically from the glass bottle top.

RESULTS AND DISCUSSION

The representative uniform SiO₂ spheres with smooth surface and diameter of 200 nm were synthesized *via* Stöber method^[29] (see Fig. S1a in supporting information, SI). Ag NPs formed onto the surface by *in situ* reduction of AgNO₃ for 40 min, achieving the SiO₂@Ag composite spheres^[30]. Diameter of the Ag NPs is $\sim$ 10 nm (Fig. S1b in SI). After selectively etching SiO₂, individual Ag NPs are released. The Ag NPs are isolated at the sphere surface. After a shorter period of reaction (20 min), Ag NPs are reduced to 4–6 nm (Fig. S1c in SI), while with a longer reaction time (60 min), Ag NPs further grow and are partially coalesced (Fig. S1d in SI). The composite spheres are only dispersible in water. The silica surfaces of SiO₂@Ag composite spheres (Fig. S1b in SI) are coated with a hydrophobic layer after a selective modification with *n*-octyltrimethoxysilane (C8-TMS). Surface morphologies of the C8-SiO₂@Ag composite spheres are preserved (Fig. S2 in SI). The spheres are dispersible both in water and in oil. Upon dissolving the Ag NPs, the sphere surface becomes smooth (Fig. S3 in SI). The newly formed fresh silica domains are flat, which can evolve into concave dents after etching with NH₄F. At a slight etching degree (20 min), the dents are shallow and isolated with a size of $\sim$ 10 nm similar to the Ag NPs (Fig. 1a). A C8-SiO₂ patchy sphere is obtained with the deeper and larger dents in a high etching degree

(60 min, ~ 30 nm). Some partially interconnected dents imply that the C8-modified silica surface has been etched at the dent periphery (Fig. S4 in SI). In order to confirm the presence of Si—OH at the dent surface, Ag NPs are favorably grown by *in situ* reduction of AgNO_3 (Fig. S5 in SI).

After the C8-SiO₂ patchy spheres are added into the copolymer THF solution under stirring overnight, the spheres are collected by centrifugation and washed with THF. The absorbed copolymer experiences a phase separation at the dents upon substitution of THF with a PS selective solvent, for example cyclohexane. The PS blocks are extended outwardly, while the P4VP blocks are collapsed, leading to the formation of Janus copolymer clusters. After adding 1,5-diiodopentane in the dispersion, the P4VP side selectively crosslinked to form robust NPs (cP4VP). The cP4VP-PS is detached *via* breaking the hydrogen bonding after adding acid. The cP4VP NPs are visualized under TEM with the diameter about 2–3 nm (Fig. 1b). After staining with RuO₄, the PS domain is distinguished and surrounds one side of the cP4VP NP (Fig. 1c). The cP4VP-PS di-segment Janus NPs are parachute-like with a total height 8–12 nm. The average hydrodynamic diameter of cP4VP-PS in THF is 13.8 nm measured by dynamic light scattering (DLS) (Fig. S6 in SI). Similarly, another cP4VP-PS Janus NPs can be afforded from the copolymer P4VP_{35k}-*b*-PS_{93k} (Fig. 1d) with a longer chain. Both cP4VP and PS segments are larger with the average hydrodynamic diameter of 16.7 nm. In order to evidence the method is robust and irrelevant with uniformity of copolymers, a mixture of P4VP_{10k}-*b*-PS_{9.8k}/P4VP_{35k}-*b*-PS_{93k} (1:1) is used to form the NPs. Similarly, the parachute-like cP4VP-PS di-segment Janus NPs are also achieved. The total height of the NPs is 9–15 nm (Fig. S7 in SI) and the average hydrodynamic diameter is 15.9 nm. At lower dosage level of P4VP_{10k}-*b*-PS_{9.8k}, for example 0.25 wt% and 0.075 wt%, the Janus NPs shorten to 5–12 and 3–8 nm (Fig. S8 in SI). The average hydrodynamic diameter decreases accordingly (Fig. S9 in SI). Meanwhile, the size distribution becomes much broader. It is noticed that the recycled SiO₂ spheres maintain the patchy microstructure (Fig. S10a in SI), which makes cP4VP-PS Janus NPs with the same morphology (Fig. S10b in SI). Such an approach is highly economic and effective.

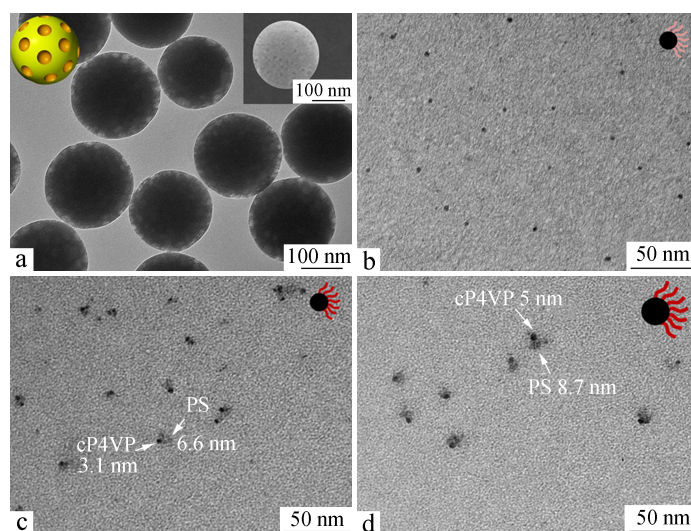


Fig. 1 (a) TEM and inset SEM images of C8-SiO₂ patchy spheres; TEM images of cP4VP-PS di-segment Janus NPs prepared from P4VP_{10k}-*b*-PS_{9.8k} (b) before and (c) after staining with RuO₄, and (d) the Janus NPs from P4VP_{35k}-*b*-PS_{93k}. All the samples were prepared after drying the dispersions in THF (Copolymer concentration: 1.0 wt% of C8-SiO₂ patchy spheres).

It is well known that there are hydrogen bonding between Si—OH and pyridyl-group^[31], which can induce a preferential absorption of P4VP-based copolymers on the dents, for example P4VP_{10k}-*b*-PS_{9.8k}. The peak shifts from 1597 cm⁻¹ to 1606 cm⁻¹ (Fig. 2), suggesting that most of the pyridine rings form hydrogen bonds^[32]. After the P4VP side is selectively crosslinked to form robust NPs (cP4VP) with 1,5-diiodopentane, a new peak appears

at 1638 cm^{-1} that is assigned to the quaternized pyridyl-groups^[33]. The small peak at 1597 cm^{-1} indicates that cP4VP-PS contains some free P4VP units. It is noted that the hydrogen bonded pyridine rings with the stretching vibration at 1606 cm^{-1} disappears. The cP4VP-PS is detached *via* breaking the hydrogen bonding after adding acid.

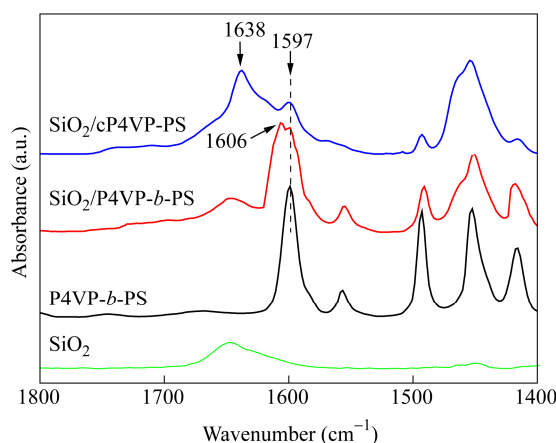


Fig. 2 FTIR spectra of the SiO₂ spheres, P4VP-*b*-PS, SiO₂/P4VP-*b*-PS and SiO₂/cP4VP-PS composite spheres

As aforementioned, there are some residual free pyridine rings in the cP4VP-PS Janus NPs, which provide them with pH sensitivity. At pH below 5.0, the dispersion is highly transparent (Fig. 3a). In comparison, at pH above 5.2, the transmittance is greatly decreased. The absorbance is decreased by reducing pH (Fig. 3b). A subtle increase in pH from 4.8 to 5.2 induces a dramatic increase in absorbance, implying the aggregation of Janus NPs. Since pK_a of pyridine is ~ 5 ^[34], the P4VP segment becomes hydrophobic after de-protonation above pH ~ 5 . The cP4VP-PS Janus NPs are individual under TEM upon drying the aqueous dispersion at pH = 3.0 (Fig. 3c). Only one narrow DLS peak is present corresponding to a hydrodynamic diameter of $\sim 11.3\text{ nm}$ (inset Fig. 3c). In comparison, some aggregates of cP4VP-PS Janus NPs are observed under TEM upon drying the aqueous dispersion at pH = 7.0 (Fig. 3d). Two broad DLS peaks are corresponded to larger aggregates (inset Fig. 3d).

The cP4VP segment can serve as a nanosized reactor to induce a favourable growth of functional materials. A huge family of composite di-segment Janus NPs are derived. As an example, Au forms within the cP4VP segment after a preferential absorption of HAuCl₄ following by *in situ* reduction. The composite Janus NP dispersion becomes pink yet transparent. The Au@cP4VP composite segment becomes darker under TEM with a diameter of 4–5 nm (Fig. 4a). Crystallinity of Au is verified by selected area electron diffraction (SAED) (inset Fig. 4a). Thiol-capped polymers, for example PEG_{16k}-SH can be grafted onto the Au@cP4VP composite segment. By staining with PTA, the PEG segment is discerned under TEM (Fig. 4b). PEG and PS segments are segregated onto opposite sides of the middle Au@cP4VP composite segment. The PEG-Au@cP4VP-PS composite tri-segment Janus NPs are dispersible in both water and oil. The aqueous dispersion is transparent and stable without aggregation within the whole pH range (Fig. S11 in SI) because the pH responsive cP4VP periphery has been covered with PEG. The PEG-Au@cP4V-PS Janus NPs can self-organize into superstructures by slowly adding water into the Janus NP dispersion in THF. As an example, superparticles are achieved after evaporation of THF from the dispersion in THF/water (1/5, *V/V*). The PS segments of all the Janus NPs are directly inward with the black Au@cP4VP segments surrounding the internal core at the exterior surface (Fig. 4c). After selectively staining with PTA, the PEG segments are discerned and cover the black Au@cP4VP layer at the outermost surface (Fig. 4d). This implies that the Janus NPs can serve as a cargo to deliver functional species such as Au NPs towards the oil/water interface. Similarly, other thiol-capped polymers such as PNIPAM-SH ($M_n = 13.3 \times 10^3$) can be grafted onto the opposite side of Au@cP4VP composite segment.

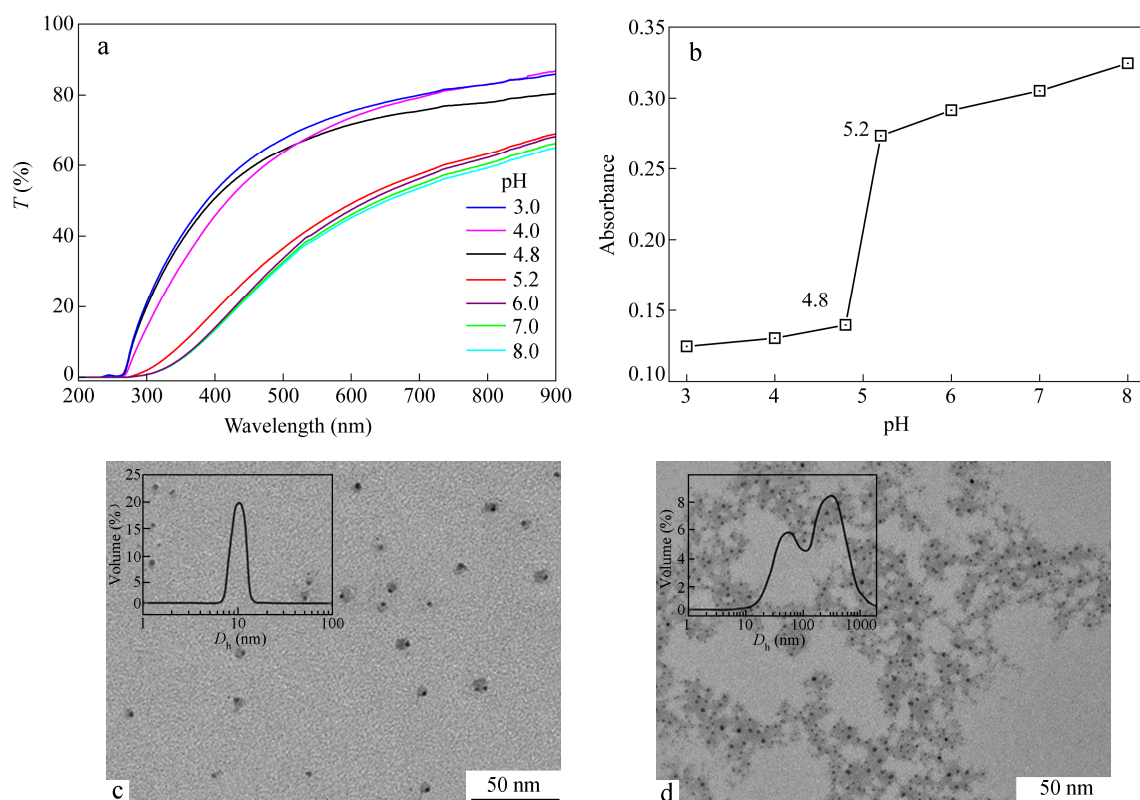


Fig. 3 (a) Transmittance curves of the cP4VP-PS Janus NPs aqueous dispersion at varied pHs; (b) Absorbance of the dispersion at 660 nm at varied pHs; TEM images and DLS curves of the cP4VP-PS Janus NPs in aqueous dispersions at two pHs: (c) pH = 3.0, (d) pH = 7.0

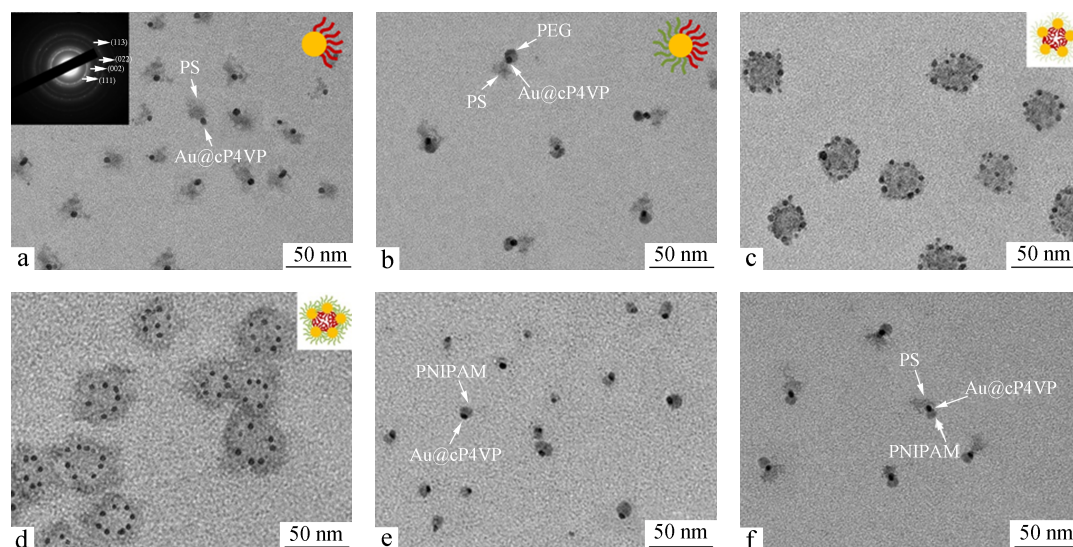


Fig. 4 (a) TEM image of the Au@cP4VP-PS composite di-segment Janus NPs, inset SAED pattern of Au; (b) TEM images of the PEG-Au@cP4VP-PS composite tri-segment Janus NPs after staining with PTA and RuO₄; TEM images of the superparticles after evaporation of THF from PEG-Au@cP4VP-PS dispersion in THF/water (1/5, V/V) (c) before and (d) after staining with PTA; TEM images of the PNIPAM-Au@cP4VP-PS composite tri-segment Janus NPs after sequential staining with (e) PTA and then (f) RuO₄

PNIPAM segment becomes distinguished after staining with PTA (Fig. 4e). After another staining with RuO₄, the PS segment on the opposite side is discerned (Fig. 4f). The PNIPAM-Au@cP4VP-PS Janus NPs are amphiphilic which is originated from PNIPAM and PS. Since PNIPAM is thermally responsive with a LCST (~ 32 °C), amphiphilic performance of the Janus NPs should be thermally triggered. A stable dispersion forms in water at low temperature. Upon increasing temperature above LCST, the aqueous dispersion becomes turbid due to the formation of precipitates.

The interactive performance of PNIPAM-Au@cP4VP-PS composite tri-segment Janus NPs is further demonstrated. The aqueous dispersion of Au@cP4VP-PS Janus NPs strongly absorb visible light at around 520 nm and especially in NIR with a peak around 800 nm (Fig. 5a). Both peaks of PNIPAM-Au@cP4VP-PS slightly blue shift. In the case of the cP4VP-PS aqueous dispersion, no absorption peaks are found. This indicates that the two absorption peaks are resulted from the nanoscaled Au. The temperature of both aqueous dispersions increase from 25 °C to 48 °C after NIR laser irradiation for 10 min (Fig. 5b). Temperature increment of the Au@cP4VP-PS Janus NPs aqueous dispersion is faster. In contrast, temperature change in either water or cP4VP-PS aqueous dispersion with NIR laser irradiation is negligible. The PNIPAM-Au@cP4VP-PS aqueous dispersion is stable below LCST (~ 32 °C) (Fig. 6a1). After NIR irradiation (808 nm, 3 W/cm²) for 50 s, the dispersion starts to flocculate although the dispersion temperature (29.7 °C) remains lower than LCST (~ 32 °C) (Fig. 6a2). This indicates that PNIPAM part has experienced a hydrophilic/hydrophobic transformation. The Au@cP4VP composite segment serves as a thermal reservoir due to the hyperthermia effect of Au under NIR irradiation. The PNIPAM segment is thus rapidly heated above LCST to drive the transformation while the temperature change of surrounding segment is delayed. A stable cyclohexane/water emulsion forms with the PNIPAM-Au@cP4VP-PS at low temperature 25.0 °C (Fig. 6b1). After 0.2 mL of the emulsion in a vessel is irradiated with NIR for 10 s, the emulsion temperature is increased to 28.5 °C and starts to destabilize. A deep pink thin top layer appears (Fig. 6b2). After NIR irradiation is switched off, the emulsion temperature gradually increases to a maximum 30.2 °C in 30 s. The system becomes completely de-emulsified. The bottom water phase becomes transparent and colorless, while the top oil phase is purple (Fig. 6b3). The Janus NPs are present in the top oil phase. After the mixture is cooled down, the oil/water interface is diffusive downwardly with a slightly pink phase. Upon shaking, a stable emulsion forms again. In comparison, the emulsion without NIR irradiation remains stable even at high temperature of 32.5 °C for a long period of time 300 s (Fig. S12 in SI). Therefore, the NIR triggered Janus performance of PNIPAM-Au@cP4VP-PS at low temperature is originated from the hyperthermia effect of Au NP and thermal energy transfer to rapidly heat the PNIPAM segment above LCST (~ 32 °C).

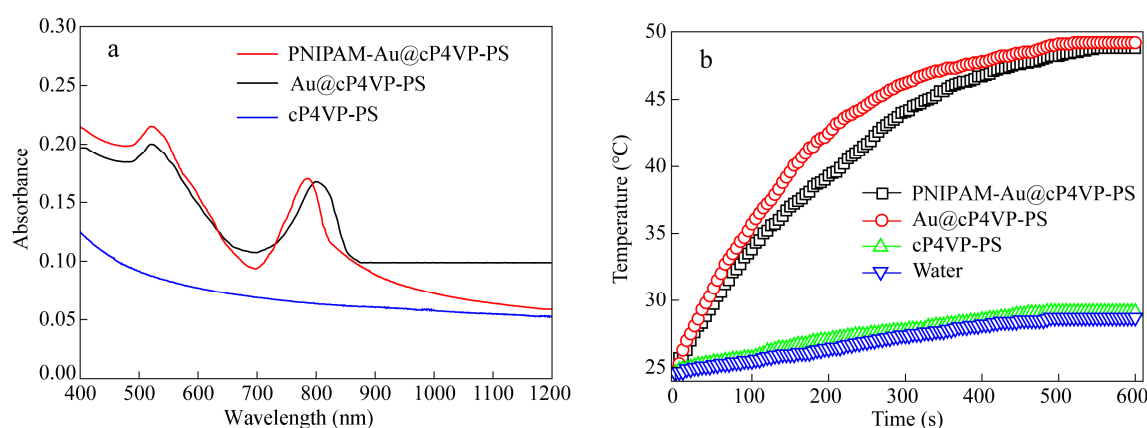


Fig. 5 (a) UV-Vis-NIR absorption curves of cP4VP-PS, Au@cP4VP-PS and PNIPAM-Au@cP4VP-PS aqueous dispersions; (b) Photo thermal curves of water, cP4VP-PS, Au@cP4VP-PS and PNIPAM-Au@cP4VP-PS aqueous dispersions under NIR laser irradiation (808 nm, 3 W/cm²)

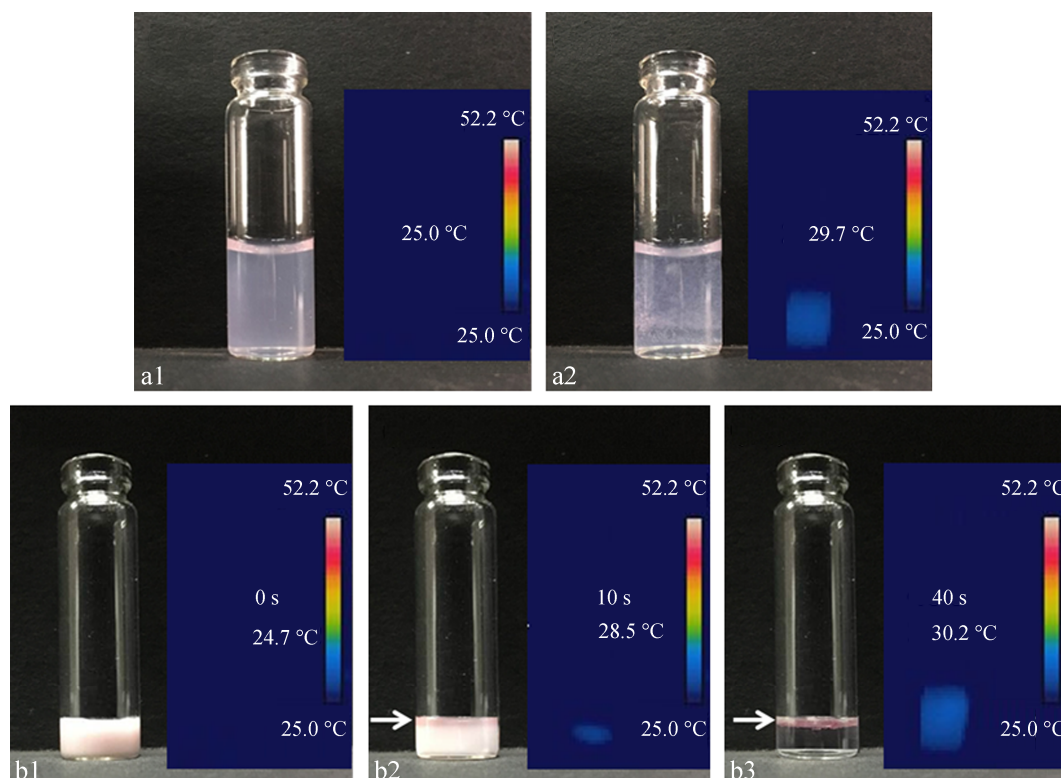


Fig. 6 The PNIPAM-Au@cP4VP-PS Janus NP aqueous dispersion (a1) before and (a2) after NIR irradiation (808 nm, 3 W/cm²) for 50 s; (b1) The cyclohexane/water emulsion stabilized with PNIPAM-Au@cP4VP-PS, (b2) after NIR irradiation (808 nm, 3 W/cm²) for 10 s, (b3) after 30 s upon switching off NIR irradiation (The emulsion volume is 0.2 mL.)

CONCLUSIONS

In summary, we have prepared polymer/metal composite segmental Janus NPs, which show interactive performances from metal NPs and polymers. PNIPAM-Au@cP4VP-PS tri-segment Janus NPs can serve as a NIR triggered responsive solid emulsifier at low temperature, which is originated from the hyperthermia effect of Au NPs and thermal energy transfer to rapidly heat the PNIPAM segment above LCST (~32 °C). Robust cP4VP-PS di-segment Janus NPs are synthesized onto a SiO₂ patchy spheres by hydrogen bonding induced absorption of P4VP-*b*-PS copolymers following by a selective crosslinking. Functional species, for example Au can be *in situ* synthesized within the cP4VP segment. Another polymer is conjugated onto opposite side of the Au@cP4VP composite segment to achieve tri-segment Janus NPs. The method is robust to tailor the molecular weight and distribution of copolymers. A huge family of functional Janus NPs will be derived by adjusting segment number and composition of polymers and NPs.

REFERENCES

- 1 de Gennes, P.G., Rev. Mod. Phys., 1992, 64: 645
- 2 Jiang, S. and Granick, S., "Janus particles synthesis, self-assembly and applications" Royal Society of Chemistry, Cambridge, 2012
- 3 Walther, A. and Müller, A.H.E., Chem. Rev., 2013, 113: 5194
- 4 Liang, F.X., Zhang, C.L. and Yang, Z.Z., Adv. Mater., 2014, 26: 6944
- 5 Lattuada, M. and Hatton, T.A., J. Am. Chem. Soc., 2007, 129: 12878

- 6 Song, Y., Liu, K. and Chen, S.W., *Langmuir*, 2012, 28: 17143
- 7 Wang, Q.G., Liang, F.X., Wang, Q., Qu, X.Z. and Yang, Z.Z., *Chinese J. Polym. Sci.*, 2015, 33(10): 1462
- 8 Lv, D.M., Ni, W., Liang, F.X., Wang, Q., Qu, X.Z. and Yang, Z.Z., *Chinese J. Polym. Sci.*, 2015, 33(9): 1344
- 9 Wurm, F. and Kilbinger, A.F.M., *Angew. Chem. Int. Ed.*, 2009, 48: 8412
- 10 Du, J.Z. and O'Reilly, R.K., *Chem. Soc. Rev.*, 2011, 40: 2402
- 11 Isojima, T., Lattuada, M., Sande, J.B.V. and Hatton, T.A., *ACS Nano*, 2008, 2: 1799
- 12 Glotzer, S.C. and Solomon, M.J., *Nat. Mater.*, 2007, 6: 557
- 13 Huang, Z.H., Dong, B.J., Chen, P.Y., Yang, Y., Zhu, G.L. and Yan, L.T., *Acta Polymerica Sinica (in Chinese)*, 2016, (8): 979
- 14 Zubarev, E.R., Xu, J., Sayyad, A. and Gibson, J.D., *J. Am. Chem. Soc.*, 2006, 128: 15098
- 15 Hu, J.M., Wu, T., Zhang, G.Y. and Liu, S.Y., *J. Am. Chem. Soc.*, 2012, 134: 7624
- 16 Jackson, A., Myerson, J.W. and Stellacci, F., *Nat. Mater.*, 2004, 5: 330
- 17 Kim, H., Carney, R.P., Reguera, J., Ong, Q.K., Liu, X. and Stellacci, F., *Adv. Mater.*, 2012, 24: 3857
- 18 Kim, B.J., Bang, J., Hawker, C.J., Chiu, J.J., Pine, D.J., Jang, S.G., Yang, S.M. and Kramer, E.J., *Langmuir*, 2007, 23: 12693
- 19 Glogowski, E., He, J., Russell T.P. and Emrick, T., *Chem. Commun.*, 2005, 32: 4050
- 20 Andala, D.M., Shin, S.H.R., Lee, H.Y. and Bishop, K.J.M., *ACS Nano*, 2012, 6: 1044
- 21 Wang, B.B., Li, B., Zhao, B. and Li, C.Y., *J. Am. Chem. Soc.*, 2008, 130: 11594
- 22 Nie, L., Liu, S.Y., Shen, W.M., Chen, D.Y. and Jiang, M., *Angew. Chem. Int. Ed.*, 2007, 46: 6321
- 23 Jiao, Y. and Akcora, P., *Macromolecules*, 2012, 45, 3463
- 24 Yao, X.H., Jing, J.Y., Liang, F.X. and Yang, Z.Z., *Macromolecules*, 2016, 49: 9618
- 25 Mavila, S., Eivgi, O., Berkovich, I. and Lemcoff, N.G., *Chem. Rev.*, 2016, 116: 878
- 26 Liu, Y.F., Abetz, V. and Müller, A.H.E., *Macromolecules*, 2003, 36: 7894
- 27 Erhardt, R., Bölker, A., Zettl, H., Kaya, H., Pyckhout-Hintzen, W., Krausch, G., Abetz, V. and Müller, A.H.E., *Macromolecules*, 2001, 34: 1069
- 28 Zhou, P., Liang, F.X., Liu, Y.J., Deng, R.H., Yang, H.L., Wang, Q., Qu, X.Z. and Yang, Z.Z., *Sci. China Mater.*, 2015, 58: 961
- 29 Stöber, W., Fink, A. and Bohn, E., *J. Colloid Interface Sci.*, 1968, 26: 62
- 30 Kim, K., Kim, H.S. and Park, H.K., *Langmuir*, 2006, 22: 8083
- 31 Burtovyy, R. and Luzinov, I., *Langmuir*, 2008, 24: 5903
- 32 Ruokolainen, J., ten Brinke, G., Ikkala, O., Torkkeli, M. and Serimaa, R., *Macromolecules*, 1996, 29: 3409
- 33 Ruokolainen, J., Tanner, J., ten Brinke, G., Ikkala, O., Torkkeli, M. and Serimaa, R., *Macromolecules*, 1995, 28: 7779
- 34 Malynych, S., Luzinov, I. and Chumanov, G., *J. Phys. Chem. B*, 2002, 106: 1280