

## Research Article

# Asymmetric Composite Nanoparticles with Anisotropic Surface Functionalities

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Asymmetric inorganic/organic composite nanoparticles with anisotropic surface functionalities represent a new approach for creating smart materials, requiring the selective introduction of chemical groups to dual components of composite, respectively. Here, we report the synthesis of snowman-like asymmetric silica/polystyrene heterostructure with anisotropic functionalities via a chemical method, creating nanostructure possibly offering two-sided biologic accessibility through the chemical groups. Carboxyl group was introduced to polystyrene component of the snowman-like composites by miniemulsion polymerization of monomer on local surface of silica particles. Moreover, amino group was then grafted to remained silica surface through facile surface modification of the composite nanoparticles. The asymmetric shape of these composites was confirmed by TEM characterization. Moreover, characteristics of anisotropic surface functionalities were indicated by Zeta potential measurement and confocal laser microscopy after being labeled with fluorescent dyes. This structure could find potential use as carriers for biological applications.

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## 1. Introduction

Recently, there have been extensive research efforts on the surface functionalization with controlled properties of the colloid particles [1, 2] and the fabrication of the new programmable building blocks for assembly [3]. Several new methods have also been reported on the design and control of the surface functionalization, including deposition of molecules on particles [4], surface-initiated heterophase polymerization [5], and adsorption of colloids [6]. One of the research interests has been focused on the preparation of asymmetrically functionalized particles stemmed from its potential applications in biomedicine due to the fact that the anisotropic particles provide additional functionality compared to their isotropic counterparts [7]. The previously developed methods have been mainly utilized for synthesizing the micrometer scale particles including microcontact printing [8], partial deposition [9, 10], anisotropic decoration [11], gel trapping method [12], laser photochemical deposition [13], micropatterning using a laminar

flow microfluidic device [14], layer-by-layer assembly of polymer [15], and electrohydrodynamic jetting [16, 17]. These asymmetric composites have significantly potential applications in biomedicine and electronic displays due to their asymmetric chemical, physical, and surface properties [18]. However, there have been a few research focused on the development of anisotropically surface-functionalized nanostructures. Therefore, novel methods are critically needed to synthesize composites that are surface functionalized to exhibit high degree of anisotropy in nanoscale.

Here, we report experimental results on the synthesis of nanometer scale, asymmetrically dual-functionalized silica/polystyrene (PS) composites through a chemical approach. That is, a PS nodule with surface carboxyl group and an amino-ended silica particle formed a composite dimer. As will be shown, surface functionalization can take place selectively on either the inorganic or organic surface regions of the composite nanoparticles. Indeed, the synthesized composite nanoparticles possess pronounced structural anisotropy with tunable surface properties.

## 2. Experimental Details

**2.1. Materials.** Tetraethoxysilane (TEOS), ammonium hydroxide (25% w/w), absolute ethanol, triethylamine, toluene, sodium dodecyl sulfate (SDS), sodium bicarbonate, and styrene were purchased from Shanghai Chemical Reagents Company, (Shanghai, China). Hexadecane (99%) and *n*-octadecyltrimethoxysilane (ODMS) were purchased from Acros Organics (NJ, USA). (USA). 3-aminopropyl-triethoxysilane (APS), 4,4'-Azobis(4-cyanopentanoic acid) (ACPA), and tetramethylrhodamine-5-isothiocyanate (TRITC) were purchased from Sigma-Aldrich (MO, USA). 5-(and-6)-carboxyfluorescein succinimidyl ester (NHS-FITC) was purchased from Molecular Probes Inc. (OR, USA). EDC·HCL was purchased from Shanghai Medpep Co. Ltd. (Shanghai, China). Styrene was washed with 5 wt% sodium hydroxide solution first and then with distilled water three times, and stored at 4°C. Deionized water was used for preparation of all aqueous solutions.

**2.2. Synthesis and Local Surface Modification of Silica Particles.** 120 nm monodispersed silica particles were prepared according to the developed Stöber method [19]. Ammonium hydroxide (0.5 M), deionized water (2.1 M), and TEOS (0.12 M) were introduced into 300 cm<sup>3</sup> of absolute ethanol at ambient temperature under vigorous magnetic stirring for 6 hours. 90 cm<sup>3</sup> of TEOS was then added dropwise to the above prepared solution. After 24-hour reaction, the silica particles were collected by centrifugation (9500 rpm for 10 minutes) and frozen dry for 16 hours.

Preparation of the locally modified silica particles: [20, 21] 0.4 cm<sup>3</sup> of ODMS in 20 cm<sup>3</sup> of toluene was impregnated into 0.6 g of the w-silica powder immersed in 0.3 g of water. After addition of 0.8 cm<sup>3</sup> of triethylamine, the suspension was further stirred for 40 hours at room temperature. Then the solid was collected by centrifugation (3000 rpm for 10 minutes) and followed by washing/centrifugation circles with ethanol for three times and thermo treatment at 110°C for 3 hours under vacuum. The obtained locally modified silica particles were kept in a vial until use.

**2.3. Preparation of Asymmetric Composites with Dual Functionalities.** First, the dispersion of 0.1 g locally modified silica particles in the mixture of 4.38 g styrene and 0.17 g hexadecane was introduced into the mixture of 0.114 g SDS, 0.004 g of sodium bicarbonate, and 50 g of deionized water. The whole system was emulsified by stirring at 150 rpm for 1 hour with purged nitrogen. The emulsion was miniemulsified by being ultrasonified at 350 w for 30 minutes. Then under nitrogen protection, the carboxyl-composite particles were obtained by polymerization of styrene initiated by 0.4 g ACPA at 70°C and finished within 3 hours.

Then 0.01 cm<sup>3</sup> APS was added into the dispersion of 35.8 mg carboxyl composite particles in the mixture of 9.1 cm<sup>3</sup> water and 19.9 cm<sup>3</sup> ethanol. The reaction system was magnetically stirred at PH 2.0 for 21 hours and then at PH 12 for 2 hours. At last, the dual-functionalized composites

were obtained when the PH was adjusted back to neutral by several circles of centrifugation and redispersion with water.

**2.4. Labeling the Fluorescence to the Asymmetric Composites.** Labeling the TRITC to the silica part of composites: 0.5 mg TRITC was firstly dissolved in the 11 g absolute ethyl alcohol. 31.4 mg functionalized silica/PS polystyrene composite nanoparticles were dispersed in the 4.8 g absolute ethyl alcohol. The reaction started when the alcohol dispersion of the composites was added in the TRITC alcohol solution rapidly and was magnetically stirred in dark place for 24 hours.

Labeling the NHS-FITC to the PS nodules of the composites: the 2.1 mg EDC·HCL and the 0.7 mg NHS-FITC were dissolved in the 3.5 cm<sup>3</sup> of absolute ethyl alcohol. The 10 mg TRITC labeled composites were dispersed in 1.5 cm<sup>3</sup> of absolute ethyl alcohol. The reaction runs for 5 hours with end-over-end process in dark place after the two dispersions were mixed.

The fluorescence-labeled composite nanoparticles were washed with each 8 cm<sup>3</sup> of ethanol for eleven times to erase the excess TRITC or NHS-FITC by centrifugation/redispersion circles (Sigma Laboratory Centrifuge 3 K 15, Harz, Germany).

**2.5. Characterization.** Transmission electron microscopy (TEM) experiments were performed with a JEOL 2010 microscope (accelerating voltage of 200 kV). Zeta potential measurement was performed at Zetasizer 2000 instruments (Malvern Co., Worcestershire, UK). Confocal micrographs were obtained at Leica TCS SP2 instrument, (Leica Microsystems Co. Ltd., Wetzlar, Germany).

## 3. Results and Discussion

In this case, the negatively charged carboxyl group was loaded on PS part of the composite through miniemulsion polymerization of monomer initiated by an initiator with carboxyl group. The positive amino group was then attached on the silica surface of the composite via grafting with an alkylsilane. Figure 1 illustrates the complete preparation process of the dual functionalized asymmetric composite nanoparticles. As shown in this figure, first, the 120 nm silica particles are prepared. Then, in step (1), the locally modified silica particles are obtained via modification of the partial surface of silica particles by ODMS. In other words, only a limited local region on each silica particle is modified [20, 21]. In step (2), the miniemulsion polymerization of the styrene monomer is performed based on the locally modified silica particles initiated by ACPA. In completion of above steps, the asymmetric silica/PS composite nanoparticles with carboxyl groups on polystyrene surface are prepared. In step (3), grafting of the coupling agent APS on the remained silica surface is performed to introduce the amino groups into the composite nanoparticles. Thus, the dual-functionalized asymmetric composite nanoparticles are obtained. As can be seen in Figure 1, the anisotropic

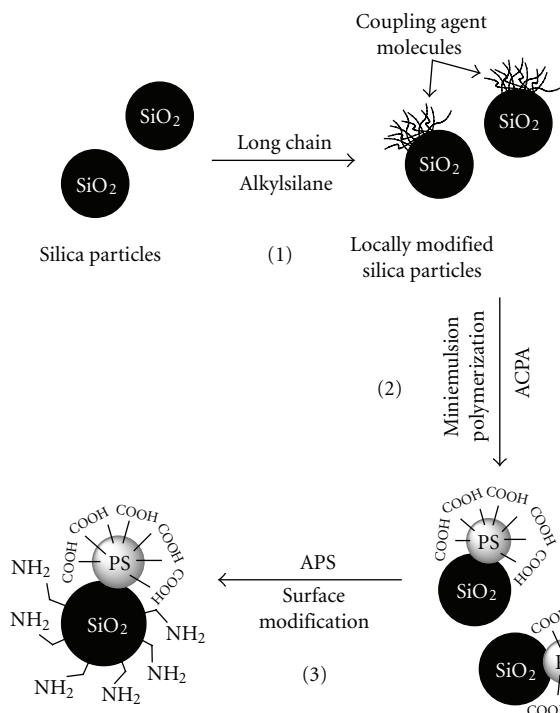
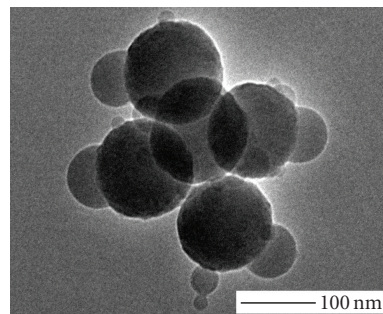


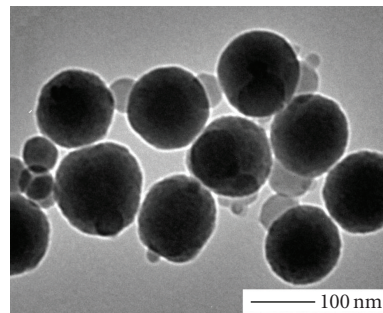
FIGURE 1: Scheme of the pathway for preparation of dual functionalized asymmetric composites nanoparticles.

surface functionalization starts from the miniemulsion polymerization of styrene monomer (step (2)). The asymmetric morphology of the silica/PS composite and the surface carboxyl groups on polystyrene nodules is synchronously created via the miniemulsion polymerization of monomer and local surface modification of silica particles is the key for the formation of the asymmetric inorganic/organic nanocomposites [22]. Due to the selective nucleation and growth of styrene on the partial surface of silica (steps (1) and (2)), further functionalization of the amino group on the remained silica surface can be realized successfully. Thus, as depicted at step (3) in Figure 1, the amino groups are loaded on the silica particles of the composites through grafting of APS.

In this experiment, the anisotropic functionality was established based on the formation of the asymmetric silica/PS composites with snowman-like structure [23]. Figure 2(a) shows the TEM image of the asymmetric composite nanoparticles with carboxyl groups on the surface of PS nodules. The snowman-like pair is composed of a 65 nm polystyrene nodule and a 120 nm silica particle. Figure 2(b) shows the asymmetric nanocomposites with anisotropic dual-functionalities, carboxyl groups on PS nodules, and amino groups on surface of silica particles, respectively. We can see that the composite nanoparticles possessed stable asymmetric morphology after being dually functionalized. Moreover, the asymmetric composites exhibit obvious amphiphilic characteristics. Figure 3 shows comparison of interfacial behavior of the asymmetric composites to that

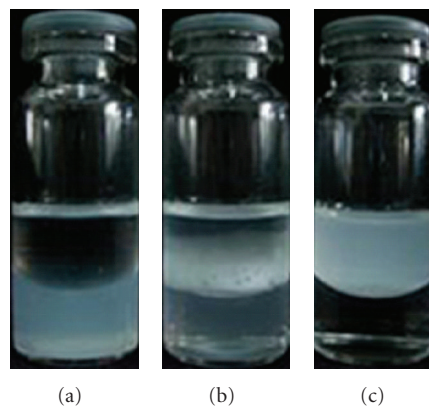


(a)



(b)

FIGURE 2: TEM images of (a) asymmetric nanocomposites with only carboxyl group on the polystyrene nodule, (b) dual-functionalized asymmetric nanocomposites with carboxyl groups on polystyrene nodules and amino groups on silica surface.



(a)

(b)

(c)

FIGURE 3: Photograph of the interfacial behavior of three kinds of particles in the water-toluene dual-phase system: (a) w-SIO particles, (b) asymmetric composite particles, and (c) o-SIO particles.

of pure hydrophilic silica particles (w-SIO) or hydrophobic silica particles (o-SIO) in the water-toluene dual-phase system. It can be seen in Figure 3(b) that asymmetric composite nanoparticles could preferentially exist at the dual-phase interface [24]. In contrast, the unmodified w-SIO particles are dispersed in water (Figure 3(a)), while the o-SIO particles, modified by ODMS thoroughly, are dispersed in toluene (Figure 3(c)).

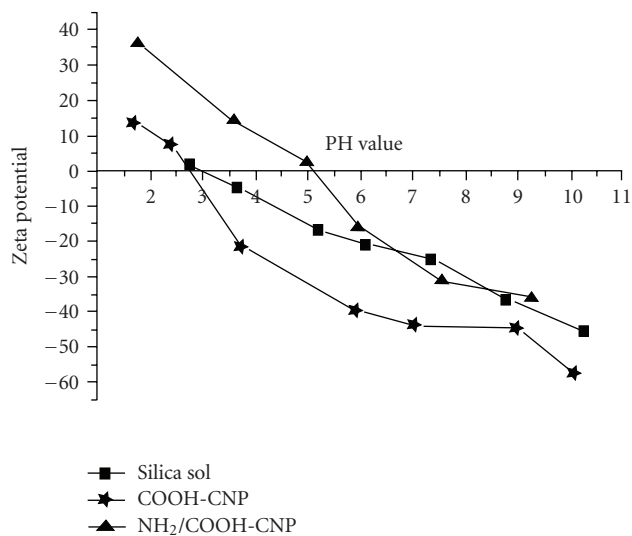
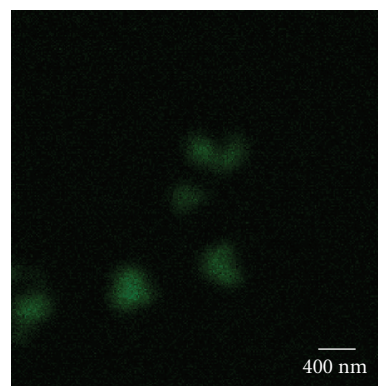


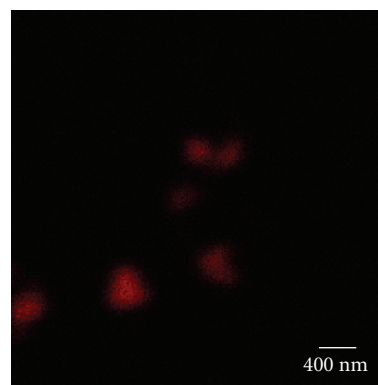
FIGURE 4: Zeta potential curves as a function of PH value of different kinds of particles.

Variation in surface potential of the dual-functionalized composites was characterized by Zeta potential measurement. Figure 4 shows the variation of Zeta potential as a function of PH value. As can be seen, there is obvious difference of the isopotential points between three kinds of aqueous dispersion of the silica particles, carboxyl-ended composite nanoparticles (COOH-CNP), and dual-functionalized composite nanoparticles (NH<sub>2</sub>/COOH-CNP). The isopotential points are 3.2, 2.8, and 5.2, respectively. Meanwhile, the quantity of surface charge of different composites at a certain PH value varies significantly due to different surface functionalities. As can be seen in this figure, the maximum negative charge value of COOH-CNP is about  $-58$  mv at PH 10, slightly higher than  $-45$  mv of silica particles due to the presence of carboxyl groups. In contrast, the positive charge value of the NH<sub>2</sub>/COOH-CNP is about  $37$  mv, much higher than that of the COOH-CNP at the PH 1.7 due to the presence of the amino groups.

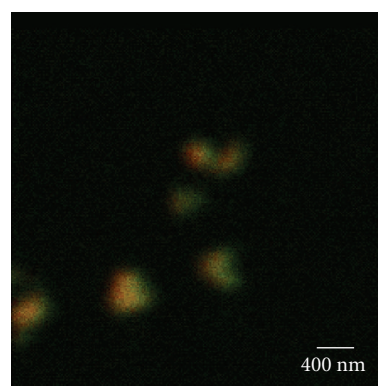
To investigate the possibilities of the as-synthesized dual-functionalized asymmetric composite nanoparticles as the biologic dual-component supporters, the anisotropic functionalities of the composites were labeled with two different fluorescent molecules, respectively. In this case, the dye of TRITC was first used to label the amino group on silica surface through an isothiocyanate functional group that only could be coupled to the amino group of APS specifically. The dye of NHS-FITC was then labeled to the carboxyl group on PS nodules intermediated by EDC·HCL. It is worth noting that TRITC was superfluously used to occupy nearly all available amino groups on the silica surface to avoid the reactions between FITC and remained amino groups. The fluorescent properties of the labeled asymmetric composite were examined by using the confocal laser scanning microscopy (CLSM). Figure 5 shows confocal micrograph of the dual-functionalized composite nanoparticles labeled with two kinds of fluorescences. Figures 5(a) and 5(b)



(a)



(b)



(c)

FIGURE 5: Confocal laser microscopy images showing the dual-functionalized composite particles labeled with different fluorescent molecules: (a) FITC fluorescence; (b) TRITC fluorescence, and (c) overlay. Scale bar: 400 nm.

show the CLSM images obtained at different individual excitation wavelengths of 488 and 543 nm, corresponding to the fluorescences of NHS-FITC and TRITC, respectively. Figure 5(c), superposition of Figures 5(a) and 5(b), indicates the anisotropic fluorescent property of the composite particles with interfacial yellow color, coexisting with the red and green visible from both sides.

The confocal results gave a direct evidence for the anisotropic surface functionalities of the silica/PS composites and the reactive activity of the anisotropic functional groups.

The dual functionalized composite nanoparticles could be used as the selective carriers for two independent ingredients or biological molecules such as DNA or enzyme [25].

#### 4. Conclusion

In conclusion, we have demonstrated a viable synthesis route for making the asymmetric composite nanoparticles with dual functionalities through a two-step chemical approach. The method combining the miniemulsion polymerization of the organic component to local surface modification of the inorganic component may be extended to the introduction of other chemical groups into the asymmetric composite nanoparticles. The as-synthesized composite nanoparticles with controlled distribution of the bioreactive surface functionalities will find important applications in biosensors, cell sorting, and fabrication of smart display.

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