Preparation and characterization of dual-responsive spiropyran-based random copolymer brushes via surface-initiated atom transfer radical polymerization

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ABSTRACT
Silica nanoparticles (SiO 2) were grafted with the precursor random copolymer of 1′-(2-acryloxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2′-indoline) (SPMA) and tert-butyl methacrylate (tBMA) by surface-initiated atom transfer radical polymerization (SI-ATRP), and SiO 2-g-P(SPMA-co-methacrylic acid (MAA)) was obtained via chemical hydrolysis of the resulting precursor random copolymer in acidic conditions. From transmission electron microscopy, we observed the spherical morphology of monodispersed silica nanoparticles and core-shell structure of SiO 2-g-P(SPMA-co-MAA). Energy dispersive spectroscopy, Fourier transform infrared spectra, X-ray photoelectron spectroscopy, and the thermogravimetric analysis indicated that the polymer had been successfully grafted onto the surface of silica nanoparticles. The dual-responsive properties were characterized by means of ultraviolet-visible spectrophotometer and dynamic light scattering. The average hydrodynamic diameter of SiO 2-g-P(SPMA-co-MAA) increased from 185.7 to 212.7 nm under ultraviolet light irradiation for 5 min. Also, the particle size of SiO2-g-P(SPMA-co-MAA) increased with the rising pH value of surrounding condition.

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1. Introduction
In recent years, silica nanoparticles (SNPs, SiO 2) have received vast attention and become a research hotspot because there are a lot of hydroxyl groups on their surface which can be easily functionalized. They have been widely used in drug release control,[1] bioimaging,[2] biomedicine,[3] catalyst,[4] biosensor,[5] gene delivery,[6] diagnosis, and therapeutics,[7] etc. Modified SNPs can keep all the properties of the inorganic nanoparticles and have special properties such as stimulus response and highly efficient adsorption of heavy metal ions.[8,9]

The surface modification of silica nanoparticles is an important method for improving their properties and expanding their application, especially by preparing polymer brushes.[10,11] Generally, polymer brushes can be obtained via covalent attachment approaches which usually contain ‘grafting to’ and ‘grafting from’ methods. Compared with ‘grafting to’, ‘grafting from’ method has no restrictions on terminal functional groups, and the grafting density is easy to control. Surface-initiated polymerization (SIP, ‘grafting from’) approach, based on initiators being immobilized with a surface to initiate polymerization, is a good choice to control the thickness, functionality, and density of polymer brushes with molecular precision.[12–15] Therefore, surface-initiated atom transfer radical polymerization (SI-ATRP) is one kind of the effective method for preparing structure-controlled polymer brushes.[16–23] With the development of the research on the smart material, stimuli-responsive polymers have attracted significant interest. When they are subjected to external environmental stimuli,[24] such as the changes of solvent,[25] temperature,[26–28] ionic strength,[29] pH,[30,31] and light irradiation,[32,33] the molecular chains of the corresponding stimuli-responsive polymer brushes will generate a conformational change, leading to the changes in the properties of polymer brushes.

Spiropyran is a well-known photosensitive molecule which has a broad spectrum and near-quantitative property in both directions during the photoisomerization process.[34–38] The combination of spiropyran units (SP) into polymer and then attaching them onto SNPs can sharply reduce the fatigue of light-responsive polymer brushes.[39] As smart dynamic materials, the spiropyran-based copolymers have particular advantages for profound and lasting applications. Under the irradiation of ultraviolet (UV) light, a ring-closed and colorless spiropyran (SP) form switches into a ring-opened and strongly colored merocyanine (MC) form, and under visible (vis) light irradiation, the isomerization equilibrium will move to the reverse direction. Because the energy of
2-bromoisobutyrate-functionalized SNPs were prepared. Next, hybrid silica nanoparticles coated with P(SPMA-co-tBMA) were constructed by SI-ATRP. Finally, the resulting polymer brushes were hydrolyzed at acidic conditions, and ultimate P(SPMA-co-MAA) brushes were obtained.

2. Experimental

2.1. Materials

The precursor monomer tertiary-butyl methacrylate (tBMA, 99%, Aladdin) was passed through a column of basic alumina to remove inhibitors before use. Ethyl 2-bromoisobutyrate (EBiB, 98%, TCI) as the initiator, cuprous chloride (CuCl, ≥99.95%, Aladdin) as the catalyst, 1,1,4,7,10,10-hexamethylenetetramine (HMTETA, 97%, J&K) as the ligand, N,N-dimethylformamide (DMF, ≥99.5%), trifluoroacetic acid (TFA, 99%, Aladdin), ammonium hydroxide (25%), tetraethyl-orthosilicate (TEOS, 99.5%), ethanol (≥99.7%), tetrahydrofuran (THF, 99%), 2-bromoisobutyl bromide (BiBB, 99%, J&K), dichloromethane (DCM, 99%, J&K), pyridine (99%, Aladdin), (3-aminopropyl)-triethoxysilane (APTES, 99.6%, J&K), and toluene (≥99.5%) were used as received. The light-responsive monomer 1′-(2-acryloxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2H-1-benzopyran-2′,2′-indoline) (SPMA) was synthesized as described in literature.[44]

2.2. Preparation of polymer brushes

2.2.1. Preparation of monodispersed SNPs (SiO$_2$) by Stöber method

Under the condition of room temperature, ammonium hydroxide (25 mL) and ethanol (500 mL) were added into
a two-neck round-bottom flask and stirred at a rotating speed of 300 rpm for 10 min. Next, the mixture of TEOS (12.5 mL) and ethanol (14 mL) was added into the flask at the rate of 1 mL/min by dropping funnel. The reaction was stopped after continuous stirring at room temperature for 20 h, and a white silica suspension was obtained. The SNPs were centrifugally separated from the suspension and washed with ethanol for four times, and then the resulting SNPs were dispersed in ethanol (50 mL) with ultrasound.

2.2.2. Preparation of amino-functionalized SNPs (SiO$_2$–NH$_2$)
The SNPs suspension (45 mL) was placed in a 100-mL flask, and then the flask was sealed with rubber plug. Subsequently, the flask was immersed in an oil bath at 60 °C, and then ammonium hydroxide (50 μL) and APTES (0.4 mL) were added into reaction system dropwise. After 12 h, the reactant was cooled to room temperature and exposed to air. The obtaining mixture was washed and centrifugally separated with toluene for four times, and the resulting SiO$_2$–NH$_2$ was dispersed in toluene (50 mL).

2.2.3. Synthesis of 2-bromoisobutyrate-functionalized SNPs (SiO$_2$–Br)
The amino-functionalized SNPs suspension (45 mL) and pyridine (0.3 mL) were placed in a 100-mL flask. Then, BiBB (0.25 mL) was added into the flask by syringe dropwise, and the mixture was stirred at 0 °C for 12 h. Then, the similar purification with SiO$_2$–NH$_2$ was carried out, and the final sediment (SiO$_2$–Br) was dried under vacuum at 50 °C overnight.

2.2.4. Synthesis of hybrid silica nanoparticles coated with P(SPMA-co-tBMA) brushes (SiO$_2$-g-P(SPMA-co-tBMA))
In a typical polymerization, SiO$_2$–Br (100 mg), SPMA (73.6 mg), tBMA (582 μL), CuCl (2.7 mg), toluene (2 mL), DMF (0.1 mL), and EBiB (2 μL) were poured into a Schlenk tube equipped with a rubber septum, and the mixture was degassed three times using the freeze–pump–thaw procedure. Thereafter, HMTETA as the ligand (45.6 μL) was injected into the mixture and the tube was placed in an oil bath at a preset temperature (90 °C) for 24 h. The polymerization was manually stopped by exposing the reactant to air. The resultant was dispersed in THF, and centrifugally separated four times. On the one hand, the copper catalyst was removed by passing the centrifugal liquid through a neutral alumina column, and precipitation of the resulting transparent solution gave the free P(SPMA-co-tBMA) which was analyzed using GPC. On the other hand, the resulting solid from centrifugal separation was carefully washed with THF, and the nongrafted polymer was further removed by Soxhlet extraction for 24 h. SiO$_2$-g-P(SPMA-co-tBMA) was obtained and dried under vacuum at 50 °C for 20 h.

2.2.5. Preparation of SiO$_2$-g-P(SPMA-co-MAA) by hydrolysis
SiO$_2$-g-P(SPMA-co-tBMA) particles (60 mg), dichloromethane (30 mL), and trifluoroacetic acid (1 mL) were stirred at room temperature for 24 h. Then, the mixture was washed and centrifugally separated with dichloromethane and ethanol alternatively for four times, and ultimate P(SPMA-co-MAA) brushes were obtained and dried under vacuum at 50 °C overnight.

2.3. Characterization
The size and morphology of bare SiO$_2$ and SiO$_2$-g-P(SPMA-co-MAA) were determined by transmission electron microscopy (TEM) using a Titan G2 60–300 on a copper grid with a carbon membrane.

The dispersion stability of the nanoparticles was evaluated by the $n$-value as reported in the previous literatures.

![Figure 1. TEM images of monodispersed silica nanoparticles (bare silica nanoparticles).](image-url)
3. Results and discussion

3.1. Synthesis and characterization of SiO$_2$-g-P(SPMA-co-MAA)

The preparation route of hybrid silica nanoparticles coated with double responsive random copolymer P(SPMA-co-MAA) is shown in Scheme 3. TEM images of bare silica nanoparticles and hybrid nanoparticles SiO$_2$-g-P(SPMA-co-MAA) dispersed in anhydrous ethanol are shown in Figures 1 and 2, respectively. Monodispersed and ordered silica nanoparticles are obviously observed in Figure 1(a) and (b), and their morphology is almost spherical with the diameter of 40–50 nm.

As can be seen from Figure 2(a) and (b), the thickness of the grafting polymer layer is about 5–8 nm. In the previous report, $n$-value is utilized to assess the dispersion stability of the nanoparticles suspension. The higher the $n$-value is, the better the dispersion stability is. In the present work, it is determined by the absorbance at different wavelengths according to the following equation:

$$\tau = a\lambda^{-n}$$

where $\tau$ is the absorbance of the suspension; $\lambda$ is the wavelength used in the experiment; $a$ is a constant.

Then, $n$-value can be calculated from the plotting between $\ln \tau$ and $\ln \lambda$ as shown in Figure S1 (see the Supporting Information). For the nanoparticles in our system, the relatively high $n$-value ($n = 2.3$) indicates that the resulting nanoparticles have good dispersion stability. This is because the whole reaction is carried out in the solvent which avoids particle aggregation caused by repeated drying.

In order to further confirm the structure of the polymer brush, EDS is employed to identify the element compositions of SiO$_2$ and SiO$_2$-g-P(SPMA-co-MAA), and the results are shown in Figure 3. Compared with bare silica nanoparticles, carbon element content in hybrid nanoparticles increases significantly while silicon element as well as oxygen element content decreases obviously. At the same time, the peaks of bromine and nitrogen element are observed in the curve of hybrid nanoparticles. In addition, the appearance of copper element is caused by copper grids in the EDS experiments. These phenomena prove that the silica surface has been grafted with a layer of polymer, which is consistent with the TEM results.

Successful preparation of SiO$_2$-g-P(SPMA-co-MAA) is also affirmed by FT-IR spectroscopy in Figure 4. It is evident that characteristic absorption peaks of major functional groups appear in the curve of bare silica as demonstrated in Figure 4(a). The strong and wide absorption peak at 1098 cm$^{-1}$ is ascribed to antisymmetric stretching vibration of Si–O–Si bond. The absorption peaks at 796 and 466 cm$^{-1}$ can be assigned to symmetric stretching vibration and bending vibration of Si–O bond. The absorption peak at 1639 cm$^{-1}$ appears from the bending vibration of H–O–H bond in water. At the same time, the absorption peak at 958 cm$^{-1}$ is assigned to antisymmetric stretching vibration of Si–O–Si bond. The absorption peaks at 796 and 466 cm$^{-1}$ can be assigned to symmetric stretching vibration and bending vibration of Si–O bond. The absorption peak at 1639 cm$^{-1}$ appears from the bending vibration of H–O–H bond in water. At the same time, the absorption peak at 958 cm$^{-1}$ is assigned to bending vibration of Si–OH bond. Compared with bare silica in Figure 4(a), there are a few new characteristic peaks for SiO$_2$-g-P(SPMA-co-MAA) in Figure 4(b). The out-of-plane bending vibrations of C–H bond which is connected with carbon–carbon double bond and benzene ring appear at 649 and 712 cm$^{-1}$, respectively. The weak absorption peak at 1384 cm$^{-1}$ is ascribed to deformation vibration of C–H which is derived from the methyl. These results indicate that the polymer molecules have been grafted on the surface of silica nanoparticles.

As we know, XPS is usually used to analyze the status of surface chemical bond, and the result is demonstrated...
Meanwhile, the new peaks at 401.52 and 68.15 eV are clearly observed from the XPS spectrum of SiO₂–Br in Figure 5(b), assigning to the binding energy of N1s and in Figure 5. The spectrum of SiO₂ in Figure 5(a) has the strong peaks at 284.87, 532.92, and 103.49 eV, attributing to the binding energy of C1s, O1s, and Si2p, respectively.

**Scheme 3.** Synthesis route of SiO₂-g-P(SPMA-co-MAA) by Si-ATRP and chemical hydrolysis.

**Figure 2.** TEM images of hybrid nanoparticles SiO₂-g-P(SPMA-co-MAA).
Figure 3. EDS spectrograms of (a) bare silica nanoparticles and (b) hybrid silica nanoparticles coated with P(SMA-co-MAA).

Figure 4. FT-IR spectra of (a) bare silica nanoparticles and (b) hybrid silica nanoparticles coated with P(SMA-co-MAA).
In addition to the weight loss of physically absorbed water, the second weight loss at 210 °C is due to the decomposition of ATRP initiator grafted on the particles, and finally weight retention stabilizes at about 69.73%. TGA curve of the hybrid silica nanoparticles coated with P(SPMA-co-MAA) in Figure 7(d) can be divided into three stages. The initial weight loss stage ranging from room temperature to 110 °C is caused by desorption of physically absorbed water and dehydroxylation. The second weight loss stage ranging from 110 to 210 °C shows a moderate decrease which results from the loss of the initiator decomposition. The last sharp weight loss stage ranging from 210 to 800 °C is mainly attributed to the P(SPMA-co-MAA) which are grafted on the surface of silica nanoparticles, and the final remaining weight percentage is 56.28%.

The weight loss measured by TGA enables us to calculate the initiator grafting density ($G_i$) as described in the literature:[46] where $W\%$ is the weight loss of various nanoparticles from TGA analysis, $N_A$ is the Avogadro’s number, $M_{initiator}$ is the molar mass of the grafted initiator, and $S_{sp}$ is the specific surface area. According the BET result, we can know $S_{sp} = 135 \text{ m}^2/\text{g}$ (Figure S2 in the Supporting Information), so the initiator grafting density is about 4.65 molecules/nm$^2$.

In addition, the polymer grafting density ($G_p$) can be also determined from the TGA results as presented below:
where $M_{n, \text{grafted polymer}}$ is the number average molecular weight of the grafted polymer. We get it from GPC result of the free polymer, since the molar weight of the free chains by the sacrificial initiator usually matches those of the grafted chains as reported elsewhere. In the present work, the number average molecular weight of the free P(SPMA-co-MAA) is about 47,700 (Figure S3 in the Supporting Information), so we can calculate the number average molecular weight of P(SPMA-co-MAA) as 30,300 according to $^{1}H$ NMR spectrum as shown in Figure S4 (see the Supporting Information). Then, polymer grafting density can be approximately determined as 0.053 chains/nm$^2$, which is consistent with Save and Charleux's report.

In addition, we can give a rough estimate on the length of the grafted chains ($L$) from polymer grafting density according to the following relationship$^{[47]}$:

$$L = \frac{G_P M_{n, \text{grafted polymer}}}{\rho N_A}$$

where $\rho$ is the density of grafted polymer chains, and it can be approximately thought as 1. In a typical experiment, the

![Figure 6. High-resolution XPS spectra and curve fitting of O1s of (a) SiO$_2$ and (b) SiO$_2$-P(SPMA-co-MAA).](image)

![Figure 7. The thermogravimetric analysis of (a) SiO$_2$, (b) SiO$_2$-Br, and (d) SiO$_2$-P(SPMA-co-MAA).](image)
length of the grafted chains is about 3 nm, which is in good agreement with the thickness of the grafting polymer layer from TEM analysis.

3.2. Stimuli-responsive behaviors of hybrid nanoparticles SiO$_2$-g-P(SPMA-co-MAA)

To explore the light/pH double responsive behaviors of polymer brushes, UV–vis absorption spectrometer is used to record the changes of absorbance upon different light conditions, and DLS is utilized to get the changes of particle sizes on different pH values.

Under the visible light irradiation for 10 min, it is interesting that there is an appearance of an absorption peak at 556 nm in Figure 8. This is due to the influence of carboxylic groups in MAA unit, and it leads to the ring-opening of spiropyran unit. After the polymer is grafted onto the silica surface, the free movement of the molecules is restricted to some extent. Full ring-closure of the spiropyran unit is difficult to be achieved even if it is under the relatively long irradiation of visible light. When it is irradiated with UV light for 1 min, the absorbance at 556 nm goes up from 0.11349 to 0.13254. Expectedly, with the extension of irradiation time, the absorbance increases gradually, meaning that more spiropyrans transform to MC isomers. These results verify that the spiropyran-based random copolymer brush SiO$_2$-g-P(SPMA-co-MAA) has a good photo-responsive behavior.

With the purpose of investigating the photosensitive behaviors of hybrid nanoparticles, DLS spectra are presented in Figure 9. As can be seen, the average hydrodynamic diameter increases from 185.7 to 212.7 nm under UV irradiation for 5 min. This reason is that SPMA is activated by ultraviolet light, and then the hydrophobic structure has become the hydrophilic structure. The particle sizes increase with the decrease of hydrophobic interaction and the enhancement of hydrophilic interaction.

The DLS characterization is employed to study the effect of pH on particle sizes and distribution of SiO$_2$-g-P(SPMA-co-MAA), and the results are shown in Figure 10. As can be seen, the hydrodynamic diameter of hybrid silica nanoparticles SiO$_2$-g-P(SPMA-co-MAA) rises from 140.0 to 185.7 nm when pH value changes from 1 to 7. The hydrodynamic diameter increases from 185.7 to 326.7 nm when pH value changes from 7 to 13. The schematic illustration of pH-responsive behavior is shown in Scheme 4. It is noted that the wide particles size distribution at pH 13 is caused by the deprotonation of carboxyl (–COOH) in the MAA unit. Under the condition of alkali, the MAA unit in the random copolymer brushes is hydrophilic, and the electrostatic repulsion between the carboxyl anions (–COO$^-$) makes them mobile.
the copolymer brushes more fluffy and swelling which leads to the increase in particle size. Moreover, because the copolymer on the surface is random, the strength of the electrostatic repulsion is unequal in different chain units, and this contributes to the appearance of a broad peak. The other reason is that the hydrophobic isomer of SPMA is transformed into the hydrophilic MCH isomer under acidic condition, and the resulting MCH isomer usually switches into hydrophilic MC isomer under alkaline condition.

4. Conclusion

In this study, we report the successful synthesis of organic/inorganic hybrid nanoparticles SiO$_2$-g-P(S1PMA-co-MAA) by SI-ATRP and chemical hydrolysis, and the double stimuli-sensitive behaviors of the hybrid nanoparticles have been investigated. TEM is used to show core/shell structure of the hybrid nanoparticles, and EDS demonstrates the change of element content before and after SI-ATRP. Both FT-IR and XPS verify the existence of chemical bonding on the interface between inorganic silica and polymeric layer. Also, the three-stage TGA curve of hybrid silica nanoparticles coated with P(S1PMA-co-MAA) three stages is observed. The dual-responsive properties are characterized by means of UV-vis spectrophotometer and DLS. The average hydrodynamic diameter of SiO$_2$-g-P(S1PMA-co-MAA) increases from 185.7 to 212.7 nm under ultraviolet light irradiation for 5 min. Also, the particle size of SiO$_2$-g-P(S1PMA-co-MAA) increases with the rising pH value of surrounding condition.

All the results in the present work indicate that the hybrid particles are dual-sensitive, which may provide a diverse range of potential applications such as drug delivery, diagnostics, tissue engineering, biosensors, coatings, and textiles. As one of ‘grafting from’ methods, SI-ATRP can offer dense and strong ‘living’ centers for the polymeric molecular chains. In addition, the grafting density and molecular weight of the resulting polymers can be better controlled by SI-ATRP than by traditional polymerization process.

Supporting information available

The plotting between ln $\tau$ and ln $\lambda$ in the absorbance experiment to assess dispersion stability, nitrogen adsorption/desorption isothermal curve of the silica nanoparticles, GPC result of the free copolymer P(S1PMA-co-tBMA) obtained from the sacrificial initiator, and $^1$H NMR spectrum of the precursor copolymer P(S1PMA-co-tBMA) in CDCl$_3$.

Disclosure statement

No potential conflict of interest was reported by the authors.

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