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Facile and large scale in-situ synthesis of the thermal responsive fluorescent SiNPs/PNIPAM hydrogels

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Xiao-Yan Zhang, Yan Zheng, Chun-Hua Liu,* Ping-Hua Wang, and Yuan-Yuan Zhu*

We herein report the synthesis of fluorescent silicon nanoparticles (F-SiNPs) with uniformly small sizes and stable fluorescence, and further preparation of the F-SiNPs/Poly(N-isopropylacrylamide) (F-SiNPs/PNIPAM) composite hydrogels by in-situ polymerization. This type of hydrogels displayed visible thermal-sensitive phase transition properties. Upon heating, the fluorescent intensity of the hydrogels decreased sharply beyond the lower critical solution temperature (LCST) of PNIPAM. The process of the fluorescence quench and recover was reversible after repeated heating and cooling cycles. This result suggests that the present organic/inorganic hybrid F-SiNPs/PNIPAM hydrogels will have potential applications in visual detection as fluorescence-based temperature sensors.

1. Introduction

Currently, the studies on silicon nanoparticles (SiNPs) with uniformly small sizes and special fluorescent properties have attracted broad and sustained interest in the field of chemistry, materials science and nanotechnology.¹⁻⁷ The SiNPs can yield strong fluorescence at small sizes (diameter equal to or smaller than 5 nm) because of indirect-to-direct band gap transitions arising from a quantum-size confinement effect. Wide researches have demonstrated that the SiNPs exhibit great promise for wide-ranging optoelectronic and biotechnological applications because of their advantageous merits including excellent optoelectronic properties, facile surface modification, and biocompatibility, etc.⁸⁻¹⁵ In order to achieve the widespread applications of SiNPs, synthetic chemists have developed several synthetic methods to prepare fluorescent SiNPs such as solution-phase reduction, laser ablation, mechanochemical method, microemulsion, and microwave irradiation, etc.^{4,16-25} Very recently, He and Lee et al reported a elegant photochemical strategy which can facilely prepare F-SiNPs in large quantity at low cost and mild condition.^{13,26}

Embedding colloidal nanoparticles into polymer matrices has proved to be an effective approach to construct functional composite materials. The nano-scale composites based on polymers and functional nanoparticles possess lots of merits in multifunction integration, chemical sensor, optical materials as well as reinforcing materials.^{4,27-31} On the basis of the luminescent properties of nanoparticles and phase transition behaviors of polymers, several composites from responsive

polymers and fluorescent nanoparticles have been synthesized and employed as luminescent sensor successfully.³²

Thermo-sensitive hydrogels are sensitive to external temperature stimuli. By this token, they have aroused wide attention over the recent years for potential applications in many fields, involving sensors, shape memories, switches and so on.³³⁻³⁹ Poly(N-isopropylacrylamide) (PNIPAM) is one of the most representative stimulus-responsive polymers. Owing to the existence of the hydrophilic amide groups (-CONH-) and hydrophobic isopropyl (-CH(CH₃)₂) on the side chains of the PNIPAM, both the linear PNIPAM aqueous solution and cross-linked PNIPAM hydrogels all display rapid temperature response. Specifically, when the temperature is higher than its lower critical solution temperature (LCST), which is about 32 °C in water, the PNIPAM hydrogels will undergo a phase transition from a hydrophilic, water-swollen state to a hydrophobic, globular state and this kind of phase transition process is reversible.^{36,40,41} Among the various reversible and stimuli-responsive gels, fluorescent gels are most promising because of their excellent and adjustable optical properties.^{34,42} We proposed that the combination of stimuli-responsive polymers and fluorescent nanoparticles will endow PNIPAM hydrogels with luminescent emission. This new type of hybrid materials will simultaneously possess strong photoluminescence and temperature sensitivity properties, which will display potential applications in visual detection especially in biological systems.

In this contribution, we facilely integrated F-SiNPs into PNIPAM polymer matrix to prepare F-SiNPs/PNIPAM composite hydrogels by in situ polymerization in a large-scale quantity. The functionalization of PNIPAM hydrogels by immobilizing F-SiNPs endowed the hydrogel matrix with luminescent properties. The fluorescent properties of the F-SiNPs in thermal-sensitive PNIPAM hydrogels could be affected by the environmental temperature. This type of thermal

School of Chemistry and Chemical Engineering, Hefei University of Technology and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei 230009, China. E-mail: lchh88@hfut.edu.cn; yyzhu@hfut.edu.cn

† Electronic Supplementary Information (ESI) available: XPS spectra of F-SiNPs, SEM images and UV-vis spectrum of F-SiNPs/PNIPAM hydrogels. See DOI: 10.1039/x0xx00000x

sensor also exhibited excellent reversibility under the repeated change of temperature. Our study suggests that the present thermal responsive composite hydrogels will exhibit potential application in the fluorescence-based temperature sensor.

2. Experimental

2.1 Materials and instrumentation

All solvents and reagents for synthesis were of analytical grade and used without further purification. (3-Aminopropyl)trimethoxysilane (KH540, 97%) was purchased from Aladdin and 1,8-naphthalimide was purchased from Xiya Reagent. N,N-methylenebisacrylamide (MBA, 97%), N,N,N,N-tetramethylethylenediamine (TEMED) (Biochemicals), ammonium persulfate (APS) (analytical grade) and N-isopropylacrylamide (NIPAM) were purchased from Sinopharm Chemical Reagent Co., Ltd.

UV-vis spectra were recorded on a UV-4820 spectrophotometer (Hitachi, Japan) equipped with exclusive quartz cuvettes at room temperature (20 °C). Photoluminescence spectra was performed on a Fluorescence spectrophotometer (F-4600FL, Hitachi, Japan) equipped with exclusive quartz cuvettes at room temperature (20 °C). (Excited wavelength: 340.0 nm; Emission wavelength range: 360 to 900 nm; Excited slit: 10.0 nm; Emission slit: 10.0 nm; PMT Voltage: 400 V). Field emission Scanning electron microscopy (SEM) was performed on a SU8020 electron microscope (Hitachi, Japan) at 20 kV. Field emission transmission electronic microscopy (TEM) was performed on a JEM-2100F electron microscope (Hitachi, Japan) at 200 kV. Infrared adsorption spectrum IR were recorded on Nicolet 6700 (KBr disk) Fourier-transform infrared (FTIR) spectroscopy (Thermo Nicolet company, USA). The UV lamp (450 W, 365 nm) was supplied by Qing Da UV Technology Co., Ltd. Dong Guan, Guangdong. Freeze Dryer (FD-1B-50) was supplied by bo yi kang experimental instrument co., Ltd. Beijing.

2.2 Preparation of F-SiNPs

The blue-emitting SiNPs were synthesized according to the previously reported procedure in literatures.^{13,26} Firstly, 1,8-naphthalimide (2 g) was dispersed in Milli-Q water (90 mL). Then KH540 (10 mL) was added slowly. The mixture was thoroughly stirred for about 15 min and the colour of nanoparticles was monitored by a UV lamp. After UV irradiation, the as-prepared F-SiNPs sample was collected after cooling to 25 °C naturally. 1,8-naphthalimide was precipitated through centrifugation at 6000 rpm for 15 min. At this low centrifugation rate, the resultant remained in clear supernatant would not precipitate. The residual KH540 (MW < 1 kDa) was further removed by dialysis (MWCO, 1000, Bomei/HC148) against Milli-Q water. The F-SiNPs with molecular weights larger than 1 kDa were collected and further diluted by Milli-Q water. The purified F-SiNPs aqueous solution was freeze-dried and weighed.

2.3 Preparation of F-SiNPs/PNIPAM hydrogels

The F-SiNPs/PNIPAM composite hydrogels were synthesized facily by in-situ polymerization of NIPAM in the presence of F-SiNPs at room temperature. Specifically, the F-SiNPs powdered sample (0.1g) was added into Milli-Q water (10 mL).

After its complete dissolution, the monomer N-isopropylacrylamide (NIPAM) (1.0 g, 0.009 mol) and crosslink reagent N,N-methylenebisacrylamide (MBA) (0.03 g, 0.0002 mol) were added to the as prepared F-SiNPs aqueous solution. After the reaction system had been completely mixed and deaerated by circulating water vacuum pump, certain amount of ammonium persulfate (APS, 0.03g, 0.0001 mol) aqueous solution were quickly added to the above mixture to initiate the polymerization. Finally, the reaction bulb was incubated for 24 h at room temperature. In our experiment, the polymerization reactions were facily scaled up 10, 50 and 100 multiples as well, so we could prepare this composite hydrogels in large scale (see Figure S1). For comparison, the pure PNIPAM hydrogel without F-SiNPs was prepared and accelerated by N,N,N,N-tetramethylethylenediamine (TEMED) as well.

3. Results and Discussion

3.1 The structure characterization and spectra properties of F-SiNPs.

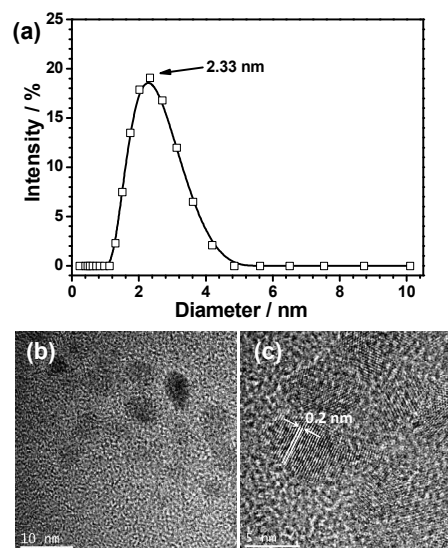


Fig. 1 (a) The results of size distribution of F-SiNPs through dynamic light scatter (DLS) and (b,c) the HRTEM of F-SiNPs.

According to the literature method, the F-SiNPs were prepared by a simple and cost-efficient method developed by He and Lee et al.^{13,26} The size and the dispersibility of the prepared F-SiNPs were characterized by dynamic light scatter (DLS) and field emission transmission electronic microscopy (FE-TEM). According to DLS measurement shown in Figure 1(a), the concentration of F-SiNPs aqueous solution is 0.05 mg/mL. The average diameter of F-SiNPs is smaller than 3 nm, indicating that the F-SiNPs possess good monodispersity in water. Further high-resolution TEM (HRTEM) images show that the prepared F-SiNPs possess favorable monodispersity with size distribution ranging from 2 to 4 nm and all the F-SiNPs display

spherical shape. The HRTEM image clearly displays the distinct lattice planes (220) of ~ 0.2 nm spacing, revealing that the fine crystallinity of the resultant F-SiNPs (see Figure 1 (c)).¹³

Optical characterization of F-SiNPs was then carried out to investigate the luminescent property. Figure 2 shows the UV-vis spectrum of the F-SiNPs aqueous solution (10 mg/mL) at 25 °C, exhibiting a resolved absorption peak at 340 nm. The photoluminescence emission of F-SiNPs were investigated by exciting the lowest-energy absorption maxima band, which displays a emission peak at 396 nm and exhibits a strong blue fluorescence emission. In addition, the elemental composites of the F-SiNPs were confirmed by the X-ray photoelectron spectroscopy (XPS) spectrum (see Figure S2).

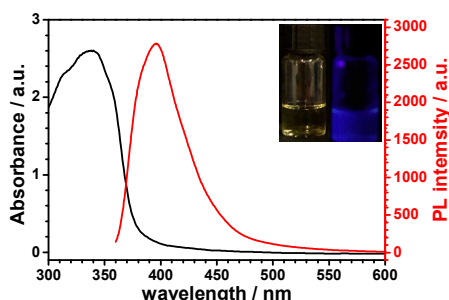


Fig 2. The UV-vis (black) and photoluminescence (red) spectra of F-SiNPs. Inset pictures: the colour of F-SiNPs under ambient light (left) and 365 nm UV light (right).

3.2 The characterization and spectra properties of F-SiNPs/PNIPAM hydrogels.

The Scheme in Fig. 3 shows the flow-chart to construct the F-SiNPs/PNIPAM composite hydrogels, according to which, the hydrogels were fabricated by in-situ polymerization of monomer NIPAM and a little amount of cross-linking agent MBA in the presence of radical initiator APS. During the polymerization process, the numerous amino groups on the surface of F-SiNPs could interact with the amide groups in the PNIPAM polymer networks through hydrogen bonding, which would result in the F-SiNPs being success-fully entrapped inside the in-situ formed PNIPAM networks⁴³⁻⁴⁵.

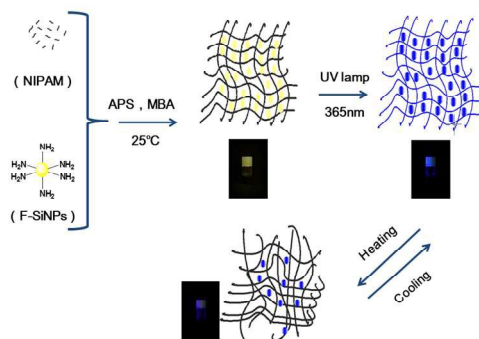


Fig 3. Schematic illustration of the preparative strategy for the thermal responsive fluorescent SiNPs/PNIPAM hydrogels and their photographs under different temperatures.

In order to gain more understanding about the structure of the hydrogels, The F-SiNPs/PNIPAM composite were then characterized by FT-IR spectra and Scanning electron microscopy (TEM) spectra. Figure S3 displays the comparison of FT-IR spectra of pure PNIPAM, F-SiNPs, and F-SiNPs/PNIPAM hydrogels. Apparently, these two hydrogels possess similar infrared absorption patterns, indicating that the addition of F-SiNPs do not affect the structure of pure PNIPAM gel. For F-SiNPs/PNIPAM hydrogels, the weak absorption peak near 1030 cm^{-1} is assigned to the vibrational stretch of Si-O bonding, showing the existence of F-SiNPs in the hydrogel matrix. The Field emission Scanning electron microscopy (FE-SEM) images show that the freeze-dried F-SiNPs/PNIPAM hydrogels possess well-defined porous network, and the presence of these interconnected holes display the typical characteristics of hydrogels (see Figure S4). In order to determine the elemental composites of the F-SiNPs/PNIPAM hydrogels, XPS measurement was carried out as well (see Figure S5).

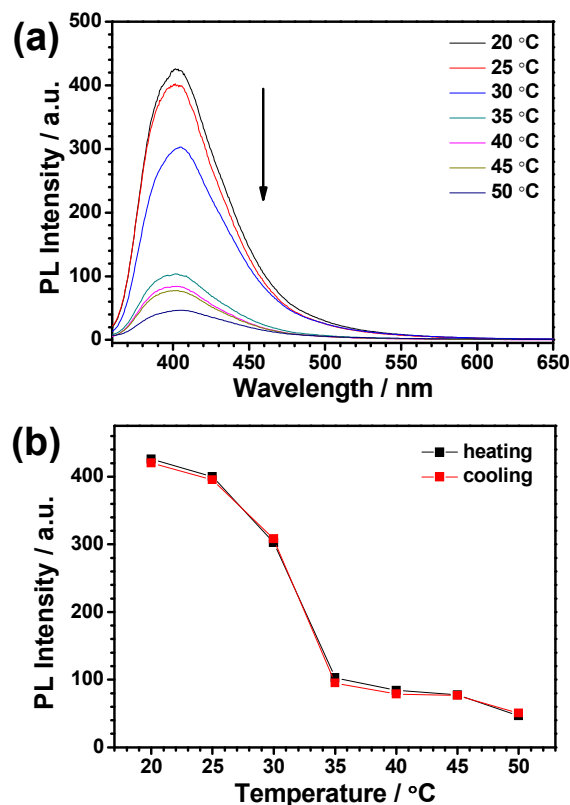


Fig 4. Effects of temperature on the PL spectra of the F-SiNPs/PNIPAM composite hydrogels.

3.3 Thermal responsive ability of the F-SiNPs/PNIPAM hydrogels.

In addition, the spectral measurements were carried out so as to investigate the relationship of fluorescence and thermal responsive behavior of this F-SiNPs/PNIPAM composite hydrogels. Figure S6 shows the UV-vis measurement of F-SiNPs/PNIPAM hydrogels, in which a resolved absorption peak near 300 nm can easily be observed. So that the photoluminescent properties were examined by exciting the lowest-energy absorption maxima band at 300 nm according

to the UV-vis absorption. As expected, the fluorescent spectra of F-SiNPs/PNIPAM composite hydrogels were measured from 20 °C to 50 °C under the gradual temperature change. It could be seen that the fluorescence intensity of hydrogels decreased abruptly with the raise of the temperature in the narrow range of 20–35 °C and vice versa (see Fig. 4). At low temperature range, the hydrogel network is homogeneous. The F-SiNPs are uniformly dispersed in the transparent gel matrix and can display strong fluorescent emission. However, when the temperature is higher than the LCST, the PNIPAM undergoes a phase separation and the hydrogel networks become heterogeneous. The intrachain of the PNIPAM networks collapsed and become turbid.⁴⁴⁻⁴⁵ The collapsed PNIPAM particles work as the strong scattering center, which result in the dramatic decrease of fluorescence intensity of the F-SiNPs. So the fluorescence of F-SiNPs is suppressed considerably at high temperature range.

It should be noted that our F-SiNPs/PNIPAM hydrogels also exhibits excellent reversibility. Fig. 5 shows the reversible switching of the F-SiNPs/PNIPAM hydrogels between 20 and 50 °C, from which one can learn that fluorescent intensity the hydrogels can be readily switched between the two states with excellent reversibility. This result suggests that the present F-SiNPs-based is an effective thermosensitive sensor. The stability of this F-SiNPs/PNIPAM hydrogels were test as well. After the composite hydrogels were immersed in deionized water at room temperature for 3 days. Then, the PL spectra of the hydrogels and the aqueous phase were detected respectively. The hydrogels still displayed strong blue fluorescence while no emission could be detected from the aqueous phase (see Figure S7). This result demonstrates that the interaction of F-SiNP and PNIPAM is strong enough after in-situ polymerization, so that the leaching of F-SiNPs nanoparticles from the polymer matrix is difficult.

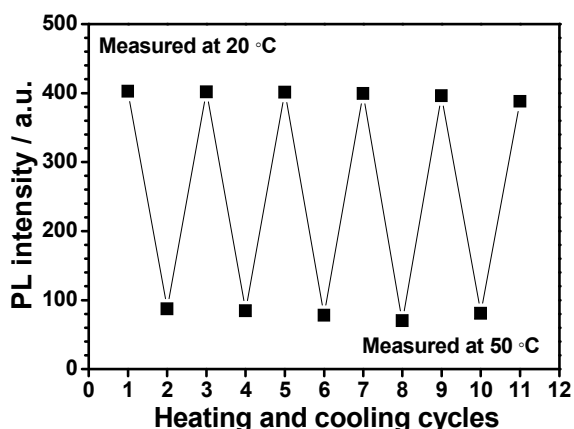


Fig. 5 The fluorescent intensity of F-SiNPs/PNIPAM between low temperature (20 °C) and high temperature (50 °C) for 6 cycles.

Conclusions

In summary, a novel type of inorganic/organic hybrid network, the F-SiNPs/PNIPAM composite hydrogels, was successfully prepared by using in-situ polymerization. The combination of PNIPAM and F-SiNPs successfully endowed the thermal

responsive polymer with fluorescent behavior. The composites hydrogels were highly photoluminescent and the fluorescent intensity was reversibly sensitive to external temperature stimuli. The reversible temperature-sensitive fluorescence properties make it promising candidate for thermo-sensitive sensors. We believe that this work has provided a new composites material in developing F-SiNPs-based thermo-sensitive devices or sensors. Further applications of this composite hydrogels in biological system are underway.

Acknowledgements

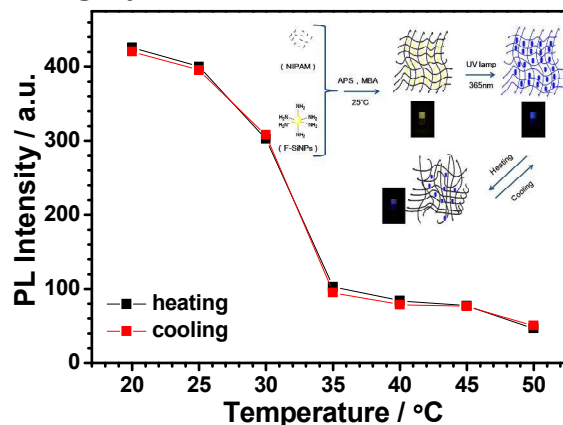
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TOC graphic



A new type of F-SiNPs/Poly(N-isopropylacrylamide) (F-SiNPs/PNIPAM) hydrogels was prepared by in-situ polymerization. The composite hydrogels display visible thermal-sensitive phase transition properties.