Amino-Modified Hollow Mesoporous Silica Microspheres Loaded with Cresol Red-Boric Acid for Potent Reversible Thermochromic Performance

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Abstract— In this study, two reversible thermochromic composites were obtained, hollow mesoporous silica (HMS) and amino group-modified hollow mesoporous silica (HMS-NH\textsubscript{2}) microspheres loaded with cresol red-boric acid (CR-BA), respectively. Owing to the rigid structure of hollow interior and mesoporous shell layers, CR-BA was easily encapsulated into a relatively high loading capacity micro-carrier. The composites analysed were characterized by Fourier transform infrared spectroscopy transmission electron microscopy, scanning and transmission electron microscopy and dynamic light scattering. By amino functionalization, a more obvious thermal colour-change was observed in HMS-NH\textsubscript{2} loaded with CR-BA. In addition, both HMS and HMS-NH\textsubscript{2} loaded with CR-BA illustrated a sever colour reversibility, which were 5min and 3min respectively.

1. Introduction
Thermochromic materials has been received significant attention in recent years due to their potential applications, the related research is ranging from the original simple metal oxides, double salt, complex development to the present all kinds of organic matters, such as liquid crystal, polymer and biological macromolecules\textsuperscript{1-3}. The different colour-changing mechanisms can be attributed to their different properties and thermodynamic characteristics. Otherwise mainly low temperature inorganic thermochromic materials are always reversible, such as metal, metal halide\textsuperscript{4}, transition metal complexes\textsuperscript{5}, metallic oxide\textsuperscript{6} and double salts\textsuperscript{7}. However, as most of them or their composites are heavy metals, the high biosafety risks lead restrictions in practical applications. Compared with inorganic substances, the simple mechanism and easy preparation lead to the organic thermochromic dyes well developed. They included polymer\textsuperscript{8}, Schiff bases\textsuperscript{9}, spiropyran and spirooxazine\textsuperscript{10}, lactone derivatives\textsuperscript{11} and liquid crystals\textsuperscript{12}. Mainly organic substance’s thermochromic mechanisms were achieved by chemical structural change, included the opening and closing of ring structures or conformation transition of chemical bonds during heating, and after cooling and the original structure is restored. In addition, the colour-changing process involves the gain and loss of electrons or a change in pH value. However, as organic thermochromic materials in general with benzene ring are easy to produce new harmful gases and substances when heating by high temperature heating and burning, alternative environmentally friendly thermochromic systems are still the target of further research.
By using an acid-base indicator cresol red as colour former and boric acid as chromogenic agent, a reversible thermochromic dye system with low-toxicity, good reversibility, low colour change temperature has been developed. To enhance the stability and biosafety, such thermochromic dye system can combine with base materials, solvents and additives with less polarity.

Hollow-structured mesoporous silica (HMS), by integrated mesoporous shell layer structure with hollow interiors structure, was observed the high loading capacity amount. To enhance the adsorption performance of mesoporous silica, certain organic group can functionalize the surface of hollow-structured mesoporous silica. Hence, the amino-group modification on mesoporous silica can provide access to enhance the thermochromic performances of hollow-structured mesoporous silica (HMS) that combined with dye system.

In this study, we selected cresol red-boric acid (CR-BA) to load with the base material hollow-structured mesoporous silica (HMS) and 3-aminopropyltriethoxysilane (APTES) modified hollow-structured mesoporous silica (HMS-NH$_2$). The two groups of the reversible thermochromic composites were termed as HMS/CR-BA and HMS-NH$_2$/CR-BA, respectively. Transmission electron microscopy (TEM) was used to observe the composite microspheres and thermogravimetric analysis (TGA) was used to measure the loading amount of CR-BA composites, dynamic light scattering (DLS) was used to investigated the increase loading capacity. After the APTES on the surface of the HMS microspheres to introduce amino groups, the load capacity of CR-BA can be enhanced. Furthermore, CR-BA endowed the composites with excellent high rapid thermochromic reversibility. Because of the low-temperature thermochromic reversibility and low toxicity, the composites obtained in this work have certain application possibility in indicator, sensor, package coating, decoration and anti-counterfeiting packaging industry.

2. Materials and Method

2.1. Materials
Analytical reagent styrene (St) and azobisisobutyronitrile (AIBN) provided by Shanghai Chemical Reagents Co., Ltd., Shanghai, China, were purified by vacuum distillation and by recrystallization from ethanol, respectively. Analytical reagent polyvinylpyrrolidone (PVP), ammonium hydroxide (NH$_3$•H$_2$O), hexadecy trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), ethanol, cresol red (CR) and boric acid (BA) were directly purchased from Shanghai Chemical Reagents Co., Ltd., Shanghai, China. 3-aminopropyltriethoxysilane (APTES) was purchased from Aladdin Reagents (Shanghai) Co., Ltd., Shanghai, China. Deionized water was used in all experiments.

2.2. Preparation of polystyrene (PS) microspheres
PVP (1.0 g) was dissolved in a solution of ethanol (100 mL) and water (10 mL) under mechanical stirring. Then St (10 g) and azobisisobutyronitrile (AIBN) (0.158 g) were added into the solution under N$_2$ protection. The mixture were heated at 70℃ for 24 hand cooled down to the room temperature, then the PS microspheres were synthesized. The PS microspheres were collected by centrifugation and washed with ethanol twice and dried in a vacuum oven at 50℃ for 24 h.

2.3. Preparation of PS@SiO$_2$ microspheres
CTAB (2.7 g) was dissolved in a solution of water (45 mL) and ethanol (60 mL). Ethanol (30 mL) was added into an aqueous dispersed solution of PS microspheres (10 wt%) (50 mL) and slowly dropped into the above mixture under mechanical stirring. Then NH$_3$•H$_2$O (3 mL) and TEOS (60 mL) were added into the reaction system. After reaction at room temperature for 48 h, the PS@SiO$_2$ microspheres were collected by centrifugation and washed with ethanol twice, and the microspheres dried in a vacuum oven at 50℃ for 24 h.
2.4. Preparation of HMS
The PS@SiO$_2$ microspheres were heated inside a muffle furnace from the room temperature to 550°C (heating rate of 5°C/min) and keep for 5 h then cooled naturally. All the processes were performed in air. The final product was noted as HMS.

2.5. Amino group modification on HMS
Anhydrous toluene (50 mL) and HMS (1.0 g) were placed in a flask and the mixture was sonicated for 30 min, followed by the addition of APTES (2 mL). The mixture was stirred at 120°C for 24 h with nitrogen gas protection. The resultant microspheres were collected by centrifugation 600rpm and washed with toluene and ethanol three times each, and dried under vacuum. The final product was HMS-NH$_2$.

2.6. Preparation of HMS-NH$_2$/CR-BA and HMS/CR-BA composites
CR and BA were added into a solution of ethanol (1.0 mL) and water (5.0 mL), followed by heating to 80°C. Then microspheres (HMS and HMS-NH$_2$ microspheres) were added rapidly into the above dye system. The mixture was sonicated for 5 min and kept at 80°C for 5 min, followed by centrifugation while the system was still hot. Finally, the collected products were dried in the air naturally. The detailed composition of the HMS-NH$_2$/CR-BA and HMS/CR-BA composites prepared is listed in Table 1. All the composites were heated to 70°C and cooled naturally. Colour changes were recorded by using a digital camera.

| Label | HMS-NH$_2$(mg) | CR(mg) | BA(mg) | Label | HMS(mg) | CR(mg) | BA(mg) |
|-------|----------------|--------|--------|-------|----------|--------|--------|
| A     | 30             | 1      | 100    | E     | 30       | 1      | 100    |
| B     | 50             | 1      | 100    | F     | 50       | 1      | 100    |
| C     | 70             | 1      | 100    | G     | 70       | 1      | 100    |
| D     | 90             | 1      | 100    | H     | 90       | 1      | 100    |

Scheme 1. Illustration of the preparation processes of HMS-NH$_2$/CR-BA

The preparation process of HMS-NH$_2$/CR-BA was illustrated in Scheme 1. In the first step, PS microspheres were synthesized by PVP under the solution of ethanol/water and St/AIBN. In the second step, the mesoporous structure PS@m-SiO$_2$ microspheres was prepared by hydrolysis and TEOS with CTAB loaded on the surface. In the third step, APTES modified PS@m-SiO$_2$ and CR-BA loaded into the microspheres (HMS-NH$_2$/CR-BA).
2.7. Characterization
Transmission electron microscopy Morphological (TEM) was used for observation of the mesoporous silica microspheres (Hirachi H-7650, Tokyo, Japan, 100 KV). Thermogravimetric analyzer (TGA) was used for Q5000IR Thermogravimetric analysis (Washington, US). Zeta-potential values were determined by a Malvern Zetasizer Nano ZS-2S90 dynamic light scattering (DLS, CORDOUAN, Paris, France) system at 25°C. Fourier transform infrared spectra (FTIR) were conducted by using a Bruker Tensor 27 FTIR spectrometer (Scotia, NY, US). Digital camera (Nikon, NY, US) was used for record colour changes.

3. Test Results and Discussions
3.1. Characterization of HMS-NH₃/CR-BR and HMS/CR-BR composites
According to the Transmission electron microscopy Morphological (TEM) observation, the PS microspheres were synthesized with an average diameter of 1.07 μm (Fig. 1(a)). After the hydrolysis of TEOS, uniform microspheres with a porous shell and a mean diameter of 1.31 μm are obtained, as observed by TEM (Fig. 1(b)). Subsequently, the HMS were produced by calcining at 550°C for 5 h the corresponding TEM image is shown in Fig. 1(c), which clearly shows that a hollow structure with a well-defined mesoporous shell was obtained. The average diameter of the microspheres was about 1.26 μm and the average thickness of the mesoporous shell was estimated to be 190 nm. The mesoporous were homogeneously arranged, generating efficient channels for CR-BR diffusion and loading.

![TEM images of mesoporous silica microspheres](image)

Figure 2(a) presents the FT-IR spectra of Cresol red, boric acid, HMS, HMS-NH₃, HMS/CR-BR and HMS-NH₃/CR-BR. All of the samples were recorded at room temperature from 400 to 4000 cm⁻¹ in transmittance mode. After modification by APTES, the HMS microspheres were functionalized to gain amino group (-NH₂), the curve of HMS-NH₂ microspheres appeared a new peak at ~950 cm⁻¹ from the HMS group. It should be attributed to the N-H deformation vibration of the primary amine. After the HMS-NH₂ microspheres were loaded with CR-BR, it was observed that the extending vibration peak of O-H at 3226 cm⁻¹ from the HMS/CR-BR and HMS-NH₂/CR-BR composites, attributed to hydroxyl group of boric acid. It can be indicated the CR-BR was loaded with the HMS-NH₂ microspheres.

TGA analysis was conducted to determine the relative ratio of the different components in the composites, as shown in figure 2(b). The results reveal that the weight losses of HMS, HMS-NH₂, HMS/CR-BR and HMS-NH₂/CR-BR were 2%, 15%, 29% and 39%, respectively. The TGA curves of HMS and HMS-NH₂ showed that when the temperature is above 325°C, an obvious weight loss occurred, due to the decomposition of APTES modified on the surface of HMS microspheres. As for HMS/CR-BR, the mass loss above 100°C represents the decomposition of CR-BR. Thus, the weight loss between 100 and 325°C on the TGA curves of HMS-NH₂/CR-BR belonged to the decomposition of CR-BR, while the weight loss above 325°C should be attributed to the decomposition of APTES.
As a result, the APTES modified HMS microspheres increased the load capacity of CR-BA. The loading capacity of the HMS-NH₂ and HMS microspheres were 0.51 and 0.38 g/g, respectively. It was observed that the zeta potential became positive after the modification of amino groups (Fig. 2(c)), suggesting that the APTES was successfully loaded into the HMS microspheres. Otherwise the HMS microspheres and CR-BA are negatively charged in deionized water. It was contributed by the electrostatic repulsion hinders the adsorption of the HMS microspheres to CR-BA. After the introduction of amino groups, the zeta potential of the HMS-NH₂ microspheres became positive, and the loading capacity to CR-BA increased.

3.2. Thermochromic performances of HMS/CR-BA and HMS-NH₂/CR-BA composites

Owing to the APTES modification, the original colour of HMS-NH₂/CR-BA composites presented as green-yellow, whereas HMS/CR-BA composites was light pink and at the room temperature 20°C in this study, shown in Fig 3. 1-3 g composites were taken from the eight prepared groups of HMS-NH₂/CR-BA and HMS/CR-BA composites (Table 1), and placed on plates, then heated the plates at the rate of 5°C/min. The colour changes were recorded by digital camera at different temperatures. It can be seen from figure 4(a), when heated to 50°C, the HMS-NH₂/CR-BA appeared an obvious colour change, and when the temperature increased to 70°C, the green-yellow powder turned to rose-purple. Furthermore, by increasing the mass ratio of HMS-NH₂, significant colour change occurred at lower temperatures. For the composites of HMS /CR-BA (Fig.4 (c)), the light pink showed an obvious colour darken at the temperature of 40°C, and when heated to 70°C, the composited changed into rose-purple. The mass ratio of HMS also affected the colour change temperature and time as shown in Fig. 4(c) and (d). When cooling the composites, the HMS-NH₂/CR-BA composites required only 3 min to recover their initial colour. As a contrast, the HMS/CR-BA required approximate 5 min to recover their initial colour as shown in Fig. 4(d), and the colour stayed light pink after the temperature maintained at room temperature. The prominent change in colour and rapid recovery colour features for the HMS-NH₂/CR-BA composites endows an excellent loading capacity for dye pigment and rapid colour change ability.
4. Conclusion

In this work, the low toxic reversible thermochromic composites that showed high temperature sensitivity and rapid reversible performance were built in simple process. FT-IR spectra indicated the amino group and hydroxyl group of boric acid were loaded into hollow-structured mesoporous silica. According to TGA analysis, with the APTES modification, the obtained HMS-NH$_2$ microspheres possessed an excellent CR-BA loading capacity of 0.51g/g which was higher than HMS. The DLS determined the zeta-potential values and showed that APTES was successfully modified the HMS microspheres. From the thermochromic performances observation, both HMS-NH$_2$/CR-BA and HMS/CR-BA had pleased colour change and good sensibility to the temperature change. Furthermore, the amino-group modification endowed the HMS-NH$_2$/CR-BA composites with a more prominent colour change of colour in response to elevated temperatures (from green-yellow to rose-purple to green-yellow) and a rapid reversibility of colour once it cools down (only 3 minutes).

Compared with other thermochromic materials\textsuperscript{3,8,11}, the colour change of HMS-NH$_2$/CR-BA and HMS/CR-BA composites can appear at relative low temperature (50 to 70 °C), which provides a thermal-safety way in indicator and sensor applications. In this study, the thermochromic performances study offset the thermochromic reverse time research limitation in former research\textsuperscript{9,12}. The thermochromic materials synthesized in this work can be applied in expected applications owing to the characteristics of high sensitive, low toxicity and rapid reversibility.

Acknowledgments

This work was financially supported by the Science and technology Project of China Tobacco Yunnan Industry Cooperation (2018 No.2018CL01).

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