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Reactive nano-essential oils for sustained release of essential oils and application to wallpaper

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ABSTRACT

Essential oils are a volatile and aromatic substance with a variety of active biological activities. However, the excessive volatility and inconvenience of the use of essential oils limit their applications. In this study, we developed a reactive mesoporous silica nanoparticle (rMSNs) based on cyanuric chloride modification for essential oil encapsulation and commodity adhesion. The large pore volume and specific surface area of rMSNs facilitate the nanoparticles adhering to a large amount of essential oil and achieve the sustained release of essential oil, thus prolonging the fragrance retention time of essential oils. The reactive nano-essential oils can form covalent bonds with the wallpaper, thereby remarkably improving the adhesion of the reactive nano-essential oils on the wallpaper and preventing the reactive nano-essential oil from de-adhering from the wallpaper. The active nano essential oil simultaneously overcomes the intense volatility of the essential oil and inconvenience in use, has a simple preparation process and low cost, and has great application potential.

Essential oils are volatile aromatic substances extracted from animals or plants. Essential oils have multiple functions, such as regulating central nervous system function [1-3], bactericidal action [4-6], and anti-inflammatory action [7-9]. However, essential oils are highly volatile, making them difficult to store, have a short useful life, and have an uncontrolled release of aroma [10-12]. Besides, the use of essential oils is not convenient enough. These defects severely limit the use of essential oils. Therefore, the key to improving the application potential of essential oils is to reduce the volatility of essential oils and improve their use convenience.

A variety of nanomaterials are capable of slowly releasing molecules [13-21]. For example, amphiphilic molecule-based self-assembly nanoparticles such as micelles and liposomes can encapsulate molecules and achieve the molecules' slow release [22-29]. Many biological macromolecules such as cyclodextrin can also reduce the release rate of the molecules [30-33]. However, most nanomaterials can only reduce the release rate of molecules in aqueous solutions. In contrast, mesoporous materials have large specific surface areas and pore volumes, thus possessing a strong adsorption capacity to encapsulate and slowly release essential oils [34-36]. In particular, the mesoporous silica nanoparticles (MSNs) are simple in structure, controllable in the preparation process, and low in cost. The MSNs are thus suitable for encapsulating essential oils. The adhesion of essential oils-encapsulated MSNs to daily necessities such as wallpaper can significantly improve the convenience of using the essential oils. Therefore, improving the interaction between nanoparticles and wallpaper is particularly important.

In this study, we prepared reactive MSNs (rMSNs) for essential oils encapsulation and wallpaper adhesion. As shown in Fig. 1A, amino-modified MSNs were synthesized by the sol-gel method. Subsequently, cyanuric chloride (CYC) was modified by condensation reaction on amino-modified MSNs. Further adsorption of

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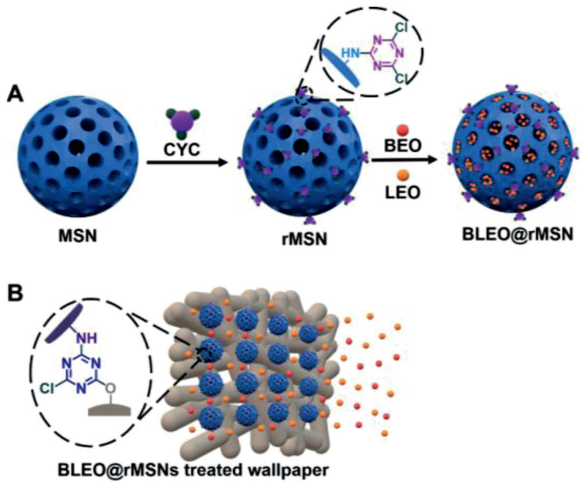

Fig. 1. (A) The schematic diagram of the reactive nano-essential oils' preparation process. (B) The schematic diagram of reactive nano-essential oils adhering to wallpaper.

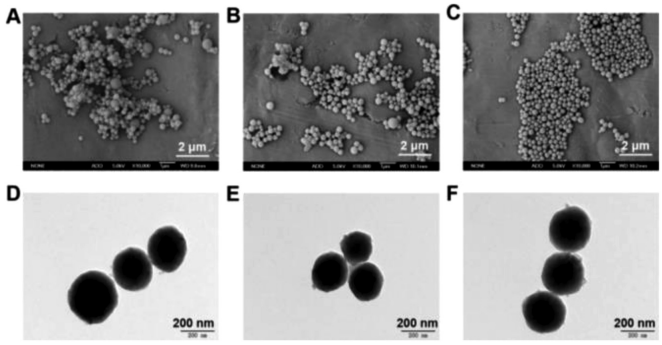

Fig. 2. The SEM images of (A) MSNs, (B) rMSNs and (C) BLEO@rMSNs. Scale bars: 2 μm. The TEM images of (D) MSNs, (E) rMSNs and (F) BLEO@rMSNs. Scale bars: 200 nm.

bergamot essential oil (BEO) and lemon essential oil (LEO) by rMSNs resulted in the preparation of nano essential oils (BL@rMSNs). BLEO@rMSN could chemically react with hydroxyl groups on the wallpaper to form covalent bonds, thus firmly adhering to the wallpaper (Fig. 1B). Therefore, BL@MSNs-CYC is reactive nano-essential oils. The BLEO@rMSNs treated wallpaper could slowly release the essential oils, reducing the essential oils' volatility and improving the essential oils' convenience.

Hexadecyltrimethylammonium bromide (CTAB, 99%), (3-aminopropyl)triethoxysilane (APTES, 98%), superdry tetrahydrofuran (THF, 99.5%) and *N*,*N*-diisopropylethylamine (DIPEA, 99%) were purchased from J&K Chemical. Cyanuric chloride (CYC, 99%) was purchased from Energy Chemical. Bergamot oil and lemon oil were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. Ammonium hydroxide (AR, 25%–28%), hydrogen chloride (HCl, AR, 36%–38%), ethanol (AR), acetone (AR), dimethylsulfoxide (AR, DMSO) cyclohexane (AR), methanol (AR) and dichloromethane (DCM) were obtained from Sinopharm Chemical Reagent Co., Ltd. CORT (97%) was purchased from TCI.

CTAB (1000 mg) was added to deionized water (160 mL) under the ultrasound condition for 10 min. Ammonium hydroxide (5 mL) was added to the solution under stirring for 1 h. Cyclohexane (20 mL), TEOS (4.5 mL) and APTES (0.5 mL) were added into the solution under stirring for 12 h. The white precipitates (MSNs) were obtained by centrifugation at 5000 rpm and washed with ethanol. The residual organic solvent was removed in a vacuum drying oven. MSNs (2000 mg) were dispersed into the mixture of

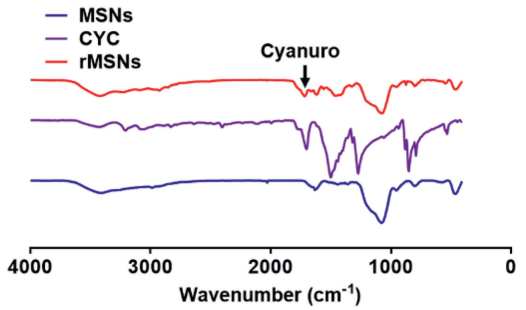

Fig. 3. The FT-IR spectra of MSNs, CYC and rMSNs.

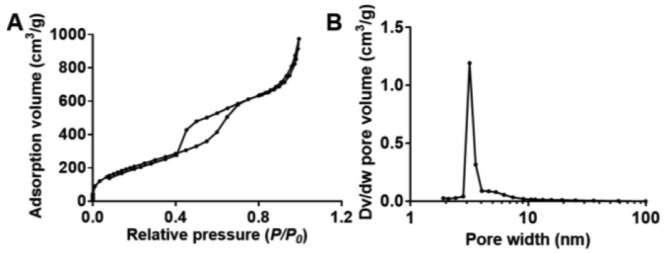

Fig. 4. (A) The nitrogen adsorption-desorption isotherm of rMSNs. (B) The pore diameter distribution of rMSNs.

ethanol (100 mL) and HCl (1 mL) to remove CTAB. After refluxing at 80 °C for 24 h three times, white precipitation was centrifuged at 5000 rpm and washed with ethanol and deionized water. The residual organic solvent was removed in a vacuum drying oven. MSNs (500 mg) and CYC (500 mg) were dissolved in THF (10 mL) under stirring at 0 °C for 30 min. Then, DIPEA (2.5 mL) was added in the solution under stirring at 0 °C for 12 h. The white precipitate (rMSNs) was centrifuged at 5000 rpm and washed with DCM, acetone, methanol, and dichloromethane successively. The residual organic solvent was removed in a vacuum drying oven.

The chemical structure of rMSNs was characterized by Fourier transform infrared spectroscopy (FT-IR). The morphology of rMSNs was observed by scanning electron microscopy (SEM, JSM-6700F) at 10 kV and transmission electron microscopy (TEM, JEM2100) at 100 kV. The pore properties of rMSNs were measured by nitrogen adsorption-desorption isotherm. rMSNs was heated at 180 °C for 8 h, and their specific surface area, pore size and pore volume were measured and calculated using the Brunauer-Emmet-Teller (BET) method.

The rMSNs (80 mg) was added into the mixture of bergamot oil (5 mL) and lemon oil (5 mL) under stirring for 24 h. The content of essential oils was determined by thermogravimetric analysis (TGA).

The content of essential oils in BLEO@rMSNs was determined at predetermined time intervals by TGA.

The wallpaper was completely immersed in the BLEO@rMSNs solution under stirring at room temperature. After 5 h, the wallpaper was dried at 50 °C for 30 min to obtain the BLEO@rMSNs-treated wallpaper. The morphology of the wallpaper was obtained by SEM.

The BLEO@rMSNs-treated wallpaper was soaked in water under stirring for 1 day, 2 days, 3 days, 4 days, 5 days, 6 days and 7 days. The wallpaper was observed by SEM.

Amino-modified MSNs were first synthesized by the sol-gel method. As shown in Fig. 2A, MSNs were spherical nanoparticles with uniform grain structure and morphology. After modifying CYC, the morphology and particle size of rMSNs were changed significantly (Fig. 2B). After the BEO and LEO encapsulation, the morphology and size of BLEO@rMSNs remained unchanged (Fig. 2C). We then observed MSNs, rMSNs, and BLEO@MSNs by TEM. As

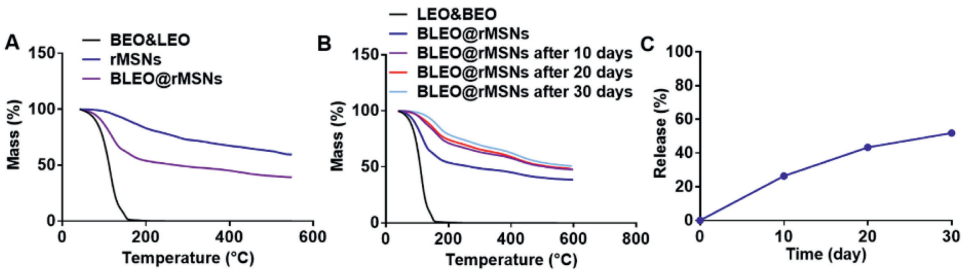

Fig. 5. (A) The TGA curves of BEO&LEO, rMSNs and BLEO@rMSNs. (B) The TGA curves of BEO&LEO, BLEO@rMSNs and BLEO@rMSNs after 10 days, 20 days, and 30 days. (C) The release of BEO&LEO from BLEO@rMSNs.

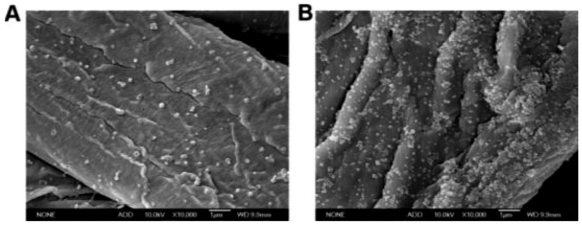

Fig. 6. The SEM images of (A) BLEO@MSNs-treated wallpaper and (B) BLEO@rMSNs treated wallpaper. Scale bars: 1 μm.

shown in Figs. 2D-F, after CYC modification and essential oils encapsulation, the nanoparticles' size and morphology were significantly changed, consistent with the SEM results. The diameters of MSNs, rMSNs, and BLEO@MSNs were all around 250 nm.

FT-IR analyzed the chemical structure of MSNs. As shown in Fig. 3, for MSNs, the peak at 3400 cm^{-1} was caused by the amino group's stretching vibration. The peak at 1640 cm^{-1} was due to the bending vibration of the amino group. This result indicated the presence of amino groups on MSNs. For CYC, 1714 cm^{-1} was the characteristic peak of the cyanuric ring. For rMSNs, the peak of the cyanuro shifted to 1730 cm^{-1}. This result indicated that rMSNs successfully modified CYC.

Then, the mesopores of rMSNs were characterized by nitrogen adsorption-desorption isotherm (Fig. 4A). The isotherm calculated the pore diameter, specific surface area, and pore volume of rMSNs. As shown in Fig. 4B, the pore diameter of rMSNs was about 3 nm, and the pore diameter distribution of rMSNs was narrow. The specific surface area and pore volume of rMSNs were 974.6 m^2/g and 1.52 cm^3/g, respectively. These results indicate that rMSNs possessed mesopores, large specific surface area, and pore volume. Therefore, rMSNs were expected to have essential oils' excellent encapsulation ability.

TGA measured the essential oils' encapsulation efficiency after the adsorption of the mixed essential oil of BEO and LEO (BEO&LEO) by rMSNs. As shown in Fig. 5A, BEO&LEO began thermal decomposition at 60 °C and decomposed completely at 156 °C. The essential oils in BLEO@rMSNs also started thermal decomposition at 60 °C and decomposed completely at 156 °C. This result further illustrated that BEO&LEO were encapsulated in rMSNs. The encapsulation efficiency of essential oils in BLEO@MSNs was about 30.38%. rMSNs had a large specific surface area and thus had a strong adsorption capacity. TGA determined the release of essential oils. As shown in Fig. 5B, the longer the time was, the less weightlessness BLEO@rMSNs exhibited. This result indicated that the encapsulated essential oils of BLEO@rMSNs gradually decreased. Further, we calculated the release of essential oil from BLEO@rMSNs. As shown in Fig. 5C, only 26.35% of the essential oil was released for ten days. Only 51.84% of the essential oils were also released for 30 days. This result indicated that BLEO@rMSNs could significantly reduce the volatility of essential oils. BLEO@rMSNs not only slowed down the release rate of the fragrances and thus increased the useful life of the essential oil. More importantly, BLEO@rMSNs could stabilize the release rate of fragrances over a long time, thereby stabilizing the fragrance content in the air over a long time and improving essential oil's use effect.

The nano-essential oils then adhered to the wallpaper. Subsequently, the nanoparticles-treated wallpaper was characterized by SEM. As shown in Fig. 6A, only a tiny number of BLEO@MSNs adhered to the wallpaper. In contrast, a large number of BLEO@rMSNs adhered to wallpaper (Fig. 6B). This result showed that the modification of CYC significantly improved the adhesion of nanoparticles to wallpaper.

The firm adhesion of nano-essential oils to wallpaper is crucial for the application of them. Therefore, we detected the de-adhesion of the nano-essential oils from the wallpaper. As shown in Fig. 7A, a large number of BLEO@MSNs de-adhered from the wallpaper on the second day. On the fourth day, there were few nanoparticles on the wallpaper. In contrast, a large number of BLEO@MSNs remained adhered to the wallpaper on the fourth day (Fig. 7B). These results indicated that the CYC-modified reactive nano-essential oils could adhere more firmly to the wallpaper, which might be due to the covalent bond formed between the reactive nanoparticles and the wallpaper. That was, BLEO@MSNs had a chemical reaction with the wallpaper and became part of it. Compared with the adhesion on the wallpaper through the traditional physical adsorption mode, the chemical reaction method enabled more nanoparticles to adhere to the wallpaper and was less prone to de-adhesion. Moreover, besides wallpaper containing hydroxyl groups, the nano-essential oils had excellent application potential for surfaces containing amino groups, such as silk and leather.

In summary, we developed reactive nano-essential oils and adhered them to wallpaper to reduce the essential oils' volatility and improve their use convenience. First, we synthesized reactive MSNs by modifying CYC with MSNs. rMSNs had a large specific surface area and pore volume, thus possessing excellent encapsulation potential for essential oils. Subsequently, a blend of bergamot and lemon essential oils was encapsulated in rMSNs. The reactive nano-essential oils were spherical nanoparticles with a diameter of about 250 nm and were homogeneous in size and morphology. The encapsulation efficiency of essential oils in the reactive nanoparticles reached 30.38%. The reactive nano essential oils showed an excellent aroma sustained-release effect. Interestingly, the reactive nano-essential oils that modified CYC significantly improved the nanoparticles' adhesion to the wallpaper. The modification of CYC could make the wallpaper adhere more nanoparticles and prevent the nanoparticles from de-adhesion from the wallpaper. Therefore, the reactive nano essential oils overcame intense volatility and inconvenient use of the essential oils and had great application potential.

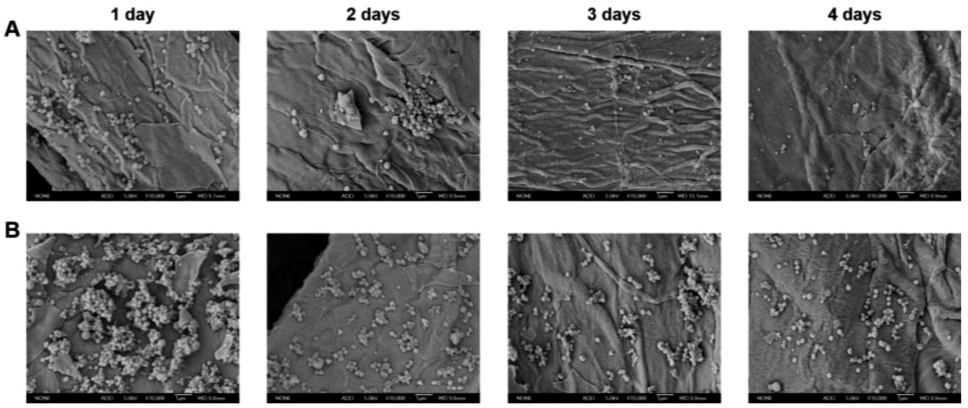

Fig. 7. The SEM images of (A) BLEO@MSNs-treated wallpaper and (B) BLEO@rMSNs treated wallpaper in the de-adhesion tests. Scale bars: 1 μm.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgments

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