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Magnetic Janus nanorods for efficient capture, separation and elimination of bacteria†

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Magnetic Janus mesoporous silica nanoparticles (MSNs) with CTAB-loading and amino-functionalization were prepared through a one-pot synthesis strategy. Janus MSNs exhibit outstanding bacterial capture and separation performance, enabling the highly efficient elimination of both Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus*, illustrating their application potential in biomedicine.

The increases in bacterial infection and contamination have received considerable attention in healthcare, cosmetics and food products industries.[1,2] Although the past several decades have witnessed the development of advanced detection and sterilization techniques, the precise detection and efficient elimination of pathogenic bacteria remain significant challenges.[3–5] To surmount these obstacles, continuous efforts have focused on the design and optimization of multifunctional platforms that achieve rapid bacterial capture and subsequently bacterial detection or elimination, which might benefit clinical diagnosis, environmental monitoring, and food safety.[6–10] Among them, magnetic nanoparticles have been widely employed to detect and kill bacteria owing to their unique properties, including a superior magnetic effect for rapid bacterial capture, convenient surface functionalization for bacteria targeting, and excellent biocompatibility.[3,11–15] However, the reduced antibacterial drug loading capacity and low bacterial capture efficiency of bare magnetic nanoparticles limit their further application.[16] In this regard, the development of magnetic-based nanoplatforms with outstanding bacterial capture, separation and elimination efficiency is highly desired.

Herein, we report a new nanoplatform with CTAB loaded on magnetic Janus mesoporous silica nanoparticles (Janus MSNs) by using a one-pot strategy. These multifunctional nanoplatforms are designed to integrate bacterial capture, separation, and elimination simultaneously into a single system. In this system, hetero-nanostructured magnetic MSNs are capable of combining the Fe_3O_4 head and mesoporous SiO_2 body together without interfering with their magnetic and mesoporous properties. The mesoporous SiO_2 body enhances the attachment of nanoplatforms to bacteria due to their large surface area for bacterial capture, while the exposed Fe_3O_4 head maintains the strong paramagnetic property for bacterial separation. Of note, hexadecyltrimethylammonium bromide (CTAB) is employed in this nanoplatform as a soft cationic template for mesoporous silica synthesis and simultaneously an anti-bacterial agent for bacterial elimination. Furthermore, the surface chemical modification of amino groups on nanoplatforms is responsible for the strong ability to bind with a broad spectrum of bacteria by electrostatic interactions. The enhanced efficiency of bacterial capture, separation and elimination of the Janus multifunctional nanoplatforms may enable their various applications in biomedicine.

The Fe_3O_4 nanospheres were synthesized by a simple sol–gel method, as we previously reported.[17] Then, the amino-functionalized, CTAB-loaded Janus MSNs were prepared by a one-step synthesis using a modified sol–gel method.[18–20] It can be observed from transmission electron microscopy (TEM) results that the Janus MSNs consisted of a Fe_3O_4 head with a diameter of approximately 100 nm and SiO_2 body with a length of approximately 200 nm (Fig. 1a). The SEM results of the Janus MSNs also illustrated the uniform morphology (Fig. 1b). As shown in Fig. 1c, the Janus MSNs possessed superb super-paramagnetic behaviour, and their saturation magnetization value was as high as 59 emu g^{-1}, which was much higher than that observed for conventional core–shell magnetic nanospheres of the same magnetic core in our previous work.[19,21] In addition, the mesoporous structure of Janus MSNs was determined by nitrogen adsorption and desorption

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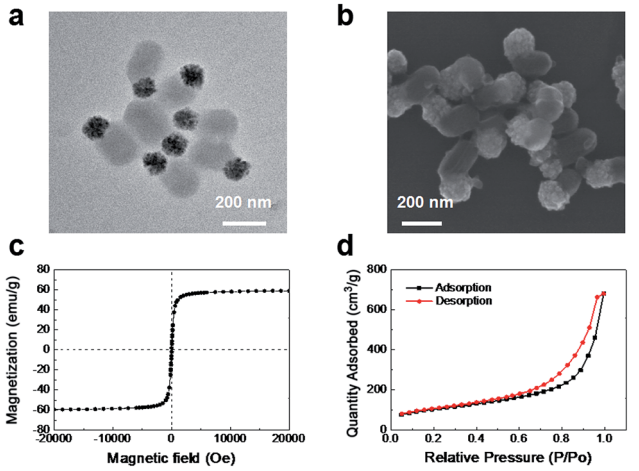

Fig. 1 The characteristics of Janus MSNs. (a) TEM images (bar = 200 nm); (b) SEM images (bar = 200 nm); (c) magnetic hysteresis loops of Janus MSNs at 300 K; (d) nitrogen adsorption and desorption isotherms of Janus MSNs.

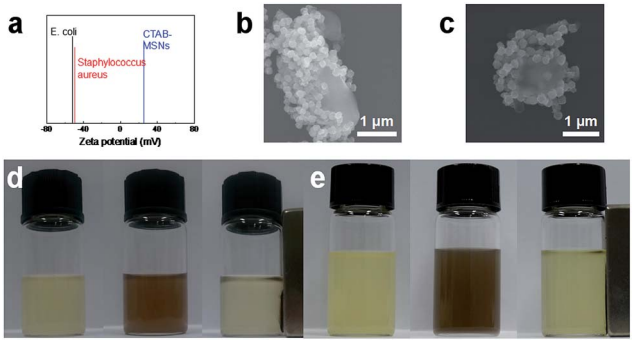

Fig. 2 (a) Zeta potential of Janus MSNs (CTAB-MSNs), *Escherichia coli* and *Staphylococcus aureus* in deionized water; SEM images of *Escherichia coli* (b) or *Staphylococcus aureus* (c) captured by Janus MSNs; optical pictures of the sterilization and separation process of Janus MSNs (100 μg mL^{-1}) in *Escherichia coli* (d) or *Staphylococcus aureus* (e) suspension (about 10^7 CFU mL^{-1}), separated by an external magnet.

isotherms (Fig. 1d), which can be classified as IV-type curves. The Brunauer–Emmett–Teller (BET) surface area, average mesopore size and total pore volume of the Janus MSNs are 657.5 m^2 g^{-1}, 2.5 nm and 0.45 cm^3 g^{-1}, respectively. In addition, the FTIR spectra further confirmed the CTAB and amino group on the surface of Janus MSNs (Fig. S1, ESI†). Collectively, these results demonstrated that the as-prepared Janus MSNs exhibited uniform morphology and both high superparamagnetic and good mesoporous properties, which indicated that this nanoplatform would be useful for bacterial capture and separation.

It is well known that magnetically responsive antibacterial materials may greatly improve the efficiency of bacterial capture and separation.[22,23] In addition to superior superparamagnetic properties, the mesoporous silica bodies of our Janus MSNs offer an easy interaction between nanoparticles and bacteria due to their large surface areas. More importantly, amine groups and CTAB modifications on the surface of Janus MSNs are nonselective ligands that bind both Gram-positive and Gram-negative bacteria *via* electrostatic attraction.[24–26] Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* were employed in this study as model bacteria. As expected, all the bacteria were negatively charged, whereas the Janus MSNs were strongly positively charged (Fig. 2a). Because the size of the bacteria was approximately one order of magnitude larger than the Janus MSNs, multiple positively charged Janus MSNs could attach strongly to the surface of negatively charged bacteria through attractive electrostatic interaction, subsequently achieving magnetically induced separation. To evaluate the bacterial-capture performance of the Janus MSNs, the separation of a bacterial suspension was conducted. As shown in Fig. 2b and c, the SEM of bacteria showed that several Janus MSNs adhere on a bacteria surface, oriented with the magnetic head outside and the silica body inside. These observations can be illustrated by the different hydrophilic/hydrophobic and charge properties on the opposite sides of Janus MSNs, which may lead to the adsorption of the silica body onto the bacterial surface. Moreover, when Janus MSNs were mixed with *Escherichia coli* or *Staphylococcus aureus* solution for 10 min, both types of bacteria were collected and retrieved from the suspension in less than 1 min under the external magnetic field (Fig. 2d and e), suggesting that the outstanding magnetic response of Janus MSNs enabled their various applications in bacterial capture and separation. Collectively, these findings indicate that Janus MSNs could rapidly achieve bacterial capture and separation due to their unique structure-related properties.

To further quantify the bacterial capture efficiency, the optical density (600 nm, OD_{600}) of the supernatants from *Escherichia coli* or *Staphylococcus aureus* samples was measured to calculate the bacterial capture efficiency after treatment with different concentrations of Janus MSNs. As shown in Fig. 3a and (Fig. S2 and S3, ESI†), the initial value, *i.e.*, the bacterial suspension after the same incubation condition without the

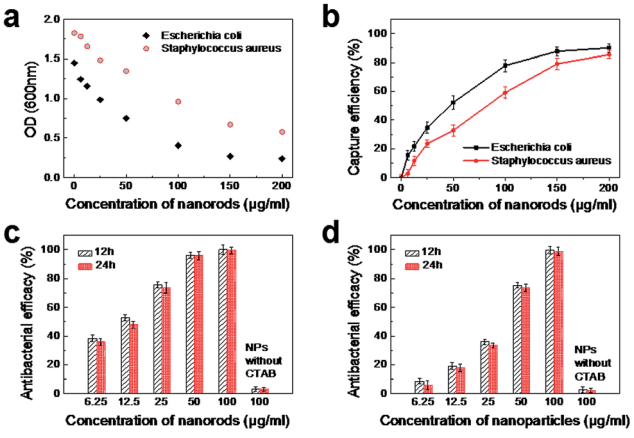

Fig. 3 (a) The optical density (600 nm) of the supernatants from *Escherichia coli* and *Staphylococcus aureus* samples after treatment with different concentrations of Janus MSNs; (b) the analysis of bacterial capture efficiency based on OD_{600}. Antibacterial efficacy of Janus MSNs against *Escherichia coli* (c) and *Staphylococcus aureus* (d).

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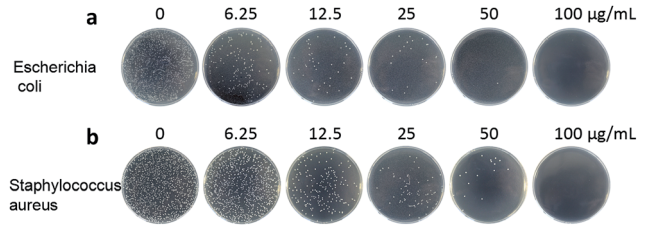

Fig. 4 (a) Antibacterial activity of Janus MSNs. Optical pictures of LB-agar plates coated with *Escherichia coli* (a) and *Staphylococcus aureus* (b) supplemented with different concentrations of Janus MSNs.

addition of any Janus MSNs, was 1.449 for *Escherichia coli* and 1.826 for *Staphylococcus aureus*, which indicated no bacteria capture. When the Janus MSNs were introduced into the suspension, and with increasing nanoparticle concentration, the OD_{600} of the supernatants decreased, indicating an increasing number of captured bacteria. The capture efficiency of *Escherichia coli* and *Staphylococcus aureus* could reach up to 90.1% and 85.4%, respectively (Fig. 3b). These results demonstrated that the Janus MSNs might be able to capture bacteria efficiently in an aqueous environment.

CTAB has been confirmed to induce superoxide stress in bacteria and cell lysis, and to lead to short-term growth suspension.[27–29] The antibacterial efficiency of the Janus MSNs was explored against both the Gram-negative bacteria *Escherichia coli* and the Gram-positive bacteria *Staphylococcus aureus*. As shown in Fig. 3c and d, the Janus MSNs without CTAB were set as the control group and exhibited a tiny antibacterial effect. More importantly, the antibacterial materials are more effective in the elimination of the Gram-negative bacteria *Escherichia coli* rather than Gram-positive bacteria *Staphylococcus aureus* after 24 h of incubation. When the concentration of Janus MSNs reached 50 μg mL^{-1}, the antibacterial efficiency against *Escherichia coli* and *Staphylococcus aureus* was 95.88% and 73.57%, respectively. The use of 100 μg mL^{-1} of Janus MSNs led to complete inhibition of all bacterial growth. The reason for these phenomenon is that the cell walls of the Gram-negative bacteria *Escherichia coli* are thinner and less compact than the cell walls of the Gram-positive bacteria *Staphylococcus aureus*. In addition, the presence of Janus MSNs on LB-agar plates can inhibit the formation of colonies for both types of bacteria, and the completely inhibitory concentration of Janus MSNs for *Escherichia coli* and *Staphylococcus aureus* are 50 and 100 μg mL^{-1}, respectively (Fig. 4a and b). Thus, the corresponding minimum inhibitory concentration (MIC) tests on LB-agar plates were consistent with the antibacterial efficiency of the Janus MSNs. These data suggest that Janus MSNs possess excellent antibacterial properties against both Gram-positive and Gram-negative bacteria.

Conclusions

In summary, Janus magnetic mesoporous silica nanoparticles have been prepared for simultaneous bacterial capture, separation and elimination. These multifunctional nanoplatforms with CTAB loading and amino-functionalization were confirmed to possess strong paramagnetic properties and high-affinity binding to bacteria. Moreover, Janus MSNs exhibit excellent antibacterial activity against both Gram-negative and Gram-positive bacteria. The enhanced efficiency of bacterial capture, separation and elimination of the Janus MSNs indicates their great potential applications in biomedicine.

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