**Fe₃O₄@Resorcinol–Formaldehyde Resin/Cu₂O Composite Microstructures: Solution-Phase Construction, Magnetic Performance, and Applications in Antibacterial and Catalytic Fields**

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**ABSTRACT:** Multifunctional Fe₃O₄@resorcinol–formaldehyde resin/Cu₂O composite microstructures (denoted as Fe₃O₄@RF/Cu₂O microstructures) were successfully constructed via a simple wet chemical route that has not been reported so far in the literature. The as-obtained Fe₃O₄@RF/Cu₂O microstructures were characterized using field-emission scanning electron microscopy, (high-resolution) transmission electron microscopy, selected-area electron diffraction, X-ray diffraction, and X-ray energy dispersive spectroscopy. The investigations showed that the as-obtained microstructures presented not only excellent antibacterial activity to *Staphylococcus aureus* (Gram-positive bacteria) and *Escherichia coli* (Gram-negative bacteria) but also highly efficient catalytic ability for the reduction of 4-nitrophenol (4-NP) in a solution with excess NaBH₄. Owing to the presence of Fe₃O₄, the antibacterial reagent and the catalyst could be readily collected from the mixed systems under the assistance of an external magnetic field. It was found that the as-obtained microstructures displayed good cycling stability in antibacterial and catalytic applications. Fe₃O₄@RF/Cu₂O microstructures still retained more than 87% of the antibacterial efficiency after 5 cycles and 89% of the catalytic efficiency after 10 cycles.

**INTRODUCTION**

Antibacterial agents have been widely used in many fields including water disinfection, textile industry, medicine, food packaging, and so on. At present, organic antibacterial agents are the main commodity on the market. However, organic antibacterial agents come with many shortcomings, such as low heat resistance, volatility, environmental pollution, poor security, and short-lived duration. To conquer the above shortcomings, therefore, inorganic antibacterial agents with improved properties were developed. Currently, several nanoscaled inorganic matters, including TiO₂, ZnO, Cu₂O, and silver, have shown a strong antibacterial activity against Gram-positive and/or Gram-negative bacteria. Among them, Cu₂O, a typical p-type semiconductor with a direct band of 2.17 eV, shows a great promise for biomedical applications because of its unique potential to combine the intrinsic antibacterial effects with multiple other functionalities. For example, Lu et al. investigated the antibacterial activities of Cu₂O with different shapes and found that all Cu₂O crystals with various shapes presented good bacteriostatic activities. Even after Cu₂O was coated with different surfactants, it still exhibited eminent antifungal activity for yeast. Furthermore, Cu₂O also presents outstanding catalytic activity for the photodegradation of organic pollutants and the synthesis of organic compounds.

Usually, it is necessary to separate antibacterial agents or catalysts from a heterogeneous system. On the one hand, the recovered antibacterial agents or catalysts can be reused to enhance the efficiency and to reduce the cost. On the other hand, recovering antibacterial agents or catalysts can avoid secondary pollution. Although traditional separation strategies such as centrifugation, free settling, and filtration have been widely adopted, they suffer from loss of antibacterial agents and catalyst, complicated operating equipment, and high operational costs. Therefore, a benign, effective, and inexpensive separation method is extremely desirable. Compared with the above separation methods, magnetic separation shows superior separation effect and draws increasing attention because of its low cost and ease of use. An antibacterial agent or catalyst carried by magnetic substances has good magnetic response to the additional magnetic field, which can achieve the goal of fast and efficient separation.
Iron oxide nanoparticles, such as magnetite (Fe₃O₄), are very interesting materials for biomedical applications because of their high biocompatibility, peculiar magnetic property, low preparation cost, high thermal and mechanical stabilities, and adaptability for large-scale production. In the current work, we attempted to construct Cu₂O nanoparticle-strewn Fe₃O₄@resorcinol–formaldehyde resin microstructures (denoted as Fe₃O₄@RF/Cu₂O microstructures) through simple wet chemical routes. First, Fe₃O₄@RF microstructures were obtained by the polymerization of RF on the surfaces of Fe₃O₄ microspheres. Then, the Fe₃O₄@RF microstructures were modified with the silane coupling agent KH550 (3-aminopropyl triethoxy silane). Finally, Fe₃O₄@RF/Cu₂O microstructures were prepared through the reduction of Cu²⁺ in the system containing Fe₃O₄@RF. It was found that the saturation magnetization (Ms) of Fe₃O₄ microspheres decreased with the formation of Fe₃O₄@RF and Fe₃O₄@RF/Cu₂O microstructures. Experiments showed that the as-obtained Fe₃O₄@RF/Cu₂O microstructures exhibited strong antibacterial ability to Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) and highly efficient catalytic activity for the reduction of 4-nitrophenol (4-NP) in excess NaBH₄ solution. Compared with the existing microstructures, the microstructure prepared in our study presented better catalytic activity. Furthermore, due to the existence of magnetic Fe₃O₄ cores, the present antibacterial reagent and the catalyst can be easily recycled under the extra magnetic field, which can efficiently reduce the cost in practical applications.
RESULTS AND DISCUSSION

Morphology and Structure Characterization. The morphologies of pure Fe₃O₄, Fe₃O₄@RF, and Fe₃O₄@RF/Cu₂O microstructures were characterized using field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) technologies. Figure 1 depicts representative FESEM images of three samples. Pure Fe₃O₄ prepared by the solvothermal technology is composed of uniform microspheres with an average diameter of ~180 nm (see Figure 1a). These microspheres were made of an abundance of small nanoparticles, which resulted in unsmooth surfaces of microspheres (see the inset in 1a). After RF was formed on monodisperse Fe₃O₄ microspheres, the product still presented spherical microstructures, but the surfaces of microspheres became smooth (see Figure 1b and its inset). Simultaneously, the sizes of microspheres increased to ~250 nm. Figure 1c shows an FESEM image of the final Fe₃O₄@RF/Cu₂O. An abundance of nanoparticles of size 5–15 nm are distributed on the surfaces of spherical microstructures, implying that Cu₂O nanoparticles have been successfully decorated on the Fe₃O₄@RF microstructures. Furthermore, it is worth pointing out that RF and KH₅S₅O play crucial roles in the formation of Fe₃O₄@RF/Cu₂O. Without either RF or KH₅S₅O, Cu₂O nanoparticles cannot be decorated on the surfaces of Fe₃O₄ microspheres.

TEM observations confirmed the results of SEM. As shown in Figure 2a, pure Fe₃O₄ microspheres are made of an abundance of small nanoparticles ~15 nm in size, which results in the roughness of the microsphere surfaces. After pure Fe₃O₄ microspheres have been coated with RF, clear core–shell structures with smooth surfaces can be easily observed (see Figure 2b). The typical TEM image of the final product is exhibited in Figure 2c. An abundance of small nanoparticles with a mean size of ~10 nm are strewn on the surfaces of Fe₃O₄@RF microspheres. Selected-area electron diffraction (SAED) pattern shown in the inset in 2c proves the good crystallinity of the final product. Bright spots are ascribed to the face-centered cubic (fcc) Fe₃O₄, and a weak spot near the (400) plane of fcc Fe₃O₄ is attributed to the (111) plane of cubic Cu₂O. Figure 2d depicts a high-resolution transmission electron microscopy (HRTEM) image of the final product. Several spherical nanoparticles are distributed on the surface of the amorphous RF layer. The clear matrix stripes imply good crystallinity of nanoparticles. The distance between neighboring planes is measured to be ~0.212 nm, which is very close to 0.21335 nm of the distance between the neighboring (200) planes of cubic Cu₂O. The above facts confirm that Cu₂O nanoparticles have indeed been successfully decorated on Fe₃O₄@RF microspheres.

The formation of Fe₃O₄@RF/Cu₂O is also confirmed using XRD and EDS analyses of the final product. Figure 3a compares the XRD patterns of the samples before and after strewing Cu₂O nanoparticles on the surfaces of Fe₃O₄@RF. Owing to the amorphous nature of RF, only the diffraction peaks of fcc Fe₃O₄ are detected before loading Cu₂O nanoparticles (see the lower pattern in Figure 3a). The other Cu₂O peaks centered at 42.3°, 61.3°, and 73.5° should overlap with the ones of Fe₃O₄ at the corresponding situations. Nevertheless, the above facts prove the successful preparation of Fe₃O₄@RF/Cu₂O. Moreover, according to the calculation result of the EDS peak areas, ~11.9 wt % of Cu₂O is loaded on the surfaces of Fe₃O₄@RF microspheres. The formation of Fe₃O₄@RF/Cu₂O is also confirmed using XRD and EDS analyses of the final product. Figure 3b shows the EDS result of the final product. O, Fe, and Cu peaks are clearly visible. Simultaneously, the strong C peak comes from organic compounds such as RF and KH₅S₅O, and the weak Si peak is attributed to the silane coupling agent. Markedly, the EDS analysis further confirms the successful preparation of Fe₃O₄@RF/Cu₂O. Moreover, according to the calculation result of the EDS peak areas, ~11.9 wt % of Cu₂O is loaded on the surfaces of Fe₃O₄@RF microspheres. It was found that the coating of RF and the subsequent loading of Cu₂O nanoparticles could obviously change the magnetism of Fe₃O₄ microspheres. Figure 4 shows the room-temperature hysteresis loops of Fe₃O₄ microspheres, Fe₃O₄@RF, and Fe₃O₄@RF/Cu₂O. Their corresponding Ms values are, in turn, 48.5, 21.7, and 14.4 emu g⁻¹. The Ms value of Fe₃O₄ decreases with the integration of RF and Cu₂O, in turn. Although the magnetism of Fe₃O₄@RF/Cu₂O markedly decreases against pure Fe₃O₄, it can still be quickly separated from a solution by an external magnetic field, which is favorable for its collection and reuse.

Antibacterial Activity. Our previous work had proven that Cu₂O owned excellent antimicrobial activities. 14 To investigate the antibacterial activity of the as-obtained Fe₃O₄@RF/Cu₂O, in the present work, S. aureus (a Gram-positive bacterium) and E. coli (a Gram-negative bacterium) are selected as the representative bacteria. Inhibition of the bacterial growth is monitored by the optical density (OD) of the system. Figure 5 shows the growth curves of ~10⁷ cfu/mL of E. coli or S. aureus.
in liquid media with different concentrations of Fe3O4@RF/Cu2O microstructures. When no antibacterial agent in the system, the bacteria rapidly breed and reach the maximum peak after 16 h for *E. coli* or 14 h for *S. aureus*. After the antibacterial agent is introduced, the reproduction of the bacteria is restrained, and the reproduction ability of the bacteria is negatively correlated to the concentration of the antibacterial agent. When increasing the concentration of the antibacterial agent to 64 μg mL⁻¹, the reproduction of *E. coli* is almost inhibited (see Figure 5a). Whereas the growth of *S. aureus* is completely inhibited, the concentration of the antibacterial agent reaches 128 μg mL⁻¹ (see Figure 5b). The above experiments indicate that the as-prepared Fe3O4@RF/Cu2O microstructures possess excellent antibacterial properties against both Gram-positive bacteria and Gram-negative bacteria and that the antibacterial effect of the antibacterial agent against the Gram-negative bacteria *E. coli* is better than that against the Gram-positive bacteria *S. aureus*. To ascertain the role of Fe3O4@RF in the antibacterial process, furthermore, we compared the changes in the OD values of *S. aureus* and *E. coli* solutions in the presence of 256 μg mL⁻¹ Fe3O4@RF and Fe3O4@RF/Cu2O, respectively. As shown in Figure 5c, in the presence of Fe3O4@RF, the OD values of *S. aureus* and *E. coli* solutions present trends similar to those of the control experiments, implying that the propagation of bacteria cannot be restrained by Fe3O4@RF. After Fe3O4@RF/Cu2O microstructures are added, however, the OD values of the two bacterial solutions hardly change within 24 h, indicating that the propagation of the bacteria is strongly restrained. The above facts confirm that the antibacterial function of Fe3O4@RF/Cu2O still comes from Cu2O nanoparticles. Figure 6a depicts the correlations between the bacteriostatic effect and the concentration of the antibacterial agent. The half-maximal inhibitory concentration (IC₅₀) against *E. coli* and *S. aureus* was 35.8 ± 3.7 and 49.5 ± 2.7 μg mL⁻¹, respectively. Obviously, the present antibacterial agent has a lower IC₅₀ value against *E. coli* than against *S. aureus*, which is in good agreement with the result shown in Figure 5. Furthermore, owing to the magnetic influence of the as-prepared Fe3O4@RF/Cu2O microstructures, the present antibacterial agent can be easily separated from a system with the assistance of extra magnetic fields. This provides the possibility of reusing the antibacterial agent.

![Figure 4. Room temperature hysteresis loops of Fe₃O₄ microspheres, Fe₃O₄@RF, and Fe₃O₄@RF/Cu₂O.](image)

![Figure 5. Reproduction curves of bacteria: (a) *E. coli* and (b) *S. aureus* in the presence of Fe₃O₄@RF/Cu₂O microstructures at various concentrations. (c) Changes in OD values of *S. aureus* (red lines) and *E. coli* (black lines) with the incubation duration in the presence of various antibacterial agents at a concentration of 256 μg mL⁻¹.](image)
NaBH₄, and 6 mg L⁻¹ absorption spectra of the system that consisted of 4-NP, some small organic molecules such as 4-NP in excess NaBH₄ also presented excellent catalytic activity for the reduction of 4-NP. The reaction can be markedly promoted by the amount of catalyst. It was also found that the as-obtained Fe₃O₄@RF/Cu₂O microstructures possess an excellent catalytic ability for the reduction of 4-NP to 4-aminophenol (4-AP), which causes the absorption peak at 400 nm to disappear and a new peak at 309 nm to appear. Figure 7a exhibits the ultraviolet–visible (UV–vis) absorption spectra of the system that consisted of 4-NP, NaBH₄ and 6 mg L⁻¹ Fe₃O₄@RF/Cu₂O after reacting for various durations. With the increase in the reaction time, the intensity of the peak at 400 nm markedly decreases, and a new absorption peak at ∼309 nm appears. After 4 min, the peak at 400 nm almost disappears, which indicates that the as-obtained Fe₃O₄@RF/Cu₂O microstructures possess an excellent catalytic ability for the reduction of 4-NP to 4-AP in excess NaBH₄ solution. To investigate the influence of the amount of catalyst on the reaction rate, 2, 4, and 8 mg L⁻¹ Fe₃O₄@RF/Cu₂O were used as the catalyst. As shown in Figure 7b, the above reduction reaction can be markedly promoted by the amount of catalyst.

However, when 8 mg L⁻¹ catalyst was used, the catalytic curve almost overlapped with that obtained in the presence of 6 mg L⁻¹ catalyst, implying that the optimum catalyst concentration was 6 mg L⁻¹ in the current work. Figure 7c compares the curves of the concentration change in 4-NP versus time in the presence of Fe₃O₄@RF and Fe₃O₄@RF/Cu₂O. When 6 mg L⁻¹ Fe₃O₄@RF was selected as the catalyst, the reduction reaction did not take place. This fact indicates that the reduction reaction of 4-NP to 4-AP is catalyzed only by Cu₂O. The kinetic constant of this pseudo-first-order reaction (k) is 0.75 min⁻¹ (see the inset in 7c). Compared with some previous reports, the present catalyst displays better catalytic activity (see Table 1). Furthermore, the presence of magnetic Fe₃O₄ cores is favorable for the collection and reuse of the present catalyst. As shown in Figure 7d, after 10 cycles, the catalytic activity of the present catalyst still remains to be 89%. Obviously, this is important for practical applications.

■ EXPERIMENTAL SECTION

Materials. FeCl₃·6H₂O, trisodium citrate dehydrate, ethylene glycol, urea, resorcinol, ammonia, formaldehyde, silane coupling agent KH550, maleic anhydride, CuCl₂·2NaOH, NH₂OH·HCl, glucose, KH₂PO₄, KH₂PO₄·H₂O, NaCl, NH₄Cl, MgSO₄·7H₂O, and CaCl₂ were purchased from Sinopharm Chemical Reagent Co., Ltd. Lactose was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were analytically pure and used without further purification. Deionized water was used in all synthesis procedures.

Characterization. The X-ray powder diffraction patterns of the products were recorded on a Bruker D8 ADVANCE X-ray diffractometer equipped with Cu Kα radiation (λ = 0.154060 nm), at a scanning rate of 0.2° s⁻¹ and 2θ ranging from 10° to 80°. SEM images were obtained on Hitachi S-4800 field emission scanning electron microscope, operated at 5 kV. TEM/HRTEM images and SAED pattern of the samples were obtained from a JEOL-2011 transmission electron microscope working at an accelerating voltage of 200 kV. The room temperature hysteresis loops of the products were measured using a superconducting quantum interference device operating at room temperature (300 K) with an applied field up to 1.0 T. UV–vis absorption spectra were recorded using a Metash 6100 UV–vis absorption spectrophotometer (Shanghai). The OD of bacteria was measured using UV-2000 spectrophotometer.

Synthesis of Fe₃O₄@RF/Cu₂O. Synthesis of Fe₃O₄@RF Microstructures. To obtain Fe₃O₄@RF microstructures, Fe₃O₄ microspheres assembled with an abundance of nanoparticles were prepared in advance using a solvothermal method as previously reported. In a typical experiment, 1.0 g of FeCl₃·6H₂O and 0.3 g of trisodium citrate dihydrate were dissolved in 30 mL of ethylene glycol under vigorous stirring. Then, 2.0 g of urea was added into the above solution under stirring. After continuously stirring for another 30 min, the as-obtained mixed mixture was sealed in a Teflon-lined stainless-steel autoclave of 40 mL capacity and heated at 200 °C for 10 h. Subsequently, the system was naturally cooled to room temperature. The black product was separated magnetically, washed with deionized water and ethanol several times, and finally dried under vacuum at 60 °C for 24 h.

Fe₃O₄ (0.1 g) microspheres prepared from the above process were placed into a 250 mL three-necked flask with 30 mL of ethanol and 70 mL of pure water. Next, 0.1 g of resorcinol and 0.5 mL of ammonia were added. After the as-obtained mixed system was ultrasonically treated for 30 min, the system was...
heated to 35 °C. Herein, 0.14 mL of 37 wt % formaldehyde solution was poured into the above system under vigorous mechanical stirring. After continuously stirring for 6 h, the precipitate was collected using a magnet, washed with distilled water and ethanol several times, and dried under vacuum at 60 °C overnight.

Synthesis of Fe₃O₄@RF/Cu₂O Microstructures. To successfully prepare Fe₃O₄@RF/Cu₂O microstructures, the surfaces of Fe₃O₄@RF microstructures must be modified by the silane coupling agent KH550 in advance. Typically, 50 mg of the Fe₃O₄@RF microstructure was first placed into a 150 mL three-necked flask with 50 mL of absolute ethanol. After the as-obtained system was ultrasonically dispersed for 30 min, a mechanical stirring was adopted. Under continuous stirring, 300 μL of KH550 was quickly introduced. The as-obtained mixed system was stirred at room temperature for 24 h. The precipitate was purified under the assistance of magnetic separation, washed with ethanol several times, and dried under vacuum at 60 °C for 24 h.

Subsequently, KH550-modified Fe₃O₄@RF microstructures were dispersed in 20 mL of dimethylformamide (DMF) and dropped into a flask containing 20 mL of DMF with 0.1 M maleic anhydride. The mixture was mechanically stirred for 24 h at room temperature. The precipitate was collected using a magnet, washed with DMF several times, and dried under vacuum at 60 °C for 24 h.

Carboxylic-functional Fe₃O₄@RF microstructures (Fe₃O₄−COOH) were obtained. The modification process of Fe₃O₄ microspheres is illustrated in Scheme 1.

Table 1. Comparison of the Catalytic Capacities of Various Catalysts Reported in the Literature for the Reduction of 4-NP to 4-AP in NaBH₄

| catalyst and its amount | kinetic rate constant (k) (min⁻¹) | ratio constant (K) (min⁻¹ mg⁻¹) | reference |
|-------------------------|----------------------------------|-------------------------------|-----------|
| hierarchical copper/3 mg | 0.27933                          | 0.093                         | 40        |
| CuO nanorods/1.0 mg     | 0.027                            | 0.027                         | 41        |
| leaf-like CuO/0.03 mg   | 2.13                             | 71                            | 42        |
| dumbbell-like CuO/0.03 mg | 0.2862                          | 9.54                          | 42        |
| Cu₂O—MWCNTs/0.02 mg    | 0.5772                           | 28.86                         | 43        |
| Cu₂O—Cu—CuO/0.5 mg     | 0.621                            | 1.242                         | 44        |
| Fe₃O₄@SiO₂—Ag/0.02 mg  | 0.33                             | 16.5                          | 45        |
| Fe₃O₄@Ag/0.01 mg        | 0.2232                           | 22.32                         | 46        |
| Fe₃O₄@Cu₂O/0.018 mg³   | 0.948                            | 94.8                          | 46        |
| Fe₃O₄@RF/Cu₂O/0.018 mg³ | 0.75                             | 41.7                          | this work |

³The calculated amount of catalyst: 3 mL of the 6 mg L⁻¹ CuO solution was used in experiments.

Figure 7. (a) UV−vis absorption spectra of the system containing 4-NP, NaBH₄, and Fe₃O₄@RF/Cu₂O microstructures for various durations; (b) concentration changes of 4-NP with the reaction time in the presence of Fe₃O₄@RF/Cu₂O catalyst of various amounts; and (c) curves of the 4-NP concentration vs time in the presence of 6 mg L⁻¹ catalysts. (d) Catalytic efficiency of Fe₃O₄@RF/Cu₂O catalyst after recycling 10 times.
Under the ultrasonication, 50 mg of the Fe₃O₄@RF−COOH sample was dispersed into 40 mL of deionized water. After 30 min, 1 mL of 0.1 M CuCl₂ solution was added. After continuous ultrasonication for another 10 min, 10 mL of 1 M NaOH was poured. Subsequently, 1 mL of 0.2 M NH₂OH·HCl solution was poured. The above mixed system was left for 2 h to allow the formation of Fe₃O₄@RF/Cu₂O magnetic microstructures. Finally, the precipitate was collected using a magnet, washed with distilled water and ethanol several times, and dried in vacuum at 60 °C overnight.

**Antibacterial Activity.** For the antimicrobial activity test, we prepared the cultivation medium containing 0.2% (w/v) glucose, 0.4% (w/v) lactose, 0.05% (w/v) K₂HPO₄, 0.05% (w/v) KH₂PO₄, 0.1% (w/v) NaCl, 0.2% (w/v) NH₄Cl, 0.002 M MgSO₄·7H₂O, and 1.0 × 10⁻⁴ M CaCl₂. The pH of the medium was 7.4.

**Measurements of Antibacterial Properties of Fe₃O₄@RF/Cu₂O Microstructures.** Gram-positive *S. aureus* and Gram-negative *E. coli* were selected as model organisms. The OD at 600 nm (OD600) of organisms was measured to reflect the variation in the amount of organisms. Before culturing bacteria, the culture medium was first sterilized by autoclaving at 121 °C for 20 min. The two bacteria were separately inoculated in liquid media at 37 °C for 24 h until an approximate OD600 of 0.8 was reached (here, the colony-forming units were ~2 × 10⁸ cfu mL⁻¹). After diluting the above suspension to 1 × 10⁻¹ cfu mL⁻¹, various amounts of Fe₃O₄@RF/Cu₂O were introduced. The concentration of the antibacterial agent in the system was, in turn, 0, 16, 32, 64, 128, 256, and 512 μg mL⁻¹. The system was placed in an orbital shaker at the rotating speed of 180 rpm. After the bacteria were incubated at 37 °C for 24 h, the OD value of the system at different durations was measured.

**IC₅₀ Test.** To obtain the IC₅₀ value, the antibacterial agent at the concentrations of 2048, 1024, 512, 256, 128, 64, 32, 16, 8, and 4 μg mL⁻¹ was separately prepared through the half times dilution method. Then, 1200 μL of the antibacterial agent at each of the concentrations was transferred into a sterile test tube. After 200 μL of bacterial liquid with 2 × 10⁸ cfu mL⁻¹ and 1000 μL of culture solution were added, the concentration of the antibacterial agent respectively became 1024, 512, 256, 128, 64, 32, 16, 8, 4, and 2 μg mL⁻¹. Furthermore, a control solution that consisted of 200 μL of the bacterial liquid with 2 × 10⁸ cfu mL⁻¹ and 2200 μL of culture solution was also prepared. All of the systems were cultured at 37 °C for 24 h. Their OD600 values were measured for the calculation of the IC₅₀ value.

**Catalytic Activity for the Reduction of 4-NP.** To investigate the catalytic property of the as-obtained Fe₃O₄@RF/Cu₂O microstructures in the reduction of 4-NP to 4-AP in excess NaBH₄ solution, a series of solutions were freshly prepared before experiment. In a typical process, appropriate amounts of 4-NP and catalysts were first mixed; then, a certain volume of NaBH₄ solution was introduced into the system to form 3 mL of the solution. Here, the concentrations of 4-NP, NaBH₄ and the catalyst were 1.0 × 10⁻⁴ mol L⁻¹, 2.0 × 10⁻² mol L⁻¹, and 2/4/6/8 mg L⁻¹, respectively. The reduction processes were monitored using a Metash 6100 UV−vis spectrophotometer.

**CONCLUSIONS**

In summary, Cu₂O nanoparticles-strewn Fe₃O₄@RF core−shell microstructures have been successfully constructed by the reduction of Cu²⁺ ions on the surfaces of Fe₃O₄@RF microstructures modified with the silane coupling agent KH550. Magnetic property studies showed that the Ms values of pure Fe₃O₄, Fe₃O₄@RF, and Fe₃O₄@RF/Cu₂O were 48.5, 21.7, and 14.4 emu g⁻¹, respectively, indicating that the Ms of pure Fe₃O₄ decreased with the integration of RF and Cu₂O in turn. Experiments showed that the as-obtained Fe₃O₄@RF/Cu₂O microstructures presented multifunctional applications in bio-antibacterial and organic catalysis fields. The reproductions of *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria) could be efficiently inhibited under the presence of appropriate amounts of Fe₃O₄@RF/Cu₂O microstructures. The IC₅₀ values against *E. coli* and *S. aureus* were 35.8 ± 3.7 and 49.5 ± 2.7 μg mL⁻¹, respectively, implying that the present antibacterial agent has stronger inhibition against *E. coli* than against *S. aureus*. Simultaneously, the as-obtained Fe₃O₄@RF/Cu₂O microstructures also displayed outstanding catalytic activity for the reduction of 4-NP in excess NaBH₄ solution. Under the presence of 6 mg L⁻¹ catalyst, 1.0 × 10⁻⁴ mol L⁻¹ 4-NP could be completely reduced within 4 min. Furthermore, because of its magnetic property, the present antibacterial agent and the catalyst could also be conveniently recovered for reuse. After five cycles, the antibacterial efficiency and the catalytic efficiency were still remaining at 87 and 90%, respectively. This is obviously favorable to cost savings in practical applications.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Hajipour, M. J.; Fromm, K. M.; Ashkarran, A. A. Trends Biotechnol. 2012, 30, 499−511.
(2) Shahid-ul-Islam; Mohammad, F. ACS Sustainable Chem. Eng. 2015, 3, 2361−2375.
(3) Musee, N.; Thwala, M.; Nota, N. J. Environ. Monit. 2011, 13, 1164−1183.
(4) Noh, M. S.; Lee, S.; Kang, H.; Yang, J.-K.; Lee, H.; Hwang, D.; Lee, J. W.; Jeong, S.; Jang, Y.; Jun, B.-H.; Jeong, D. H.; Kim, S. K.; Lee, Y.-S.; Cho, M.-H. Biomaterials 2015, 65, 124−125.
(5) Meng, Y.; Yan, X.; Wang, Y. Chem. Phys. Lett. 2016, 651, 84−87.
(6) Naik, K.; Kowshik, M. J. Appl. Microbiol. 2014, 117, 972−983.
(7) Zhao, H.; Xu, P.; Li, J. Spectrochim. Acta, Part A 2013, 110, 395−399.
(8) Sun, L.; Liu, L.; Liu, X.; Wang, Y.; Li, M.; Yao, L.; Yang, J.; Ji, G.; Guo, C.; Pan, Y.; Liang, S.; Wang, B.; Ding, J.; Zhang, H.; Shi, Y. Cancer Sci. 2014, 105, 651−659.
(9) Viciu, B.; Selyutina, A.; Garcia-Sosa, A. T.; Karonen, M.; Sinkkonen, J.; Merits, A.; Maran, U. Bioorg. Med. Chem. 2016, 24, 2519−2529.
(10) Samad, M.; Hashim, S.; Simarani, K.; Yaacob, J. J. Molecules 2016, 21, 419−432.
(11) Sun, D.; Lee, R. E. Tetrahedron Lett. 2005, 46, 8497−8501.
(12) Ananpattarachai, J.; Boonto, Y.; Kajitvichyanukul, P. Environ. Sci. Pollut. Res. 2016, 23, 4111−4119.
(13) (a) Han, H.; Ni, Y.; Sheng, E. RSC Adv. 2015, 5, 51750–51761.
(b) Li, H.; Ni, Y.; Cai, Y.; Zhang, L.; Zhou, J.; Hong, J.; Wei, X. J. Mater. Chem. 2009, 19, 594–597. (c) Zhong, Y.; Ni, Y.; Li, S.; Wang, M. RSC Adv. 2016, 6, 15831–15837.
(14) Panáček, A.; Kvitk, L.; Prucek, R.; Kolář, M.; Večeřová, R.; Pizůrová, N.; Sharma, V. K.; Nevečná, T.; Zbořil, R. J. Phys. Chem. B 2006, 110, 16248–16253.
(15) Kou, T.; Jin, C.; Zhang, C.; Sun, J.; Zhang, Z. RSC Adv. 2012, 2, 12636–12643.
(16) Chudasama, B.; Vala, A. K.; Andhariya, N.; Upadhyay, R. V.; Mehta, R. V. Nano Res. 2009, 2, 955–965.
(17) Schneider, B.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnemann, D. W. Chem. Rev. 2014, 114, 9919–9986.
(18) Zhou, D.-L.; Feng, J.-J.; Cai, L.-Y.; Fang, Q.-X.; Chen, J.-R.; Wang, A.-J. Electrochem. Acta 2014, 115, 103–108.
(19) Albo, J.; Sáez, A.; Solla-Gullón, J.; Montiel, V.; Irabien, A. Appl. Catal., B 2015, 176–177, 709–717.
(20) Xu, Y.-T.; Guo, Y.; Li, C.; Zhou, X.-Y.; Tucker, M. C.; Fu, X.-Z.; Sun, R.; Wong, C.-P. Nano Energy 2015, 11, 38–47.
(21) Chakravarty, A.; Bhownik, K.; Mukherjee, A.; De, G. Langmuir 2015, 31, 5210–5219.
(22) Huang, C.; Ye, W.; Liu, Q.; Qiu, X. ACS Appl. Mater. Interfaces 2014, 6, 14469–14476.
(23) Tsai, Y.-H.; Chanda, K.; Chu, Y.-T.; Chiu, C.-Y.; Huang, M. H. Nanoscale 2014, 6, 8704–8709.
(24) Tu, K.; Wang, Q.; Lu, A.; Zhang, L. J. Phys. Chem. C 2014, 118, 7202–7210.
(25) Pang, H.; Gao, F.; Lu, Q. Chem. Commun. 2009, 1076–1078.
(26) Giannousi, K.; Sarafidis, G.; Mourtikoudis, S.; Pantazaki, A.; Dendrinou-Samara, C. Inorg. Chem. 2014, 53, 9657–9666.
(27) Liu, L.; Ding, L.; An, W.; Liu, S.; Hu, J.; Liang, Y.; Cui, W. RSC Adv. 2016, 6, 29202–29209.
(28) Yang, L.; Luo, S.; Li, Y.; Yao, X.; Kang, Q.; Cai, Q. Environ. Sci. Technol. 2010, 44, 7641–7646.
(29) Yao, Q.; Gao, Y.; Gao, T.; Zhang, Y.; Harnooke, C.; Dong, A.; Liu, Y.; Xiao, L. Colloids Surf., B 2016, 144, 319–326.
(30) Li, M.; Wu, W.; Qiao, R.; Tan, L.; Li, Z.; Zhang, Y. J. Alloys Compd. 2016, 676, 113–119.
(31) Chen, S.-S.; Xu, H.; Xu, H.-J.; Yu, G.-J.; Gong, X.-L.; Fang, Q.-L.; Leung, K.-C.-F.; Xuan, S.-H.; Xiong, Q.-R. Dalton Trans. 2015, 44, 9140–9148.
(32) Abbas, M.; Torati, S. R.; Kim, C. Nanoscale 2015, 7, 12192–12204.
(33) Cao, J.; Li, J.; Liu, L.; Xie, A.; Li, S.; Qiu, L.; Yuan, Y.; Shen, Y. J. Mater. Chem. A 2014, 2, 7953–7959.
(34) Chalasani, R.; Vasudevan, S. ACS Nano 2013, 7, 4093–4104.
(35) Zhang, Y.; Xu, X.; Jia, Y.; Jin, Z.; Liu, J.; Huang, X. Eur. J. Inorg. Chem. 2011, 2011, 5096–5104.
(36) Zhang, T.; Yan, X.; Sun, D. D. J. Hazard. Mater. 2012, 243, 302–310.
(37) Gong, P.; Li, H.; He, X.; Wang, K.; Hu, J.; Tan, W.; Zhang, S.; Yang, X. Nanotechnology 2007, 18, 285604–285610.
(38) (a) Wang, J.; Yang, J.; Li, X.; Wang, D.; Wei, B.; Song, H.; Li, X.; Fu, S. Phys. E 2016, 75, 66–71. (b) Song, H. J.; You, S.; Jia, X. H.; Yang, J. Ceram. Int. 2015, 41, 13896–13902.
(39) Zhang, C.; Wang, X.; Sun, J.; Kou, T.; Zhang, Z. CrystEngComm 2013, 15, 3965–3973.
(40) Ghosh, S.; Das, R.; Chowdhury, I. H.; Bhana, P.; Naskar, M. K. RSC Adv. 2015, 5, 101519–101524.
(41) Bhattacharjee, A.; Ahmaruzzaman, M. Mater. Lett. 2016, 166, 171–174.
(42) Che, W.; Ni, Y.; Zhang, Y.; Ma, Y. J. Phys. Chem. Solids 2015, 77, 1–7.
(43) Liu, C.; Wang, F.; Liang, Q.; Liu, J.; Chen, Z.; Wang, S.-D. Ceram. Int. 2016, 42, 17916–17919.
(44) Alla, S. K.; Verma, A. D.; Kumar, V.; Mandal, R. K.; Sinha, I.; Prasad, N. K. RSC Adv. 2016, 6, 61927–61933.
(45) Shin, K. S.; Cho, Y. K.; Choi, J.-Y.; Kim, K. Appl. Catal., A 2012, 413–414, 170–175.
(46) An, Q.; Yu, M.; Zhang, Y.; Ma, W.; Guo, J.; Wang, C. J. Phys. Chem. C 2012, 116, 22432–22440.