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Robust microcapsules with polyurea/silica hybrid shell for one-part self-healing anticorrosion coatings

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Silica/polyurea hybrid microcapsules loaded with hexamethylene diisocyanate (HDI) as core materials were facilely prepared via a combined strategy of interfacial polymerization and *in-situ* sol-gel process in an oil-in-water emulsion, and clearly
¹⁵ characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The resultant microcapsules have diameter of 57-328 μm , shell thickness of 1-8 μm , and core fraction of 51.2-65.6 %. The diameter and shell thickness linearly related to the agitation rate in the double logarithm coordinates, and the core fraction linearly related to the agitation
²⁰ rate, indicating that the structure and component of microcapsules can be controlled effectively. The resistant properties for thermal and solvent were assessed by using

thermogravimetric analysis and titration. The results show that microcapsules had the outstanding thermal stability with the initial evaporation temperature (defined at 5 % of weight loss) increased by around 58 °C compared with that of pure core material and the good resistance to xylene with less than 25.9±0.7 wt.% reduction of core content after immersion for 100 h. Self-healing anticorrosion coatings based on microcapsules were fabricated on a steel substrate. Preliminary results indicated significant corrosion retardancy happened in the coatings under an accelerated corrosion process, showing the great potential of our microcapsules in development of catalyst-free, one-part self-healing coatings for corrosion control.

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Introduction

Corrosion of materials has attracted attention and concern for a long time due to bring considerable economic loss and even endanger human life. For the purpose of corrosion protection to various substrates surface, especially metal, the coatings mainly consisted of polymer matrix are applied universally. However, the cracks of coatings generated from the treating and using of materials lead to a re-exposure of protected metal substrate in the ambient environment, resulting in corrosion.

Microcapsules have been used extensively in many fields, such as biomedical applications,^{1,2} catalysis,^{3,4} thermal energy storage,⁵ and self-healing materials.^{6,7} Concerning the self-healing applications of microcapsules, the basic idea is a microcapsules-embedded approach. In other words, the microcapsules containing healable agents are embedded into materials matrix to achieve a self-healing of the

cracks. The healable agents are usually a flowable polymerizer. With or without catalyst, as cracks are formed in the materials because of mechanical fatigue, the embedded microcapsules are ruptured, meanwhile the encapsulated polymerizers are released, move into the cracks, form polymers, and finally re-bond the cracks. The first generation self-healing materials based on this embedding method of microcapsules with dicyclopentadiene (DCPD) core in the presence of Grubbs' catalyst particles were reported and developed by White et al.^{6,8-11} Moreover, they also explored the self-healing anticorrosion of epoxy coatings on metal substrate by the microcapsules-embedded approach.⁷

The above-mentioned self-healing materials are the typical examples of a so-called two-part self-healing system. The others include multi-part and one-part self-healing systems. Compared with the two-part and multi-part systems, the one-part system could be more promising in practical applications. Because it from one aspect minimizes the impact of introducing extra microcapsules to the material matrix, and from another aspect avoids the use of catalyst, which is of considerable economic importance. One of very promising candidates being available for one-part, catalyst-free self-healing materials is the microcapsules containing liquid isocyanates which are reactive with moisture. The microcapsules with polyurethane (PU) shell and isophorone diisocyanate (IPDI) or hexamethylene diisocyanate (HDI) core were obtained by an interfacial polymerization.¹²⁻¹⁴ The anticorrosion epoxy coatings containing the HDI microcapsules were covered on a steel substrate.^{13,14} The results indicated that the microcapsules-embedded coatings can autonomously heal the cracks of scratch, which significantly avoids corrosion happened in the cracks of coatings

under an accelerated corrosion process.

The one-part microcapsules-embedded approach seems to be realizing the termination of corrosion of materials in real life. However, as an universal and critical issue to microcapsules and other micro/nano-containers, unsatisfying resistant property is very terrible and must be overcome for a long-term storage and handling in practical applications. The prior strategies of improving resistant property of microcapsules mainly include preparing multi-layers structure microcapsules,¹⁵⁻¹⁷ introducing inorganic nanosheets into shell,¹⁸ and increasing shell thickness.¹⁹ But, their encapsulated substances had relative high chemical and physical stability. Most of them just focused on improving a single resistant property such as thermal resistance, and usually referred to multiple steps. Besides, the resultant microcapsules could not have quite good quality, and even some of them were hard to be collected. Thus, design and preparation of robust microcapsules with superior resistant property are quite significant and still extremely challenging for the application of self-healing anticorrosion coatings.

Herein, we present the robust microcapsules with polyurea/silica hybrid shell and HDI core which were facilely prepared via a combined strategy of interfacial polymerization and *in-situ* sol-gel process in an oil-in-water emulsion. The resultant microcapsules showed a significant improvement of thermal and solvent resistant properties. Besides, the structure and component of microcapsules can be controlled effectively. As an example application, the self-healing anticorrosion coatings are fabricated by dispersing the microcapsules into epoxy coating and displays good corrosion protection performance to steel substrates.

Experimental section

Materials

MDI pre-polymer (Suprasec 2644) was obtained from Huntsman. HDI (99%), gum arabic, tetraethyl orthosilicate (TEOS) (99.9%), polyethylenimine (PEI) (branched, $M_w \sim 25,000$), ammonium hydroxide solution (28-30%), hydrochloric acid aqueous solution (0.1 mol/L), bromophenol blue, sodium chloride (NaCl), and anhydrous *p*-xylene (99%) were obtained from Sigma-Aldrich. All chemicals in this study were used without further purification unless otherwise specified.

Preparation of microcapsules with silica/polyurea hybrid shell and HDI core

Preparation of microcapsules with HDI core being formed from MDI pre-polymer (Suprasec 2644), branched PEI with 25000 of M_w , and TEOS. Typical experimental procedure is as follows: At room temperature, 30 ml of 3 wt% gum arabic aqueous solution was prepared as surfactant solution in a 100 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller at a rate of 300 rpm and heated to 40 °C with a heating rate of 7 °C/min. The 0.97 g of MDI pre-polymer was mixed well with 4.8 g of HDI, and then this mixture was added into the prepared surfactant solution to develop an emulsion system. After 15 min, agitation rate and temperature were decreased to 150 rpm and room temperature, respectively. Then, diluted aqueous solution of 0.1 g of PEI (10 wt%) was dropwise added into the emulsion system to initiate the interfacial polymerization at the oil/water interface. After 30 min, the pre-

hydrolyzed TEOS as encapsulation precursor obtained by mixing and stirring 1 g of TEOS and 2 g of HCl solution (pH=2.2) at 35 °C for 30 min when the hydrolysis of TEOS was completed, was added dropwise, meanwhile 0.5 g of NH₄OH (28 wt%) was added slowly. The reaction was stopped after 60 min at room temperature, and the resultant microcapsules were washed with deionized water, filtered and air-dried at room temperature for 12 h before further analysis. The amount of dried microcapsules was about 4.5 g.

Morphology and statistic parameter of HDI microcapsules

The microcapsule formation during the reaction process was observed under an Axiotech optical microscope (Zeiss) equipped with a device camera (Sony). The surface morphology and shell thickness were examined by using scanning electron microscopy (SEM) (JOEL JSM-7600F FESEM). Mean diameter and distribution of microcapsules were determined from data sets of at least 200 measurements from SEM images and analyzed in Image-Pro Plus 6.0. For SEM observation, the samples were prepared as follow: firstly, microcapsules were well-distributed mounted on conductive adhesive tape, ruptured with a razor blade to measure shell thickness, and coated by gold.

Components of microcapsules

Pure HDI, shell and core of microcapsules were analyzed separately by using Fourier transform infrared spectroscopy (FTIR, Varian 3100) in order to confirm the constituents of the microcapsules. The spectrum in the range of 500 to 4000 cm⁻¹ was used for the observation. In order to collect the FTIR spectra of shell and core, small

amounts of microcapsules were crushed and washed by acetone for 5-7 times. After filtration and drying, pure core and shell were obtained for analysis, respectively.

Energy-dispersive X-ray spectroscopy (EDX) (JOEL JSM-7600F FESEM) was applied to reveal the elemental distribution in shell of microcapsules.

5 An X-ray photoelectron spectroscopy (XPS) (Axis-ultra, Kratos) was used to detect the chemical composition of shell. In the XPS experiment, a monochromatized Al K α X-ray source (1486.71 eV) was operated at a reduced power of 150 W (15 kV and 10 mA). The base pressure in the analysis chamber was 2.66×10^{-7} Pa. The measured binding energies were calibrated by the C1s (hydrocarbon C–C, C–H) of 285 eV.

10 **Thermal property and core fraction of microcapsules**

The thermal stability property and core fraction of microcapsules were characterized by using thermogravimetric analysis (TGA, Hi-Res Modulated TGA 2950). Typical experimental procedure is as follows: 10-20 mg of microcapsules was put in a platinum pan and heated under nitrogen atmosphere at a rate of 10 °C/min, or kept for
15 a certain time at 60 °C in air atmosphere. The peak width of the derivative of the weight loss curve was used to roughly determine the core fraction of microcapsules.

Solvent resistance

The resistant property of microcapsules with HDI core in solvent was assessed by the immersion test. Typically, 0.2 g microcapsules were immersed into 10 g anhydrous *p*-
20 xylene for a certain time at room temperature. Then 5 g upper clear liquid was absorbed and titrated by a standard method of ASTM-1572-97. The relative release percentage of HDI encapsulated in the prepared microcapsules (HDI_{release} wt%) was

calculated as follows:

$$HDI_{\text{release}} \text{ wt}\% = \frac{m_{(HDI\text{release})}}{m_{(HDI\text{encapsulated})}} \times 100\%$$

$$m_{(HDI\text{release})} = 2 \times m_{\text{solvent}} \times \frac{NCO\%}{1 - NCO\%}$$

$$NCO\% = \frac{(V_{\text{blank}} - V) \times C_{(HCl)} \times 0.042}{m_{\text{sample}}} \times 100\%$$

5 where NCO% is the percentage of NCO released into solvent, V_{blank} (ml) is the volume of standard HCl aqueous solution consumed by the blank, V (ml) is the volume of standard HCl aqueous solution consumed by the 5 g specimen, $C_{(HCl)}$ is the normality of standard HCl aqueous solution, 0.042 is the milliequivalent weight of the NCO group, m_{sample} (g) is the weight of specimen (5 g), $m_{(HDI\text{release})}$ (g) is the release
 10 weight of HDI in total microcapsules, m_{solvent} (g) is the weight of solvent (10 g), $m_{(HDI\text{encapsulated})}$ (g) is the total weight of HDI encapsulated in the initial microcapsules.

Preparation and observation of anticorrosion self-healing coating

Anticorrosion self-healing coatings were prepared by dispersing 10 wt% of synthesized microcapsules into epoxy resin (EPOLAM 5015) at room temperature,
 15 followed by mixing hardener (EPOLAM 5015). The mixture was degassed for 20 min under vacuum. A piece of steel plate with 5 × 5 cm size was polished by sand paper (grain size 350-400), degreased by acetone, and then washed by distilled water. After being dried, the steel plate was coated by the degassed self-healing coating with about 500-550 μm of thickness. After epoxy was cured completely at room temperature,
 20 scratches were applied manually on the coating by razor blade. Specimens were

immersed in 10 wt% of NaCl solution for 48 h to evaluate the accelerated corrosion process. Pure epoxy coating with the same thickness and size was prepared as a control and treated in the same manner for comparison. Corrosion situation was recorded by optical photography. The scribed areas were inspected by SEM (JEOL 5 JSM 5600LV SEM) to examine the self-healing performance.

Results and discussion

Preparation and characterization of microcapsules

As shown Scheme 1, an oil phase containing Suprasec 2644 and HDI was first dispersed into gum arabic aqueous solution to generate an oil-in-water emulsion. 10 When PEI was introduced, the primary polymerization reaction between the amino groups of PEI in the aqueous phase and isocyanate functional group in the oil phase would take place at the oil/water interface to produce a polyurea shell with positive charges surrounding the oil droplets. MDI prepolymer was much more reactive than HDI, and hence the primary reaction was between PEI and prepolymer to form the 15 shell structure, while the relatively less reactive HDI liquid was encapsulated as core material. Then the silica precursors obtained by the pre-hydrolysis of TEOS in hydrochloric acid aqueous solution with 2.2 of pH were added dropwise into the emulsion, and were attracted onto the surfaces of polyurea shell through electrostatic and hydrogen-bonding interactions between amino groups and silanol groups. It is 20 well known that the hydrolysis rate of TEOS is significantly higher than the condensation rate of the silica precursors at around 2.0 of pH closing to the isoelectric point of silica.²⁰ The resultant silica precursors including alkylsilanols and silanols are

water-soluble and transparent. Since mixing the silica precursors with emulsion, ammonia water was added dropwise into reaction system to increase pH values, resulting in an acceleration of the condensation rate of silica precursors, and thus, silica component is successfully hybridized in the polyurea shell through this sol-gel process. In addition, there were some side reactions between NCO groups from prepolymer, intermediate polyisocyanates, and HDI and hydroxyl groups from water, amino groups from NH_4OH . These side reactions also eventually produced polyurea as shell wall. But, to identify precise chemical compositions of shell wall material is beyond the scope of this study.

The nearly spherical shaped microcapsules with $328.9 \pm 92.9 \mu\text{m}$ of mean diameter were obtained as shown in Fig. 1a and d. It is seen that the microcapsules have obvious core-shell structure, and there are many particles on the outer surface of the capsules (Fig. 1b). Besides, as shown in Fig. 1c, the shell is quite compact, and the shell wall thickness is roughly uniform and about $8 \mu\text{m}$, which acts as an appropriate barrier from leakage and provides enough mechanical stiffness from rupture during post processing.

By FTIR, the chemical structure of the microcapsules was characterized. As shown in Fig. 2, pure HDI, capsule shell, and capsule core were investigated. The nearly identical spectra for HDI and core material indicated that HDI was successfully encapsulated and no prepolymer was included due to the absence of signal peaks at 1641.5 cm^{-1} and 1540.7 cm^{-1} .¹³ For the shell, the characteristic signal at 1071.2 cm^{-1} are attributed to asymmetric Si-O-Si stretching vibrations of the silica component, and signal peaks at 3311.6 cm^{-1} , 1635.9 cm^{-1} , and 1228.2 cm^{-1} are respectively assigned to

hydrogen-bonded N-H stretching vibrations, hydrogen-bonded carbonyl stretching band, and C-N stretching vibrations of polyurea component, indicating the silica/polyurea hybrid structure.

Moreover, the presence of the oxygen, nitrogen, carbon, and silicon peaks in EDX spectrum of the microcapsules' shell also reflects the hybrid shell component (Fig. 3a). By the XPS on the surface of microcapsules' shell, the oxygen, nitrogen, carbon, and silicon were detected further. Fig.3b depicts the survey spectrum recorded for the microcapsules' shell. The obvious signal peaks of four elements can be observed, as expected. By deconvolving the C 1s and Si 2p peaks, various components can be obtained. Typically, two components were identified as O=C-NH bonds (288.7 eV) and O-Si (102.8 eV) bonds, which clearly confirms the hybrid shell structure consisting of silica and polyurea.

Control of structure and core fraction of microcapsules

In the development of microcapsules-based self-healing materials, proper control of microcapsule size is a critical issue due to the great influence of diameter on the self-healing performance.¹¹ Actually, in some cases, only the microcapsules with a given range of diameters are suitable. Herein, the average diameter of microcapsules was primarily controlled by the agitation rate. As illustrated in Fig. 4, a higher agitation speed resulted in smaller microcapsule diameter. The relation between mean diameter and agitation rate was linear in the double logarithm coordinates, being consistent with the previous reports.^{21,22} At higher agitation rate, the stronger shear force led to the formation of finer oil droplets in the emulsion system, and the final

microcapsules had accordingly a smaller size. By adjusting agitation rate from 300 to 1000 RPM, microcapsules with average diameter in the approximate range of 328-57 μm were obtained.

The influence of agitation rate on the average shell thickness was also given in Fig. 4, which clearly showed that the shell thickness reduced as increasing agitation rate and their relation was linear in double logarithm coordinates. As mentioned above, at higher agitation rate, the generated oil droplets were finer, implying that total specific surface area of oil droplets was larger. When the amount of core materials was fixed and shell materials remained constant, the amount of shell materials surrounding each oil droplet would therefore be less, resulting in the thinner shell wall of the resultant microcapsules. By changing agitation rate from 300 to 1000 RPM, the average shell thickness of microcapsules can be controlled in the range of about 8-1 μm .

Besides, the core fractions of the microcapsules also can be adjusted through changing the agitation rate. As shown in Fig. 5, faster agitation led to lower core fractions, and the HDI content in the microcapsules reduced from 65.6 % to 51.2 % with the increase of agitation rate from 300 to 1000 RPM. The reason could be that the water across the thinner capsule shells formed at the higher agitation rates was easier, and accordingly more HDI was consumed by the water. Thus, the core fraction in the final microcapsules was lower at higher agitation rate.

Thermal and solvent resistances of microcapsules

In practical applications, microcapsules have to be robust enough to survive various rigorous environments during materials processing cycle, such as solvent, moisture,

exothermal reaction, acid/base, and so on.^{15,19,23} However, the preparation of robust microcapsules with superior resistant property, especially regarding to solvent and thermal attacks, is still greatly challenging.

As shown in Fig. 6a, the TGA gave the content of HDI in core which was about 5 65.6 %, indicating that the HDI was encapsulated effectively. Remarkably, the initial evaporation temperature (defined at 5 % of weight loss) at 144 °C of resultant microcapsules was obviously higher than that of pure HDI (about 86 °C), indicating an excellent thermal resistant property of the microcapsules. In addition, the isothermal experiment of microcapsules in air atmosphere showed that the residual 10 weights after heated for 12 h at 60 °C was 86.5% (Fig. 6b), showing the thermal stability of HDI in the tight-shell capsules was significantly improved in comparison with that of pure HDI (Fig. 6b). The primary reason to result in such a tremendous improvement of thermal stability could be the highly crosslinked shell to protect the leakage of liquid core upon heating.

15 For the application of self-healing anticorrosion coatings, the good resistance of microcapsules for solvents must be highlighted. Since microcapsules are emerged into a solvent like xylene or toluene as diluted agent in practical coating system, the solvent diffuses into the core domain and transfers the core materials out of microcapsules, which could significantly reduce the self-healing efficiency. By 20 titration according to ASTM-1572-97, the resistant property of silica/polyurea hybrid microcapsules in xylene was investigated. It was found from Fig. 7 that the relative released percentage of HDI calculated from titration results gradually reached a plateau after 100 h immersion, and the final value was 25.9 ± 0.7 wt.%, reflecting a

good resistance to xylene as low polar organic solvents with 2 wt.% concentration for a certain period at room temperature.

Corrosion protection assessment of self-healing coating

Following the procedure described above in experiment, epoxy coated 5×5 cm steel panels were prepared. After curing at open air for 24 h, scratches were applied manually on the self-healing coating and pure epoxy coating as a control by razor blade (Fig. 8a and d). After that, these two specimens were immersed in 10 wt% NaCl aqueous solution at room temperature for 48 h to evaluate the accelerated corrosion process. It can be seen from Fig. 8e that scratched areas of the self-healing coating was nearly fully free of rusts after 48 h immersion in salt solution. In contrast, a number of rusts can be found in the control specimen (Fig. 8b). Indeed, there was no obvious corrosion on steel panel peeled off the self-healing coating (Fig. 8f), while the severe corrosion was on surface of steel panel for control specimen (Fig. 8c). The results clearly demonstrated the excellent corrosion protection of the prepared self-healing coating towards the steel panel.

The anticorrosion performance was attributed to a self-healing ability of the microcapsules-embedded coating.¹³ The self-healing mechanism being different from the nanocontainers-based anticorrosion coating^{24,25} was that the released HDI from ruptured MCs at scratched areas reacted with moisture or water to form solid materials, filling the crack. The crack was in this way sealed and healed autonomously to retard diffusion of salt ions and thus protect substrate from corrosion process. This mechanism can be supported by SEM observations showing the cracks

of top (Fig. 9a,b) and bottom (Fig. 9c,d) surfaces for the scratched areas of self-healing coating were filled by newly formed material. The healing process of microcapsules with silica/polyurea hybrid shell and HDI core in epoxy coating was completely autonomous, and it did not require any catalyst or external intervention. So, this microcapsule is available to develop self-healing anticorrosion coating.

Conclusions

The spherical silica/polyurea hybrid microcapsules with HDI core were obtained by a combined strategy of interfacial polymerization and *in-situ* sol-gel process in an oil-in-water emulsion. The diameter, shell thickness, and core fraction of the resultant microcapsules can be controlled in the range of 57-328 μm , 1-8 μm , and 51.2-65.6 %, respectively. The initial evaporation temperature (144 $^{\circ}\text{C}$) of HDI (near 5 % of weight loss) for silica/polyurea hybrid microcapsules was obviously higher than that of the pure HDI (85.8 $^{\circ}\text{C}$), and the isothermal experiments at 60 $^{\circ}\text{C}$ in air atmosphere for 12 h showed that the final residual weight (86.5 %) of microcapsules was remarkably higher than that of pure HDI, indicating a outstanding thermal resistant property of our microcapsules. Besides, after microcapsules were immersed in xylene with 2 wt.% concentration for 100 h, the relative released percentage of HDI was 25.9 \pm 0.7 wt.%, indicating that the resultant microcapsules had an good xylene resistant property. For the accelerated corrosion process, the scratched areas of the 5 \times 5 cm steel panel coated with microcapsules-embedded self-healing coatings was nearly fully free of rusts after 48 h immersion in 10 wt.% NaCl aqueous solution at room temperature. In contrast, a number of rusts can be seen in the control specimen. The

result clearly demonstrated the excellent corrosion protection of the self-healing coating towards the steel panel under an accelerated corrosion process, revealing a great potential of our microcapsules in development of catalyst-free, one-part self-healing coatings for corrosion control.

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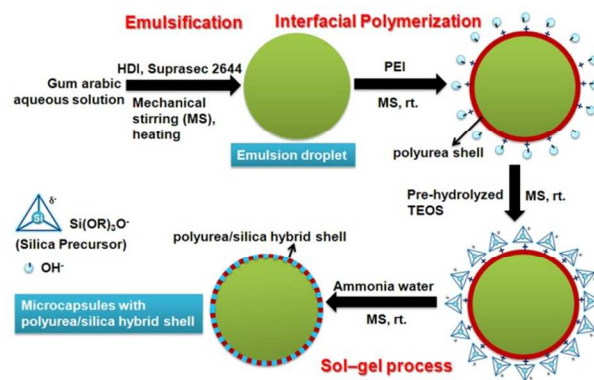
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Scheme

Scheme 1 Preparation of microcapsules with polyurea/silica hybrid shell and HDI core.



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Scheme 1

Figure Captions

Fig. 1 SEM images of (a) microcapsules, (b) their outer surface and (c) shell wall profile. (d) The histograms of microcapsules' diameter distribution

Fig. 2 FTIR spectra of microcapsules shell, microcapsules core, and pure HDI.

Fig. 3 (a) EDX spectrum of microcapsules' shell. (b) XPS survey spectrum of microcapsules' shell. (c) C 1s and (d) Si 2p core line spectra obtained from microcapsules' shell, respectively. (■) Observed data; (---) theoretical calculated spectra; (—) individual components.

Fig. 4 Diameter and shell thickness of microcapsules obtained at different agitation rates.

Fig. 5 Core fraction of microcapsules obtained at different agitation rates.

Fig. 6 (a) TGA weight loss curve of microcapsules and pure HDI with 10 °C/min of heating rate in N₂ atmosphere. (b) TGA isothermal curve of microcapsules and pure HDI at 60 °C in air atmosphere.

Fig. 7 Relative released percentage of HDI after microcapsules were immersed in xylene for different time. Concentration of microcapsules is 2 wt%.

Fig. 8 Corrosion test results for steel panels coated with control and microcapsules-embedded epoxy coating (10 wt% of content of microcapsules), respectively. Control coating: (a) before, (b) after immersion, (c) steel panel peeled off the coating after immersion. Microcapsules-embedded coating: (d) before, (e) after immersion, (f) steel panel peeled off the coating after immersion. The panels were immersed in 10 wt% NaCl solution for 48 h.

Fig. 9 SEM images of the scratched regions of top (a), (b) and bottom (c) (d) surfaces for the self-healing coating after 48 h immersion in salt water.

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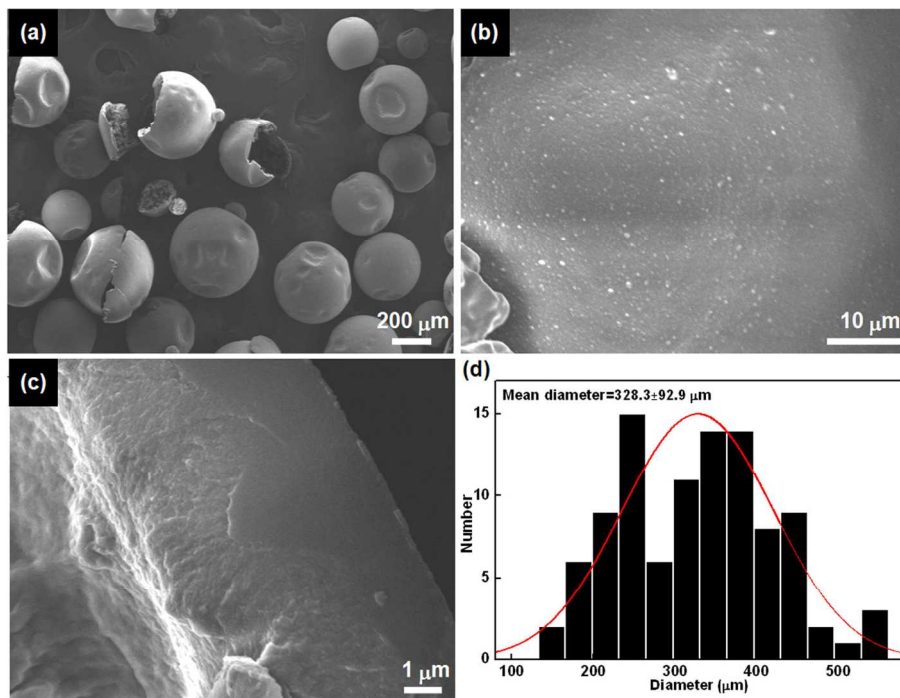


Fig. 1

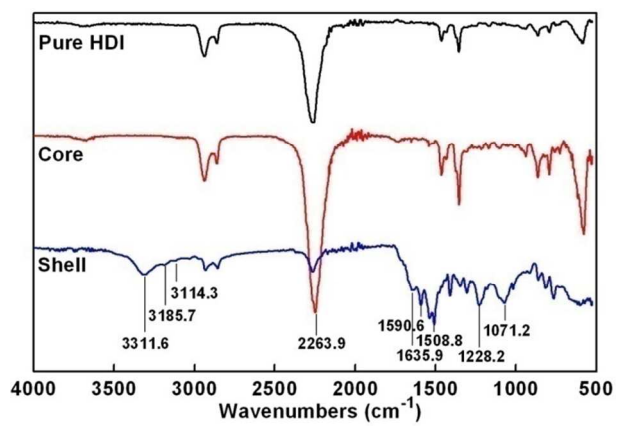


Fig. 2

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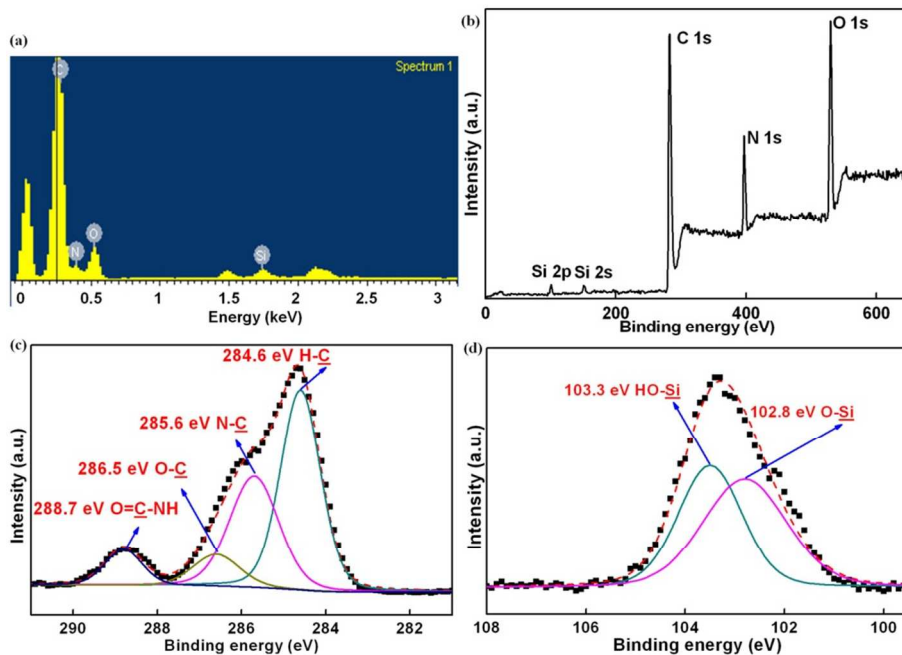


Fig. 3

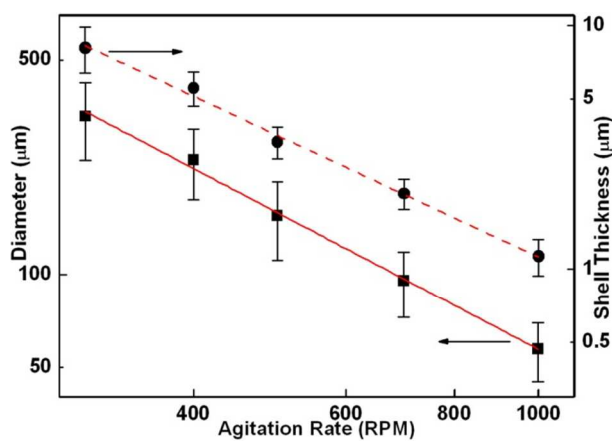


Fig. 4

5

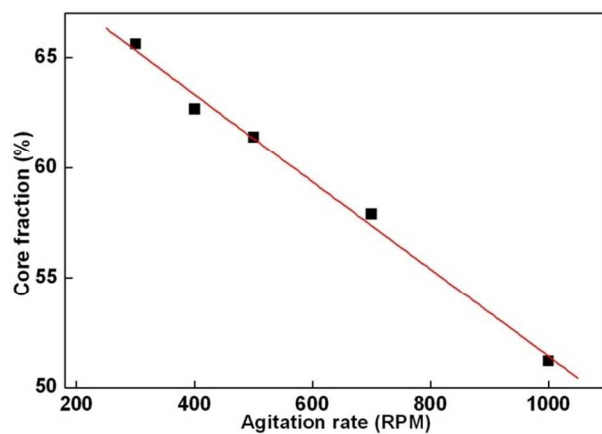


Fig. 5

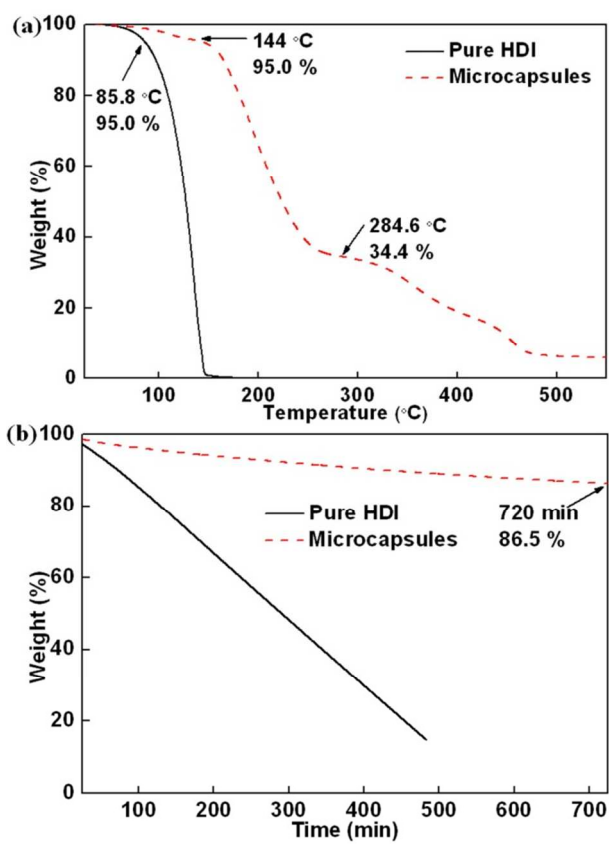


Fig. 6

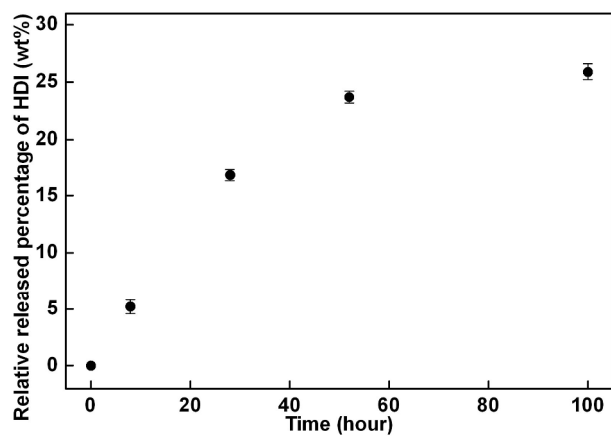


Fig. 7

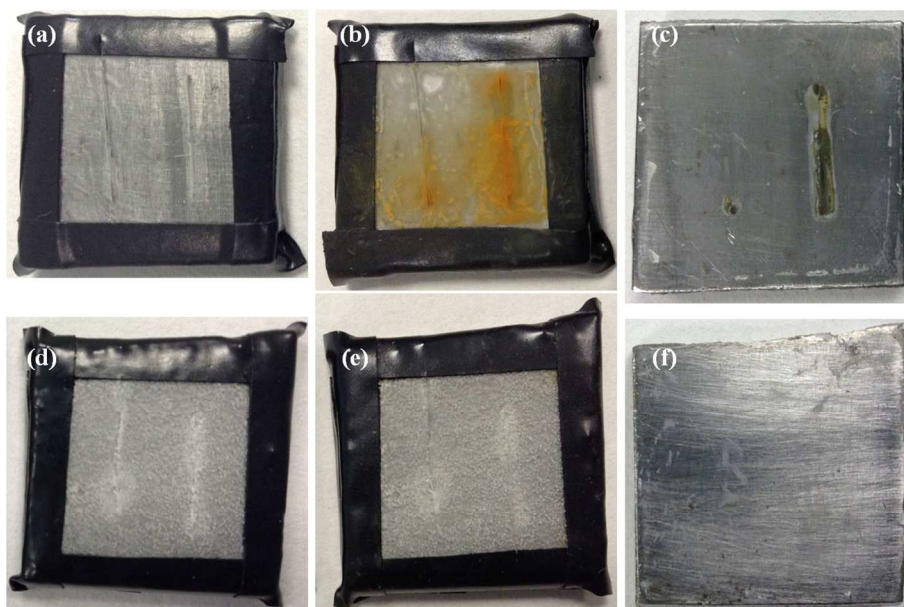


Fig. 8

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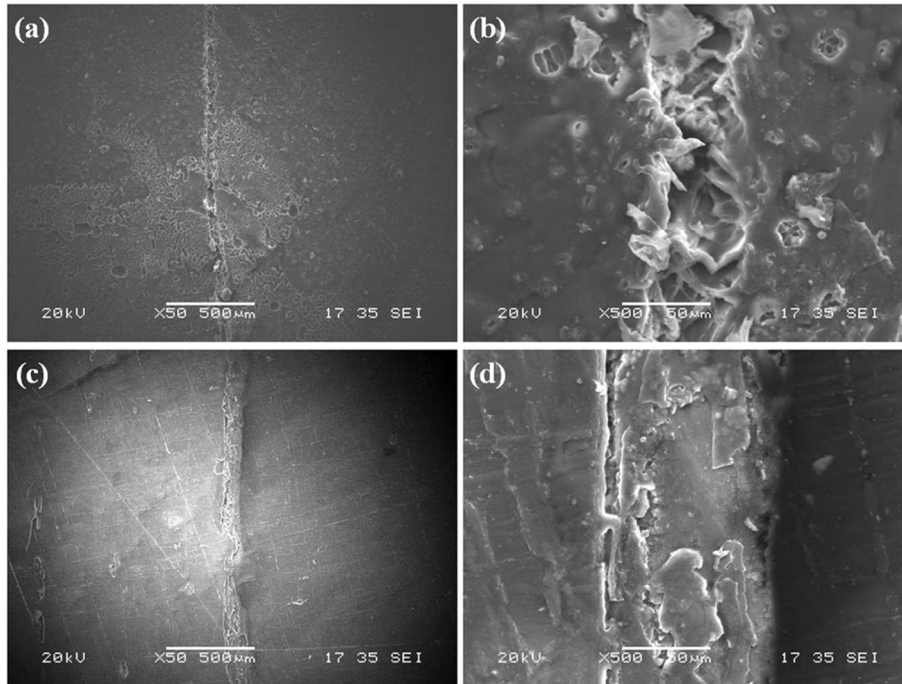
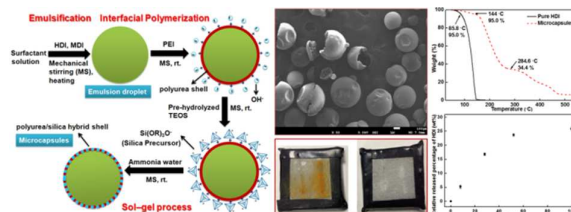


Fig. 9

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HDI-filled silica/polyurea hybrid microcapsules with superior thermal stability and solvent resistance were prepared and applied to one-part self-healing anticorrosion coatings.