Preparation and properties of NIR-Responsive microcapsules

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Keywords: photo-sensitive, near infrared responsive, microcapsule, information recording material, coating, polyurea

Abstract
In this paper, near infrared (NIR) absorbing dye and fluorane dye (FD) was successfully encapsulated into microcapsules with NIR light responsive performance. The NIR responsive microcapsules are able to be utilized in information recording and anti-counterfeiting fields. Specifically, the factors effecting on synthesis of NIR responsive microcapsules were studied in detail. Microcapsules with an average particle size of 0.2 ~ 0.5 μm were prepared by adjusting the mass ratio of shell/core material, the viscosity of oil phase and the mass ratio of water/oil (W/O) phase. It was found that the preferred reaction condition was the feeding mass ratio of shell/core materiel at 1:2 and the W/O phase mass ratio of 2:1. When the feeding mass ratio of NIR absorbing dye and FD is 1/10, the NIR responsive microcapsules have the best coloration performance. Then the NIR responsive microcapsules were coated on aluminum substrate and scanned by 808 nm near-infrared laser, the image precision reached 20 μm.

1. Introduction

Information-recording materials, which act as multifunctional materials, have been widely utilized in printing, photography, medicine, coating, and so on, due to their stimuli responsive property. There are various information-recording materials such as magnetic materials and photo-sensitive materials such as silver salt materials and ink jet materials [1]. However, the magnetic materials and silver salt materials always suffer from complicated preparation processes and high cost, and it is desirable to develop novel materials with facile fabrication and low cost.

Microcapsule material has drawn much attention in the information recording field due to its easy preparation and low-cost properties. A microcapsule is mainly composed of a core and shell. The core can be drugs, catalysts, dyes and phase change materials, and so on, which are protected from the outside environment stimuli, such as pH, surface pressure, temperature, and UV. Typically, thermal-responsive microcapsule has been widely used in medical imaging, printing, and photographic fields. However, thermal-responsive microcapsule cannot realize high image resolution printing, which is limited by the size of the thermal printing head. This material has the problems of probe pollution and printing accuracy decline because it requires the printing head to closely contact with microcapsule materials during recording. So, the photo-responsive microcapsules which use non-contacting recording mode by exposure or scanning has aroused research attention. UV light-responsive microcapsules were reported, but the UV light is known to cause skin and eye damage and ozone pollution, and poor penetration. Hence, it is important to develop photo-responsive systems upon longer (safer) wavelength irradiation.

So we fabricated a near infrared (NIR)-responsive microcapsules system to integrate the advantages of thermal-responsive microcapsules and UV photo-responsive microcapsules. It can be used for medical imaging materials. Different from thermal-responsive microcapsules, it uses non-contact imaging mode which improved imaging accuracy.
The chromogenic imaging mechanism of the NIR-responsive microcapsules is shown in Scheme 1. The NIR absorbing dyes (in the microcapsule) produce thermal effects that increase the permeability of shell, allowing the chromogenic agent (out of the microcapsule) penetrate into the microcapsule and react with the fluorane dye (FD) (in the microcapsule) by stimulation with a NIR light or NIR laser. FD of the lactone structure becomes a colored quinone structure, due to the chromogenic reaction of FD with the chromogenic agent (CA) [16,17].

Preparation methods of microcapsules include in situ/interfacial polymerization [10,18–20], emulsion polymerization [21], hierarchical assembly [9,22], optical heating technology [23], and nanometer interfacial complexation [24]. In this study, NIR-responsive microcapsules were prepared using an interface polymerization technology. The NIR absorbing dye (IR-813) and FD (ODB-2) were encapsulated as core materials with polyurea as the shell material. The schematic diagram of the microcapsules formed by interfacial polymerization is shown in Scheme 2. Oil-in-water emulsion was formed by high-speed shearing (Scheme 2(a)). Then another shell-forming material (H₂N-R’-NH₂) was added in O/W emulsion. The temperature was raised to the reaction temperature, then interfacial reaction starts at the interface between the water phase and the oil droplets (Scheme 2(b)). The scheme of interface reaction is shown in the Scheme 2(c).

The factors influencing the synthesis of the NIR-responsive microcapsules were studied in detail, including the mass ratio of the shell–core materials, the viscosity of the oil phase, and the mass ratio of the water–oil phase. Microcapsules with an average particle size of 0.2–0.5 μm were prepared. The microcapsules had the best color performance with an optical density (OD) up to 0.35 when the amount of NIR absorbing dye was 1/10th of the mass of FD. Then, the NIR-responsive microcapsules were coated on an aluminum substrate and exposed with an 808 nm infrared (IR) laser, which has an image precision of 20 μm. This method has the advantages of simplicity, high yield, high maturity, and easy applicability in industrial production.
2. Experiment

2.1. Materials

IPDI (isophorone diisocyanate) was purchased from Shanghai Aoke Industrial Co. Ltd. D-110N (Triisocyanate compound 75 wt% ethyl acetate solution, industrial grade) were purchased from Mitsui Chemical Co. Ltd. Tetraethylene pentamine (TEPA) (mass fraction 95%) was purchased from Beijing Enokai Technology Co. Ltd. 2-phenylamino-3-methyl-6-dibutylamino-fluorane (ODB-2) was purchased from Hebei Jianxin Chemical Co. Ltd. The NIR absorbing dye (IR-813) was purchased from Hubei Gurun Co., Ltd. 4’-hydroxy-4’-isopropoxy diphenylsulfone (D-8) was purchased from Zhangjiagang Gangda New Material Technology Co., Ltd. PVA224 was purchased from Japan Kalli Co. Ltd. The emulsifier alkylphenol polyoxyethylene ether (OP-10) was purchased from Jiangsu Hai’an petrochemical plant. Ethyl acetate, analytical pure, was purchased from Sinopharma Chemical Reagent Co. Ltd. Unless otherwise noted, the above materials were industrial grade and employed without further purification.

2.2. Preparation of Microcapsules

2.2.1. Preparation of the Oil Phase (O)

6.0 g ODB-2, 0.6 g IR-813 (chemical structure were shown in figures S3, SI is available online at stacks.iop.org/MRX/7/116408/mmedia), 35 g ethyl acetate and 3.0 g isocyanate IPDI or D-110N were added to a round-bottomed flask, then stirred and heated reflux to become a homogeneous phase, which become oil phase.

2.2.2. Preparation of the Water Phase (W)

10 g PVA224 was added to deionized water, heated and stirred well, yielding 200 ml of PVA224 (5 wt%). Then, 0.4 g OP-10 was added to the solution and stirred well to prepare the water phase.

2.2.3. Preparation of the NIR-Responsive Microcapsules by Interfacial Polymerization

45 g total mass of oil phase was poured into 90 g water phase under shear agitation at 10,000 RPM and emulsified for 10 min to form the oil-in-water (O/W) emulsion. Then, 40 ml deionized water and 2.6 g TEPA (at an equal molar ratio to the IPDI) were slowly added. The reaction solution was stirred at 60 °C for 3.5–4 h, then stopped when the isocyanate peak (2258 cm⁻¹ for N=C=O) disappeared by Fourier transform infrared spectrometer (FTIR), which indicated the reaction had finished. Then, the obtained microcapsules suspension was centrifuged at 1,000 RPM for 10 min to separate out the ODB-2 and IR-813 not wrapped in the microcapsules. Finally, the NIR-responsive microcapsule suspension was obtained.
2.3. Preparation of the Chromogenic Agent (CA) Dispersion

20 g D-8, 180 g PVA224 (3 wt% aqueous solution), and 10 g OP-10 (10 wt% aqueous solution) were blended into an agate jar and ball-milled for 8 h at a speed of 400 RPM with a QM-3 SP2 planetary ball mill (Nanjing Nanda Instrument Plant). The CA dispersion was obtained with particle size in the micron dimension.

2.4. Preparation of the NIR-responsive microcapsule coating

The NIR-responsive microcapsule suspensions prepared with different masses of IR-813 were mixed with the CA dispersion D-8 at a mass ratio of 3:1 to obtain the mixed coating solution. The mixed coating solution was coated on a substrate (glass or aluminum) with an RDS coating rod and then dried at 60 °C for 2–5 min to obtain the NIR-responsive microcapsule coating with a thickness of about 1.0 μm measured by a CHY-CA thickness tester.

2.5. Characterization

2.5.1. Detection methods

FTIR was utilized to inspect the microcapsule formation process, 2258 cm\(^{-1}\) for N=C=O decreased as reaction time increased (shown in figure 1(a)). FTIR was also utilized to determine the chemical composition of the microcapsule (shown in figure 1(b)). From the blue curve in figure 1(b), 1750 cm\(^{-1}\) is the lactone carbonyl peak of ODB-2, and 910 cm\(^{-1}\) is the C–H bending vibration peak of the HC=CH bond of IR-813, which indicates that ODB-2 and IR-813 are encapsulated in the microcapsule. FTIR was also utilized to determine the changes of mass ratio of ODB-2 and IR-813 before and after centrifugation of NIR microcapsules suspension (shown in figures S2, S1). The results showed that the mass ratio of ODB-2 and IR-813 capsulated was basically equal to feed ratio, only slightly decreased. The NIR-responsive microcapsule formation process was observed by transmission electronmicroscope (TEM) (HT7700), shown in figures S4, S1. The morphology of the NIR-responsive microcapsules was obtained by scanning electron microscopy (SEM) with S-4800. The size of NIR-responsive microcapsules was measured by Dynamic light scattering (DLS) with Mastersizer 2000. The coloration of the microcapsules varied with the laser power as measured by real-time infrared (RT-FTIR) and UV-visible spectrophotometer. The exposure experiment was done with an IR laser machine (MDL-III-808-5W), which was purchased from Changchun New Industry Optoelectronic Technology Co. Ltd. The scanning imaging test was done with a CTP plate maker (Trendsetter 800 III) that had a 32-channel 1.5 W 808 nm laser. The reflective optical density (OD) of NIR microcapsule coating after exposure was measured with an optical reflection densitometer, which was purchased from American Essalene Company. The imaging OD is according to the formula

\[
OD = OD_{\text{max}} - OD_0
\]

where \(OD_{\text{max}}\) and \(OD_0\) is the OD of the exposure region and non-exposure region, respectively.

2.5.2. UV–visible spectra before and after IR laser exposure

A UV-visible spectrophotometer (Hitachi u-3000 UV–vis spectrophotometer) was used to detect the coloration of ODB-2 (UV absorption peaks at 460 and 590 nm with a scanning range of 200–900 nm). The microcapsules with a 1/10 feeding mass ratio of IR-813 and ODB-2 were mixed with the D-8 dispersion at a mass ratio of 3:1,
coated on quartz colorimetric dishes, dried and tested. The laser power density gradually increased from 2.0 to 3.4 W cm\(^{-2}\), and the exposure time was 10 s. The distance between the laser head and the sample was 5 cm.

2.5.3. RT-FTIR measurement of the ODB-2 conversion

The coloration conversion of the NIR-responsive microcapsules was determined by real-time infrared spectra (RT-FTIR). The mixtures of NIR responsive microcapsules and D-8 at different ratios were placed on KBr crystals and then exposed with an IR laser at radiation power densities of 2.7 and 3.5 W cm\(^{-2}\). The time-dependent conversion of the microcapsule’s coloration was recorded by monitoring the decay of the lactone bond peak of ODB-2 in the range from 1736 to 1758 cm\(^{-1}\) under IR irradiation. Thus, the conversion was calculated by measuring the in situ peak area with prolonged reaction time according to the formula:

\[
\text{Conversion(\%)} = \frac{A_0 - A_t}{A_t} \times 100\%,
\]

where \(A_0\) and \(A_t\) correspond to the peak areas of the lactone bond at 0 s and at time \(t\) under irradiation, respectively.

3. Results and discussion

3.1. Factors Influencing the Preparation of the NIR-responsive microcapsules

3.1.1. Effect of the mass ratio of shell and core materials on microcapsule morphology and size

The morphology and size of the microcapsules were studied when the feeding mass of IPDI was 2.0 g, 3.0 g, 6.0 g and 18.0 g, accounting for 1/3th, 1/2th, 1/1 and 3/1 the mass of ODB-2, respectively, the mass of remaining substances described as section 2.2. We investigated the morphology of the microcapsule via SEM, and the particle size was measured by DLS. The corresponding data are displayed figure 2.

As indicated in figure 2(a), at a mass ratio of 1:3, the mass of IPDI was too small to encapsulate the core during shell formation, so the microcapsules adhered together, causing poor microcapsule stability. As the mass of IPDI increased, the morphology of the microcapsules became uniformly spherical, which were not adhesive and had clear outlines (figures 2(b) and (c)). As the mass of IPDI continued to increase, the average microcapsule particle size increased (figure 2(d)), which improved the stability of the microcapsules\cite{12} due to their smaller specific surface area. In contrast, high doses of IPDI caused the oil phase to disperse and the interfacial reaction to be insufficient during the emulsification stage (figure 2(d)). So, a feeding mass ratio of shell/core material at 1:2 was selected as the preferred reaction condition.

Figure 2. SEM images of microcapsules formed from different feeding mass ratios of IPDI and ODB-2. (a) 1:3. (b) 1:2. (c) 1:1. (d) 3:1. (e), (f) Particle size distribution plots of the microcapsules corresponding to SEM images (b) and (c).
3.1.2. Effect of the shell material viscosity on the particle size distribution of microcapsules

When using D-110N and IPDI as the shell materials, the average particle size and distribution width of the microcapsules synthesized by D-110N were larger than that of IPDI (figure 2(e) and figure 3(b)). The viscosity of D-110N (500 mPa·s, 20 °C) was higher than that of IPDI (15 mPa·s, 20 °C). When other conditions are equal, higher viscosity makes it more difficult for small particles to disperse. Therefore, the particle size of the microcapsules can be controlled by adjusting the viscosity of the oil phase to regulate the droplet size at the emulsification stage.

3.1.3. Effect of the water-oil (W/O) mass ratio on the particle size distribution of microcapsules

When the concentration of the PVA solution is fixed, 5 wt%, the mass ratio of the W/O phase determines the particle size and distribution of the microcapsules. The morphology and the size measurement of microcapsules were shown in figure 4 and Figures S5, SI, respectively. During microcapsule formation, PVA aqueous solution, as a stabilizer, reduces the surface energy of oil droplets and prevents oil droplet coalescence \[20\]. We fixed oil phase mass as 45 g, then changed water phase mass as 45 g, 90 g and 180 g, respectively, the mass of remaining substances described as section 2.2. As shown in figure 4, when the W/O phase mass ratio increased, the average particle size decreased, and the distribution became narrower. This shows that increasing the W/O phase mass ratio is an effective way to reduce particle size. However, when the oil phase mass concentration was too low, the number of microcapsules that were produced was too small. So, a W/O phase mass ratio of 2:1 was selected as the preferred reaction condition.

3.2. Effect of IR-813 Mass on the Microcapsule Coating OD

The properties of the microcapsules were studied when the feeding mass of IR-813 was 0.3 g, 0.6 g, and 3 g accounting for 1/20th, 1/10th, and 1/2th of the mass of ODB-2, respectively, the mass of remaining substances described as section 2.2. The morphology and the size measurement of microcapsules were shown in figure 5 and Figures S6, SI, respectively. When IR-813 was 0.6 g, the microcapsules have a clear outline and uniform average particle size (figures 5(b), 5(e)).

The microcapsule coatings with different feeding masses of IR-813 as the core material (mass of ODB-2 is fixed) were exposed with an 808 nm NIR laser at an energy density of 9.2 J cm\(^{-2}\). The OD data are given in table 1. As can be seen from table 1, when there is no IR-813 in the microcapsules, the microcapsules have weak NIR response (table 1, No. 0 control group), even with the addition of an IR absorbing dye into the mixed
coating solution. Therefore, it is essential to encapsulate IR-813 in the microcapsules to achieve an NIR-responsive performance. When IR-813 was added directly to the mixed coating solution, the IR absorbing dye aggregated and could not effectively transfer heat to the microcapsules, so the OD was rather low (Table 1, No. 1, 3). When the encapsulated amount of IR-813 was insufficient, the photothermal conversion efficiency was low and the OD was low (Table 1, No. 2). Increasing the feed amount of IR-813 greatly improved the OD in the exposure area (Table 1, No. 4). When the encapsulated amount of IR-813 reached saturation, further increasing the amount of IR-813 did not improve the OD, and even caused it to decline (Table 1, No. 5) because the excess infrared dye reduced the stability of the microcapsules.

So, the experiments show that when other conditions are equal, the mass ratio of IR-813 and ODB-2 affect the OD of the microcapsule coating. The most suitable feeding mass of IR-813 is 0.6 g, which accounts for 1/10th of the mass of ODB-2.

### 3.3. Effect of laser power density on the NIR responsive microcapsule coloration

The coloration of ODB-2 at different IR laser power densities was detected by a UV-visible spectrophotometer (shown in Figure 6). The coloration kinetics of ODB-2 at different IR laser power densities and exposure times was studied by RT-FTIR (shown in Figure 7).

From Figure 6(a), the absorption peaks at 460 and 590 nm of ODB-2 gradually increased because of the chromogenic reaction of ODB-2 under continuous IR laser irradiation. Meanwhile, the absorption peak at 830 nm gradually decreased due to the photo-bleaching effect of IR-813 [25]. The chromogenic reaction mechanism of ODB-2 is shown in Scheme 1(d). Figure 6(b) shows the absorbance difference values of the absorption peak at 590 nm plotted against the IR laser power. The NIR-responsive microcapsules have the lowest chromogenic threshold (> 26 J cm\(^{-2}\)). When the laser intensity was lower than 2.6 W cm\(^{-2}\), no chromogenic reaction occurred. When the laser intensity range was 2.8–3.4 W cm\(^{-2}\), higher power density corresponded to higher \(\Delta A_{abs}\), which means they had higher OD.

Figure 7(a) shows the RT-FTIR of the NIR-responsive microcapsule coatings. The characteristic absorption peak of the carboxyl group of ODB-2 lactone is 1748 cm\(^{-1}\). As the chromogenic reaction progresses, the lactone ring opens and turns into a carboxyl group, with the peak at 1748 cm\(^{-1}\) gradually decreasing (Figure 6(a)). Figure 6(b) shows the conversion plot of the carboxyl group of ODB-2 lactone by integrating the 1748 cm\(^{-1}\) area. In Figure 7(b), the blue curve is the conversion of the microcapsule coating without IR-813 in the microcapsule core. The conversion rate of ODB-2 lactone is almost zero, which indicates that a microcapsule coating solution.

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**Table 1. Optical density (OD) comparison of the NIR-responsive microcapsule coating.**

| No. | Feeding mass of IR-813 \(^a\) (g) | Mass of IR-813 outside \(^b\) (g) | OD |
|-----|---------------------------------|---------------------------------|----|
| 0   | 0                               | 0                               | 0  |
| 1   | 0                               | 0.3                             | 0.02 |
| 2   | 0.3                             | 0                               | 0.12 |
| 3   | 0.3                             | 0.3                             | 0.13 |
| 4   | 0.6                             | 0                               | 0.35 |
| 5   | 3.0                             | 0                               | 0.28 |

\(^a\) Feeding mass of IR813 in the encapsulation.

\(^b\) Mass of IR813 added to the coating solution.

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Figures 5. SEM images of the NIR-responsive microcapsules with different IR813 feeding masses. (a) 0.3 g. (b) 0.6 g. (c) 3.0 g.
with an IR absorbing dye is the key to IR responsivity. Compared with the green curve, the red curve has a higher exposure intensity and a shorter response time. A comparison between the red and black curves shows that the chromogenic reaction speed can improve as the proportion of microcapsules increases when the exposure intensity is the same.

The energy threshold values calculated from the red, black, and green curves in figure 7 are 5.9, 20.7, and 27.8 J cm$^{-2}$, respectively. The higher the power density, the lower the energy threshold.

There is a temperature threshold for coloration of the microcapsules. So, when the exposure laser power is low, the generated heat dissipates to the surrounding environment, making it impossible to reach the required temperature. Thus, if the laser power is less than 1.3 W, the extended exposure time cannot make the microcapsules change color.

3.4. Application

Appropriate microcapsules can be fabricated by adjusting the shell–core material feeding mass ratios, the viscosity of the shell material, and the mass ratio of the water–oil phase. In general, the particle size of the microcapsules is less than 1 μm, which implies that the microcapsules can respond to NIR stimuli in the sub-micrometer dimension [12].

According to the above optimized encapsulation conditions, the feeding mass ratio of IPDI: ODB–2 was 1:2, the W/O phase mass ratio was 2:1, and IR–813 accounted for 1/10th of the mass of ODB–2. The mean particle size of the microcapsules was 279 nm. A coating solution consisting of this NIR-responsive microcapsule suspension and a CA dispersion D–8 at a mass ratio of 3:1 was coated on an electrolytic oxidized aluminum substrate, and then dried at 60 °C for 2 min to obtain an NIR-responsive microcapsule coating with a thickness of

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Figure 6. (a) UV-Vis spectra of coated films before exposure (black curve) and after exposure (from top down is 2.6, 2.8, 3.0, and 3.4 W cm$^{-2}$). (b) Plot of peak absorbance difference at 590 nm after exposure versus 808 nm IR laser power density.

Figure 7. (a) FT-IR absorbance variance versus exposure time. (b) Conversion plot of ODB–2 in NIR responsive microcapsules exposed to an IR laser (mass ratios of the NIR responsive microcapsules suspension and D–8 dispersion were 1:1, 3:1, and 3:1, and the laser power densities were 3.5, 3.5, 3.5, and 2.7 W cm$^{-2}$, corresponding to the black, blue, red, and green curves, respectively).
of about 1.0 μm. Then, the coating was scanned by a CTP plate maker (Trendsetter 800 II) that had 32 channels of 808 nm laser diodes. The image precision of the coating reached 20 μm (figure 8).

4. Conclusion

In this paper, NIR-responsive microcapsules with an average particle size of 0.2–0.5 μm and a narrow distribution width were prepared, which can be used for imaging materials by infrared laser direct writing to achieve non-contact printing. Through above research, we screened out the optimal synthesis conditions as feeding mass ratio of shell/core material at 1/2, W/O phase at 2/1, IR-813/ODB-2 at 1/10.

The morphology and particle size distribution of the microcapsules were influenced by the amount of infrared dye. Infrared dye encapsulated in the microcapsule improved the photothermal conversion efficiency to improve the image density. The feeding mass ratio of IR-813 and ODB-2 was 1/10, with which the OD reached a maximum value of 0.35. When the mass ratio of microcapsules and CA dispersion was 3:1, the coating had a quick NIR response and high chromogenic conversion. The image precision was up to 20 μm. These NIR-responsive microcapsules have the potential to broaden the applied field of thermosensitive microcapsules and have good application prospects.

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Figure 8. A photo of the NIR-responsive microcapsule coating scanned by a Trendsetter 800 III CTP plate maker (808 nm, laser power was 1.5 W, 32-channel).