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Tunable UV-Responsive Organic−Inorganic Hybrid Capsules

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Microcapsules have attracted widespread interest because of their potential application in the areas of drug delivery, agriculture, and the food and cosmetics industries.[1−6] A versatile method that affords microcapsules with control over their size, stability, loading, and release properties is the layer-by-layer (LbL) assembly technique.[7−9] This process involves the successive deposition of various materials, assembled alternately through complementary interactions (e.g., electrostatics, H-bonding, covalent bonding), onto colloidal particles, followed by particle removal. Recent studies have focused on the development of "smart capsules" with stimuli-responsive behavior.[10−14] These include capsules functionalized with nanoparticles for near-infrared- or UV-triggered release of encapsulated substances, and capsules that can be chemically cleaved by reduction of disulfide bonds cross-linking the walls. Despite these studies, there are considerable challenges in encapsulating and releasing low-molecular-weight molecules (including drugs) from LbL-engineered capsules. The stable encapsulation of small molecules in polyelectrolyte capsules is considerably more difficult than for macromolecules, because polyelectrolyte multilayers exhibit a high permeability to low-molecular-weight compounds.[15] This permeability can be reduced by the deposition of lipid coatings on the capsules,[16] thus offering a pathway for encapsulating small molecules. However, such systems can be unstable under a variety of conditions, especially at different temperatures, as the

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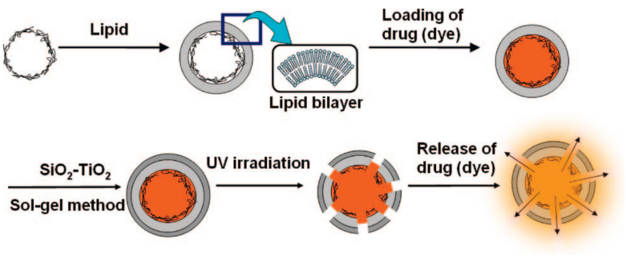
Scheme 1. Scheme for Fabricating UV-Responsive $(PSS/PDDA)_5/PSS/DDAB/SiO_2-TiO_2$ Capsules for the Controlled Release of Drugs (Dyes)



permeability of the lipid (and hence the capsules) is highly temperature sensitive. Therefore, there is a need for stable capsules loaded with low-molecular-weight materials that can be triggered to controllably release the encapsulated materials.

Herein, we report the preparation of organic−inorganic hybrid capsules by a combination of LbL assembly and sol−gel methods, and show that these capsules are suitable for the stable encapsulation of a low molecular weight dye (phenol red), which can be released upon UV irradiation. TiO_2 was selected as the UV-responsive component since it can decompose organic materials by photocatalytic reaction. Such a reaction was used to trigger rupturing of the polymer capsule walls, releasing the dye. We chose the binary inorganic oxide system SiO_2-TiO_2 because this binary oxide can be prepared by the sol−gel process with various conpositions. In addition, we have reported that anatase TiO_2 nanocrystals can be obtained from SiO_2-TiO_2 gel films via treatment at less than 100 °C.[17] Therefore, the photocatalytic activity is controllable in this system by varying the oxide composition and crystalline state. Here, we show that release of the dye can be tuned through controlling the SiO_2:TiO_2 composition and UV irradiation intensity.

Scheme 1 shows the procedure used for preparing the organic−inorganic hybrid capsules by LbL assembly and sol−gel chemistry. Polyelectrolyte capsules were fabricated by the alternate assembly of poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA) onto melamine formaldehyde (MF) particles, followed by removal of the MF particles by dissolution with HCl.[8] The capsules, terminated by a PSS layer, were subsequently coated with a cationic lipid bilayer of dioctadecyldimethylammonium bromide (DDAB). Phenol red was postloaded into the capsules by switching the lipid bilayer membrane permeability through the "gel" to "liquid crystalline" phase transition. A SiO_2 coating was deposited on the capsules by dispersing the DDAB-coated capsules in ethanol, adding tetraethylorthosilicate (TEOS), ammonia, and water to cause hydrolysis and condensation of the alkoxide. In the case of the SiO_2-TiO_2 (molar ratio = 75:25) coating on the capsules, the precursor sol was prepared from TEOS and tetra-*n*-butylorthotitanate (TBOT). TEOS, TBOT, and acetylacetone, as a chelating agent, were dissolved in ethanol. A previous report by Wang and Caruso has shown that the sol−gel coating of polyelectrolyte multilayers assembled on particles results in uniform organic−inorganic coatings.[18] Details of the preparation conditions and procedures are given in the Supporting Information.

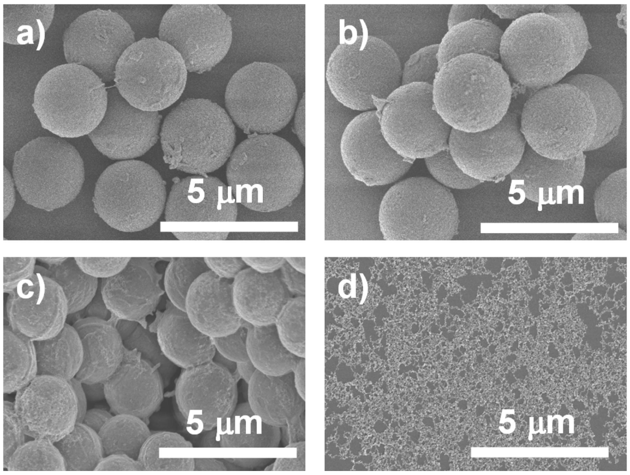


Figure 1. SEM images of (a, b) $(PSS/PDDA)_5/PSS/DDAB/SiO_2$ capsules and (c, d) $(PSS/PDDA)_5/PSS/DDAB/SiO_2-TiO_2$ (75:25) capsules (a, c) before and (b, d) after UV irradiation (20 mW cm^{-1}, 60 min).

The effect of UV irradiation on the morphology of the capsules was examined by scanning electron microscopy (SEM). Figure 1 shows SEM images of the organic−inorganic hybrid capsules before and after UV exposure. Prior to UV irradiation, the particles have a spherical structure for both SiO_2−polymer and SiO_2/TiO_2−polymer capsules. After UV irradiation, the SiO_2−polymer capsules remain spherical and intact, whereas the SiO_2/TiO_2−polymer capsules completely decomposed. In TiO_2, electron−hole pairs are generated through excitation with UV light and the holes residing in the valence band of TiO_2 have high oxidative activity.[19] Recently, Sasaki et al. have demonstrated that multilayer films formed from PSS/PDDA and TiO_2 can be converted into polymer-free inorganic films upon UV irradiation.[20] In the current study, the polyelectrolyte capsules are decomposed by the photocatalytic effect of the TiO_2 in the inorganic layer.

We next examined the effects of UV-induced release of the encapsulated dye molecules. Phenol red was selected for use in these experiments because it has been widely examined in release studies from colloidal materials, including liposomes. Phenol red can act as an indicator, changing color at different pH values.[21] The dye was encapsulated in the internal aqueous phase of the lipid-coated capsules at pH 7.0 above the phase transition temperature of the lipid membrane (ca. 40 °C). At this condition, the molecular permeability of the membrane is high. After cooling to 20 °C, the dye was sealed into the capsules because of the reduced permeability. The capsules were then washed and coated with SiO_2/TiO_2. The external aqueous phase was

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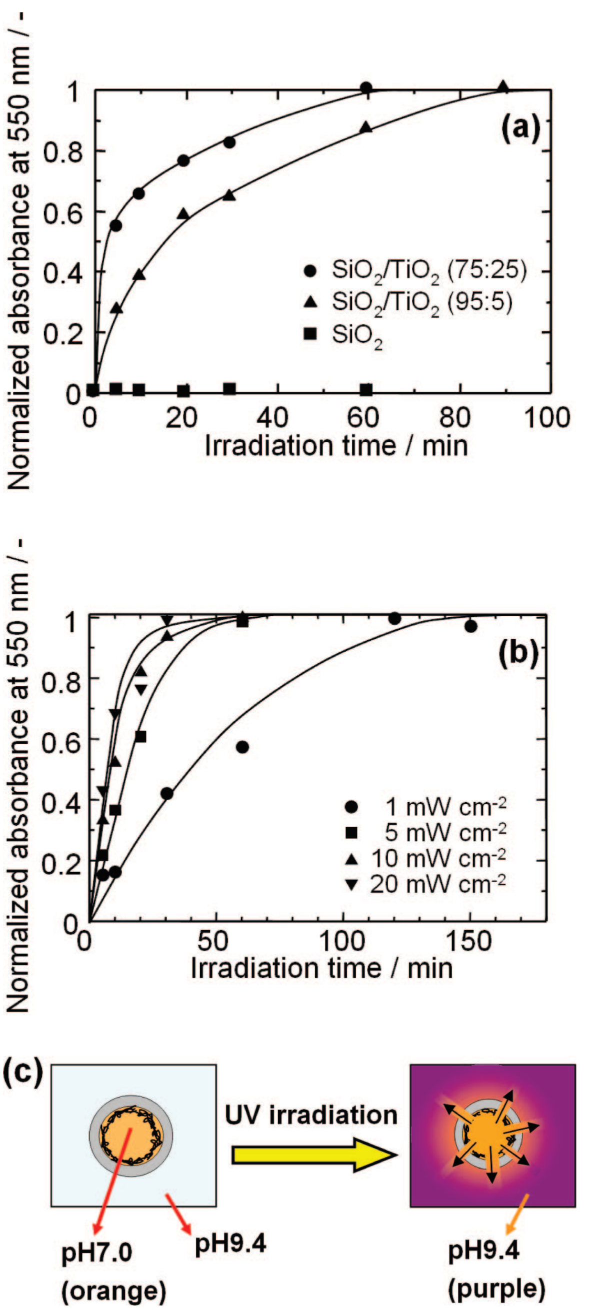

Figure 2. Release of phenol red from the organic−inorganic hybrid capsules, monitored by changes in dye absorbance at 550 nm as a function of UV irradiation time. (a) Capsules coated with SiO$_2$ and SiO$_2$/TiO$_2$ (75:25 and 95:5) were examined. The UV intensity was fixed at 20 mW cm^{-2}. (b) Several UV intensities (1, 5, 10, and 20 mW cm^{-2}) were used to irradiate capsules coated with SiO$_2$-TiO$_2$ (75:25). (c) Schematic representaion of color changes of phenol red upon release from the capsule.

changed to pH 9.4. When the dye was released to the outer phase of the capsules, the color changed to purple. Therefore, the release behavior can be detected by an increase in absorbance at 550 nm (maximum absorbance of phenol red at pH 9.4). The control experiment was examined by using SiO$_2$-coated capsules. Figure 2 shows the changes in absorbance (550 nm) with UV irradiation time. These plots are directly comparable since the same amount of encapsulated dye was employed in each experiment. The SiO$_2$-coated capsules retained the dye, with no dye release observed over a period of 24 h. When the SiO$_2$/TiO$_2$-coated capsules (SiO$_2$:TiO$_2$ = 75:25 and 95:5) were irradiated with UV light, the dye was released (Figure 2a). The dye release rate was is controllable through varying the SiO$_2$:TiO$_2$ composition in the capsules, with quicker release observed for the capsules containing a higher TiO$_2$ content. In contrast, there was negligible increase in the absorbance after irradiation for 60 min for the SiO$_2$-coated capsules, reflecting virtually no dye release. These results indicate that the presence of TiO$_2$ in the capsule shells decomposes the polyelectrolytes (and lipids), causing release of the dye. The release rate of the dye was also tunable by changing UV intensity. When UV intensities greater than 5 mW cm^{-2} were used to irradiate the SiO$_2$/TiO$_2$ (75:25)-coated capsules, the encapsulated dye was released with 60 min. In contrast, a UV intensity of 1 mW cm^{-2} resulted in considerably slower release (ca. 150 min) (Figure 2b).

In conclusion, tunable UV-responsive microcapsules, comprising PSS/PDDA multilayers coated with lipid bilayers and SiO$_2$−TiO$_2$, were prepared via the LbL colloid-templating technique and sol−gel chemistry. It was shown that low-molecular-weight dyes can be loaded into the capsules by exploiting the temperature-dependence of the lipid bilayer permeability. The encapsulated dyes can be released on demand by UV irradiation. The capsules without TiO$_2$ were unaffected by UV irradiation. Hence, the UV-induced release is attributed to the photocatalytic activity of the TiO$_2$ component to decompose polyelectrolytes, which causes the capsules to rupture. In addition, the release rate is tunable by changing the composition of SiO$_2$ and TiO$_2$. It is well-known that sunlight contains UV-light of ca. 3 mW cm^{-2} (direct sunlight). Accordingly, these systems are aimed at applications in cosmetics and agriculture, where UV light can trigger the release of encapsulated low-molecular-weight materials.

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Supporting Information Available: Detailed information for preparation procedure of the capsules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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