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Chemicals On Demand with Phototriggerable Microcapsules

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We report the development of remotely triggerable liquid-filled free-flowing solid microcapsules (MCs) with impermeable shell walls that enable the coexistence of otherwise incompatible chemical species in a single container until their reaction is desired. While liquid filled microcapsules[1] are widespread with applications as varied as carbonless copy paper, agrochemicals, or self-healing polymers,[2] remote triggering of content release is not common for free-flowing MCs. Langer et al. have described the remote release of chemicals from a microchip by dissolution of a polymer membrane triggered by application of an electric potential.[3] More commonly, release is induced through crushing or the application of other forms of mechanical stress.[1,2]

Triggering the release of the contents of MCs by light is attractive as light can easily address a small object or blanket an entire surface. To achieve this goal we have designed remotely triggered MCs in which the encapsulated liquid contains optothermally active species, such as carbon nanotubes (CNTs), which can rapidly heat up the liquid content when irradiated. Irradiation of an MC would then trigger a rupture mechanism involving an increase in internal pressure.[4] In early work, Masuhara et al. have reported the escape of toluene/pyrene droplets from an optically trapped melamine/formaldehyde microcapsule when irradiated with a second laser that caused ablation of the capsule wall.[5] Similarly, Au or Ag nanoparticles have more recently been used as optothermal triggers for the breakdown of semipermeable polyelectrolyte membranes.[6]

CNTs were selected as the optothermal-triggering element because they absorb light across the entire spectrum[7] and efficiently convert the absorbed light into heat.[8] Unfortunately, CNTs are poorly soluble in most organic solvents; therefore, it was imperative to identify a robust microencapsulation method that not only prevented the partitioning of the CNTs into the continuous phase but also permitted the isolation of free-flowing solids. The interfacial polymerization of triamines and di- or triacid chlorides in an oil-in-water emulsion, a technique thoroughly studied by Mathowitz and Cohen,[9] was found to be well suited for these purposes.

In a typical procedure, CNTs (1 mg) were sonicated in a solution of organic liquid (1 g) and terphthaloyl chloride (45 mg). The suspension was emulsified in 3 mL of a 0.4 wt % aqueous solution of polyvinyl alcohol (87−89% hydrolyzed), and then an aqueous solution of diethylene triamine (650 μL in 1 mL water) was added dropwise to the emulsion. Membrane formation around the oil droplets was nearly instantaneous but the particles were allowed to set for an additional 1.5−24 h to ensure that solid-walled and impermeable MCs were obtained. Isolation by filtration afforded free-flowing, liquid-filled MCs (Figure 1a, b) in yields ranging from 80−95%. MCs with diameters in the range of 100−1000 μm were easily accessible with the average diameter being controlled by emulsion stir rate (see the Supporting Information). Shell thickness was determined to be ∼1 μm by SEM (Figure 1d), and the liquid fill content for toluene-filled capsules was determined to be ∼95 wt % via physical crushing and removal of the volatiles *in vacuo*. Optical images (Figure 1b) revealed that the majority of the CNTs were located inside the MCs. Further SEM analysis of crushed particles showed that some of the CNTs are embedded in and on the shell material.

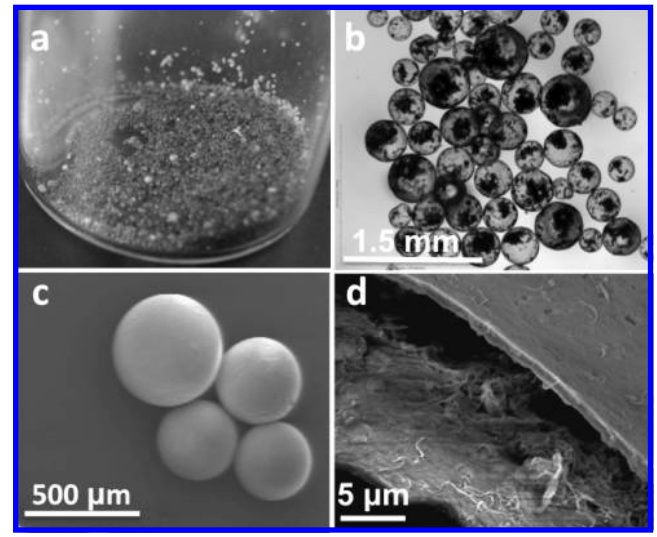

Figure 1. Toluene filled polyamide microcapsules containing 1 wt % CNTs. (a) Optical image of MCs in a scintillation vial. (b) Optical image of MCs in oil. (c) Scanning electron micrograph of MCs. (d) Scanning electron micrograph of crushed MCs. CNTs (white bundles) are visible in the interior, exterior, and incorporated into the wall.

Physical crushing of the MCs produced an audible pop and resulted in ejection of the encapsulated liquid, demonstrating the good barrier properties of the shell wall. Notably, no significant decrease in fill content of the MCs was apparent after standing in air for over 2 months (see the Supporting Information). Furthermore, leakage studies with encapsulated phenylacetylene revealed that little to none of the liquid content escaped when the MCs were immersed in solvents that do not swell the cross-linked polyamide shell wall such as *t*-butanol, benzene, and hexanes (see the Supporting Information for more information on leakage).

Having confirmed negligible leakage of the liquid contents under a broad range of conditions, we next tested if liquid release could be optically triggered with a near-IR laser.[10] Indeed, as depicted in Figure 2, encapsulated toluene can be optothermally released via laser irradiation (785 nm, 400 mW diode laser) in air. Bursting of the MCs occurred within 0.02 s, and observation of the process under an optical microscope revealed that swelling can occur immediately prior to bursting (Figures 2a−c, and Supplemental Movies S1 and S2, Supporting Information). For comparison, heating of toluene filled MCs in a standard melting point capillary resulted in considerable swelling and bursting at ∼171 °C, which correlates to an internal pressure of ∼4.5 atm.[11] Importantly, the

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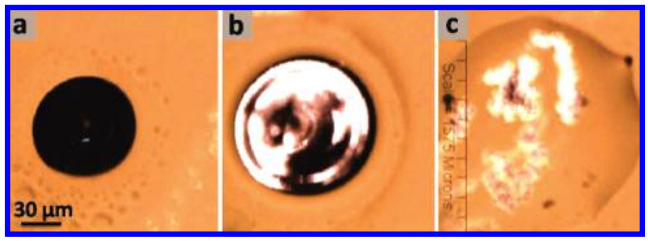

Figure 2. Optical micrographs of a nanotube filled microcapsule prior to irradiation (a), during irradiation (b), and after bursting (c). Swelling is evident during irradiation (b), resulting in an increase in internal volume on the order of 2.5 times.

MCs can also be optothermally ruptured by IR laser irradiation when immersed in liquids such as water or alcohols, and a release efficiency of >95% was obtained for phenylacetylene MCs as determined by UV−vis spectroscopy. Control particles lacking CNTs did not rupture under analogous irradiation in liquids or air.

To demonstrate the concept that mutually reactive materials can be stored in intimate proximity and remotely released "on demand," phenylacetylene/CNT MCs were immersed in a solution containing benzyl azide under highly reactive click conditions.[12] The click reaction is a useful test system because in the presence of Cu(I), phenylacetylene and benzyl azide react rapidly to give the corresponding triazole, near quantitatively. Figure 3a demonstrates the coexistence of the phenylacetylene/CNT MCs with the solution of azide and copper catalyst until laser rupture after 24 h. Laser-induced bursting of the MCs resulted in rapid consumption of benzyl azide with complete conversion within 1 h. The spatial resolution of the laser also enabled the successive triggering of several MCs, resulting in the controlled and stepwise consumption of the starting material (Figure 3b).

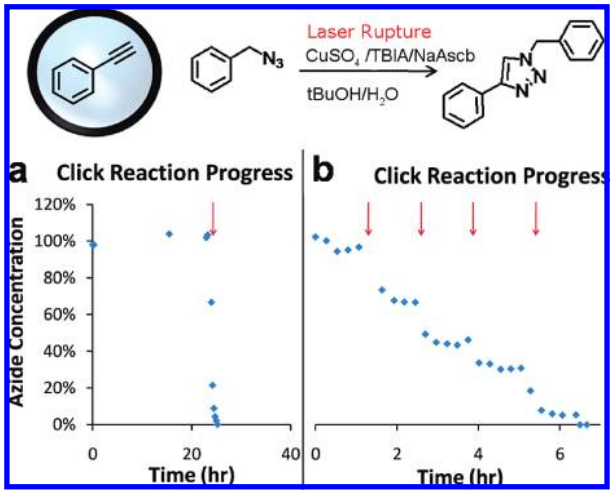

Figure 3. Click reaction progress as monitored by GC-MS via the consumption of benzyl azide. Red arrows indicate points of laser rupture. (a) Laser rupture of multiple MCs at a single time point to completely consume all of the azide. (b) Selective rupture of individual MCs among a group, showing the ability to trigger the reaction in a stepwise fashion. The difference in the size of the steps reflects the difference in the size of the MCs.

As another demonstration of remote initiation, we explored the "on-demand" laser induced polymerization of dicyclopentadiene (DCPD) via ring-opening metathesis polymerization. To this end, Grubb's second generation catalyst was encapsulated as a 5 wt % solution in toluene. These MCs can be dispersed in neat DCPD (1 mg MC/100 mg DCPD) for weeks without a noticeable increase in viscosity. In contrast, laser bursting of the capsules resulted in the polymerization of DCPD, leading to gelling within minutes and

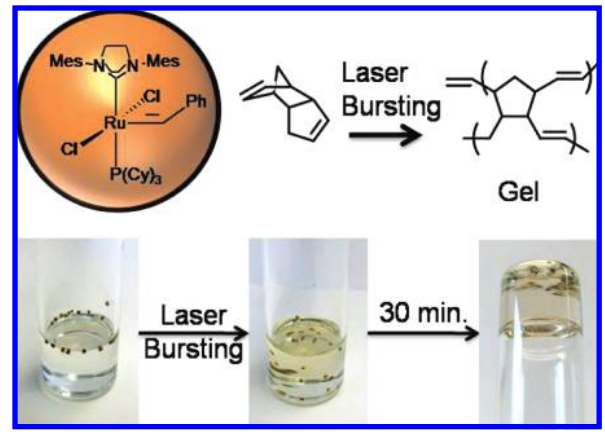

Figure 4. Ring-opening metathesis of DCPD using encapsulated Grubbs Catalyst. Images of MCs in DCPD (left), after bursting (center), and finally after gelling (right).

subsequent hardening over tens of minutes (Figure 4). This example further highlights the large "on-off" characteristics that can be obtained with these responsive MCs. The fact that the encapsulated small molecule catalyst maintains significant activity is notable, considering that free amines were used for encapsulation and that localized optothermal heating was used for release.

In conclusion, we have demonstrated the concept of light-triggerable, liquid-filled microcapsules via coencapsulation of CNTs using a simple and robust interfacial polymerization technique. The solid polyamide shell provides substantial protection from the external environment to its encapsulated liquid contents but remains breachable upon irradiation. We have demonstrated the concept of storage and remote release with mutually reactive small molecules and catalysts. While this release mechanism is robust, it may not be applicable for thermally sensitive compounds. Further exploitation of this approach is currently underway.

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Supporting Information Available: Materials and Methods, movies S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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