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Light-Regulated Supramolecular Engineering of Polymeric Nanocapsules

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Supporting Information

ABSTRACT: This article describes the light-driven supramolecular engineering of water-dispersible nanocapsules (NCPs). The novelty of the method lies in the utilization of an appropriate phototrigger to stimulate spherical polymer brushes, consisting of dual-responsive 2-(dimethylamino)ethyl methacrylate (DMAEMA) and light-sensitive spiropyran (SP) moieties, for the development or disruption of the NCPs in a controlled manner. The fabrication of the nanocarriers is based on the formation of H-type $\pi-\pi$ interactions between merocyanine (MC) isomers within the sterically crowded environment of the polymer brushes upon UV irradiation, which enables the SP-to-MC isomerization of the photosensitive species. After HF etching of the inorganic core, dual-responsive polymeric vesicles whose walls' robustness is provided by the MC−MC cross-link points are formed. Disruption of the vesicles can be achieved remotely by applying a harmless trigger such as visible-light irradiation. The hydrophilic nature of the DMAEMA comonomer facilitates the engineering of the vesicles in environmentally benign aqueous media and enables the controlled alteration of the NCPs size upon variation of the solution pH. The inherent ability of the NCPs to fluoresce in water opens new possibilities for the development of addressable nanoscale capsules for biomedical applications.

Considerable scientific interest has been devoted lately to the nanoengineering of responsive polymeric spheres with hollow interiors because of their unique features in encapsulating and releasing substances or molecules upon application of a specific external stimulus. The fabrication of such hollow capsules has been tackled using various approaches, including self-assembly of block copolymers,[1] emulsion/interfacial polymerization,[2] and colloidal templating[3] strategies. The last of these has been the preferred method because it is more facile and robust, involving the layer-by-layer assembly of polyelectrolytes[4] or stereocomplexes[5] onto particles or the grafting of polymers "to"[6] or "from"[7] the surface of spherical templates followed by the sacrifice of the latter to form the void of the capsule. The development of controlled/"living" radical polymerization methods has provided synthetic flexibility for the introduction of a variety of functionalities onto diverse substrates and allowed the covalent grafting of dense polymer films onto the surfaces of particles that can be further degraded to provide multifunctional polymer vesicles with a narrow size distribution and controlled shell thickness.[7] However, the fabrication of "smart" nanocapsules (NCPs) that can alter their size or be disrupted upon stimulation is still a challenge. In typical systems, conformational changes of the polymeric constituent of the vesicle are stimulated by classical triggers such as pH,[8] temperature,[9] and ionic strength,[10] whereas redox[11] and voltage[12] variations have recently been reported. Nevertheless, these systems often suffer from spatial restrictions and/or inefficient disruption/swelling of the NCP wall.

An important breakthrough in this direction would be the engineering of NCPs whose properties can be reversibly altered by applying a remote stimulus such as irradiation with light of a specific wavelength, which involves an easily controllable photochemical process with temporal and spatial control. To fulfill this need, the NCP walls have been doped with either metal nanoparticles or IR dyes, which upon NIR illumination absorb energy and generate local heating leading to permeability variations[13] or rupture[14] of the NCP wall. The shortcoming of this approach is light-driven local heating, which can be hazardous for certain applications. To avoid this effect, the permeability of the NCP wall can be controlled by a local pH gradient induced by irradiation of a "proton pump" molecule incorporated into the capsule shell.[15] Another approach uses polarity changes within polymer chains, arising from the photoswitching of light-sensitive molecules, to induce reversible micelle-to-vesicle transitions.[16] The incorporation of photosensitive or photolabile derivatives within self-assembled polymers has also been used for cross-linking and/or disruption of micellar or NCP structures.[17]

A well-known family of photosensitive molecules is nonpolar spiropyrans (SPs), which upon UV irradiation isomerize to the polar merocyanines (MCs), whereas visible-light irradiation of the latter regenerates the SP form.[18] This property has been used for reversible disruption of self-assembled micellar structures bearing SP moieties.[19] The tendency of the MCs to aggregate into either H- or J-type stacklike arrangements under certain circumstances[20] provides a useful tool for supramolecular engineering based on noncovalent $\pi-\pi$ interactions. Recently, the light-triggered formation of nano- or micrometer-sized particles from SP-functionalized dendrons

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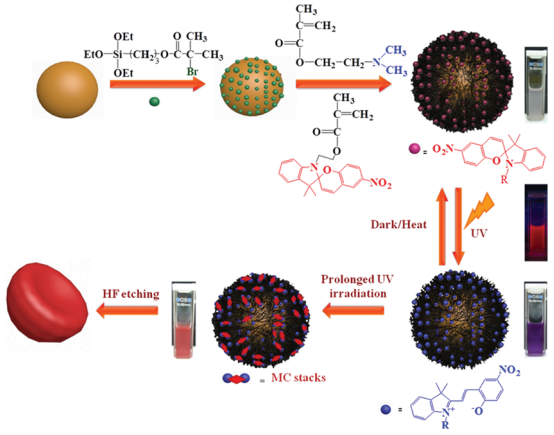
via similar intermolecular $\pi-\pi$ interactions was reported.[21] $\pi-\pi$ interactions have also been used to form highly ordered 2D assemblies[22] and 3D patterns[23] based on interparticle association of colloids bearing the chromophore units. However, the use of light-induced intraparticle $\pi-\pi$ interactions to cause noncovalent cross-linking of polymer chains is unprecedented.

Herein we describe a novel concept for supramolecular engineering of fluorescent and pH-sensitive NCPs from light-sensitive core–shell hybrid particles. The NCPs are constructed and disrupted upon irradiation with light of the appropriate wavelength. The synthetic strategy for the fabrication of the polymeric NCPs is illustrated in Scheme 1. First, a molecule

Scheme 1. Synthetic Procedure for Fabricating the NCPs



capable of initiating an atom transfer radical polymerization (ATRP) process, [3-(2-bromoisobutyryl)propyl]-triethoxysilane, was immobilized onto the surface of the silica nanoparticles. Next, the photosensitive monomer 1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2*H*-1-benzo-pyran-2,2′-indoline) (SPMA) was randomly copolymerized with 2-(dimethylamino)ethyl methacrylate (DMAEMA) via Cu-mediated ATRP from the surface of the inorganic colloids to give well-defined PDMAEMA-*co*-PSPMA copolymer brushes.

The PDMAEMA-*co*-PSPMA random copolymer brushes exhibited a number-average molecular weight (M_n) of 66 600 g/mol and a polydispersity index (PDI) of 1.29, as determined by gel-permeation chromatography (Figure S1 in the Supporting Information), and contained 6.1 mol % chromophore units, as determined by ^{1}H NMR spectroscopy (Figure S2). The hybrid core–shell structures had a polymer content of 36 wt % (Figure S3) and a polymer grafting density of 0.42 chains/nm^2. Characterization of the SiO_2 colloids and the SiO_2-*g*-(PDMAEMA-*co*-PSPMA) hybrids by dynamic light scattering (DLS) in neutral pH water showed that the bare silica particles, with a hydrodynamic diameter (D_h) of 267 nm, were successfully modified with the PDMAEMA-*co*-PSPMA random brushes to obtain hybrid core–shell structures with D_h = 464 nm (Figure S4), supporting the synthesis of a highly grafted polymer shell onto the surface of the SiO_2 particles. The morphology of the hybrids was studied by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) (Figure 1A,B, respectively). The polymer coated the silica surface uniformly, resulting in well-defined hybrids with a diameter of 245 ± 20 nm as determined

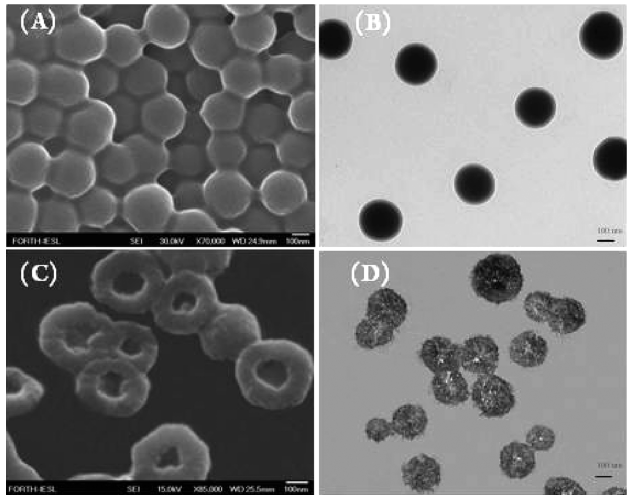


Figure 1. FESEM and TEM images of the SiO_2-*g*-(PDMAEMA-*co*-PSPMA) core–shell structures (A and B, respectively) and the hollow NCPs after HF etching of the inorganic core (C and D, respectively).

by SEM (Figure 1A). Similarly, TEM images showed a uniform, conformal coating on the surfaces of the particles. Isolated hybrid particles with diameters of 237 ± 12 nm surrounded by a 19 ± 3 nm thick polymer layer (seen as a lighter-color shell around the dark silica core) were observed (Figure 1B).

Next, the hybrid particles were subjected to prolonged UV irradiation (λ = 365 nm) to induce the SP-to-MC isomerization of the chromophore units (Figure S5) and promote the formation of intraparticle H-type MC–MC stacks within the polymeric layer, which is favored by the hydrophilic nature of the DMAEMA comonomer and the inherent steric crowding of the concentrated polymer brush. Upon HF etching of the silica core of the hybrids, the H-type aggregates act as noncovalent cross-link points within the dense polymer brush, leading to the formation of robust NCP structures. Figure S6 shows the NCPs obtained upon drying the water-swollen capsules under air, whereas Figure 1C shows the doughnut structures derived after the capsules were dried and deposited on a silicon substrate under high vacuum, which induced rupturing of the vesicle walls. The ability of the NCPs to deform is attributed to the flexible nature of the polymer wall due to the low degree of cross-linking in the shell. The doughnut structures with diameters of 336 ± 31 nm observed by SEM (Figure 1C) indicate that despite the nonpermanent character of the cross-links in the shell, the vesicle wall is robust and retains its integrity both in solution and on the surface. The absence of interparticle association of the colloids is due to the low chromophore content of the brush (6.1 mol %), which favors the observed intrasphere cross-linking. The doughnut structures on the surface after the core etching are significantly larger than the precursor core–shell hybrids for two reasons: first, the protonation of the PDMAEMA moieties at low pH induces the swelling of the polymer shell, and second, the capsules flatten on the substrate when the NCP walls fracture under vacuum. TEM also verified the successful formation of the NCPs, as indicated by the absence of the core–shell structure (no contrast) and the presence of nearly homogeneous spheres with diameters of 260 ± 44 nm (Figure 1D). The size of the NCPs determined by TEM was similar to that of the core–shell precursors. This is due to the mild conditions used for drying

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the NCPs on the carbon-coated grid, which prevented the rupture of the NCP walls.

The nature of the intramolecular interactions induced within the photosensitive brush upon UV irradiation, which govern the supramolecular engineering of the NCPs, was verified by fluorescence spectroscopy. The emission spectra (λ_{ex} = 516 nm) of the hybrids after a short irradiation time (49 s) exhibited a band at 620 nm assigned to the open MC residues,[24] whereas upon prolonged irradiation (140 min), the evolution of a new band at 566 nm was observed and attributed to the formation of H-stacks[25] that coexist with the free MC species (Figure S7A). Finally, the addition of acid (to adjust the solution to pH 2) induced the protonation of the MC isomers, which was observed as a decrease in the intensity of their emission band, whereas the intensity of the band of the H-aggregates remained unaffected in the extreme acidic environment (Figure S7A). Similarly, the emission spectrum (λ_{ex} = 516 nm) of the NCPs at pH 2 exhibited two separate maxima: an intense band at 563 nm attributed to the H-aggregates and a red-shifted peak at 605 nm attributed to the MC residues of the vesicles (Figure 2A). The above verified the formation of H-aggregates upon prolonged irradiation of the hybrid particles, allowing the development of NCPs upon core etching. These aggregates serve as cross-links that afford robustness to the NCP walls and render the vesicles stable even at low pH. Fluorescence microscopy imaging of an aqueous dispersion of the NCPs at low pH (Figure S7B) clearly showed that the vesicles exhibit orange-red fluorescence emission, in agreement with the spectrum in Figure 2A. This inherent fluorescence of the NCPs in aqueous media was unexpected because neither the SPs nor the MCs exhibit appreciable fluorescence in water. An enhanced fluorescence efficiency of MC moieties has been reported under specific circumstances, such as within hydrophobic cavities of polymeric particles.[26] In our case, the fluorescence of the NCPs is attributed to the entrapment of the chromophores in the spatially crowded environment of the polymer brush and their restricted conformational flexibility, which minimizes the nonradiative relaxation of the excited molecules.[26a] This inherent fluorescent behavior of the NCPs renders them attractive in biological fluorescent labeling applications, allowing their tracking during in vivo experiments.

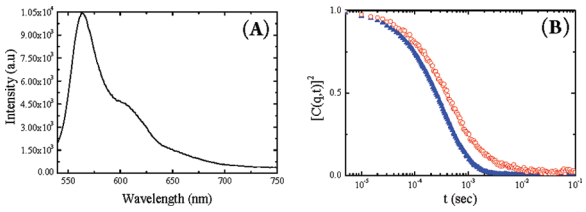

Figure 2. (A) Fluorescence emission spectrum (λ_{ex} = 516 nm) of an aqueous dispersion of NCPs at low pH. (B) Intensity autocorrelation functions of the NCPs at pH 2 (red ○) and 8 (blue ▲) at θ = 90°.

The PDMAEMA component of the copolymer brushes is a weak polybase with an effective pK_a for the tertiary amine groups of ~5.8 (Figure S8 inset), which is lower than that found for a linear homopolymer because of the confinement of the counterions within the brush structure.[27] Thus, the brush behaves as a cationic polyelectrolyte at pH below 5.8 and becomes uncharged at high pH. The SP moieties are also sensitive to a decrease in the solution pH upon addition of acid. The closed SP form first isomerizes to the open MC structure (6.15×10^{-6} mol of HCl), and next, the latter becomes protonated ($[MC-OH]^+$) (1.52×10^{-4} mol of HCl) (Figure S9).[28] This pH sensitivity of DMAEMA and SP should affect the size of the NCPs, which should expand because of the repulsive interactions between the charged amine and $[MC-OH]^+$ groups and the osmotic pressure induced by the Cl^- counterions[29] and shrink upon neutralization of the polymer at high pH (Figure S10A).

The pH-responsive behavior of the NCPs was studied by DLS. Figure 2B shows the intensity autocorrelation functions at a scattering angle (θ) of 90° for the NCPs at pH 2 and 8 (i.e., below and above the effective pK_a of the DMAEMA monomer repeat units, respectively). At low pH, the diffusion coefficient (D) was 2.2×10^{-8} cm^2/s, corresponding to a D_h of 219 nm assuming a hard-sphere model; increasing the solution pH to 8 increased D to 2.8×10^{-8} cm^2/s, indicating a reduction in the NCP size to 172 nm. The reduced NCP diameter at high pH verified the shrinkage of the NCPs upon deprotonation of the PDMAEMA units. Notably, the D_h of the NCPs at both low and high pH was significantly smaller than that of the precursor hybrids, indicating the partial collapse of the polymer shell upon dissolution of the inorganic core. The sensitivity of the NCPs to changes in the solution pH was also confirmed by FESEM imaging upon drying at pH 2 and 8 (Figure S10B,C, respectively). At pH 2, where the DMAEMA units are positively charged and the repulsive forces along the macromolecular chain are dominant, the NCPs are highly hydrated, and the average diameter of the ruptured nanospheres was 336 ± 31 nm (Figure S10B). When the pH was increased to 8, the average diameter of the ruptured capsules decreased to 302 ± 18 nm (Figure S10C), suggesting shrinkage of the vesicles in agreement with the DLS results discussed above. Moreover, the NCPs remained isolated and nonaggregated even at high pH, whereas the intraparticle stacking that provides the robust vesicle wall was not affected by pH variations. This suggests that the NCPs are robust structures whose size and wall permeability can be conveniently tuned as a function of pH, rendering them attractive nanocarriers for stimuli-responsive capture and release applications.

We recently showed that H-type MC–MC stacks can be dissociated upon visible-light irradiation as a result of MC-to-SP isomerization.[28] Here we report for the first time the disruption of NCPs upon visible-light irradiation and dissociation of the H-aggregates. An aqueous dispersion of the NCPs at low pH was irradiated with visible light for various time intervals, after which DLS measurements were performed. Figure 3A shows the intensity autocorrelation functions of an aqueous dispersion of the NCPs at pH 2 measured at θ = 90° after different exposure times. The scattering intensity decreased gradually

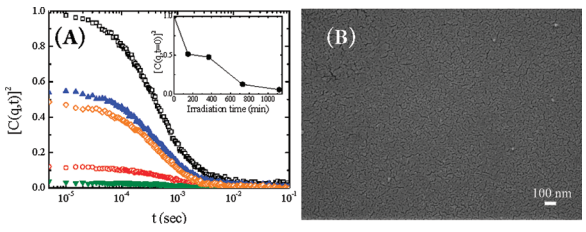

Figure 3. (A) Intensity autocorrelation functions of the NCPs measured at θ = 90° after visible-light irradiation for various times: 0 (black □), 150 (blue ▲), 371 (orange ◇), 731 (red ○), and 1121 (green ▼) min. (B) SEM image of the sample irradiated for 1121 min.

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with irradiation time. Since the autocorrelation functions were measured at the same scattering angle ($\theta = 90°$), the changes in scattering intensity upon irradiation are due to variations in the optical contrast and the volume of the scatterers according to the scattering theory of dilute solutions. The reduction in the scattering intensity as a function of irradiation time (Figure 3A inset) verified the dissociation of the H-type MC−MC stacks that act as cross-link points in the NCP walls and thus the gradual destruction of the vesicles (Scheme S1).[30] The disruption of the NCPs was further verified by FESEM imaging of the NCPs after exposure to visible light for 18.7 h (Figure 3B). The absence of the polymer vesicle structures indicated that the NCPs were effectively dissociated to their constituent polymeric chains, which formed a homogeneous polymeric film on the substrate. We anticipate that this light-induced disruption of the polymeric vesicles presents particular advantages for their use in controlled release by means of a harmless stimulus such as visible light, and we will explore this in future work.

In summary, we have proposed a novel approach for the supramolecular engineering of NCPs in water based on the controlled formation and dissociation of H-type $\pi-\pi$ interactions among MC chromophore units in a polymer shell layer triggered by irradiation with light of appropriate wavelengths. The development of the NCPs is based on the ability of the MC isomers to form stacks within a sterically crowded polymer brush on silica particles upon UV irradiation. Moreover, the robust NCPs derived following HF etching of the silica core of the hybrids can be progressively disrupted in a controlled manner by applying a harmless stimulus such as visible-light irradiation. The pH-responsive character of the NCPs provides a facile route for altering their size by varying the pH, whereas their inherent ability to fluoresce opens new possibilities for the development of nanoscale capsules that can function in environmentally benign aqueous media.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods and processes, characterization details, and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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