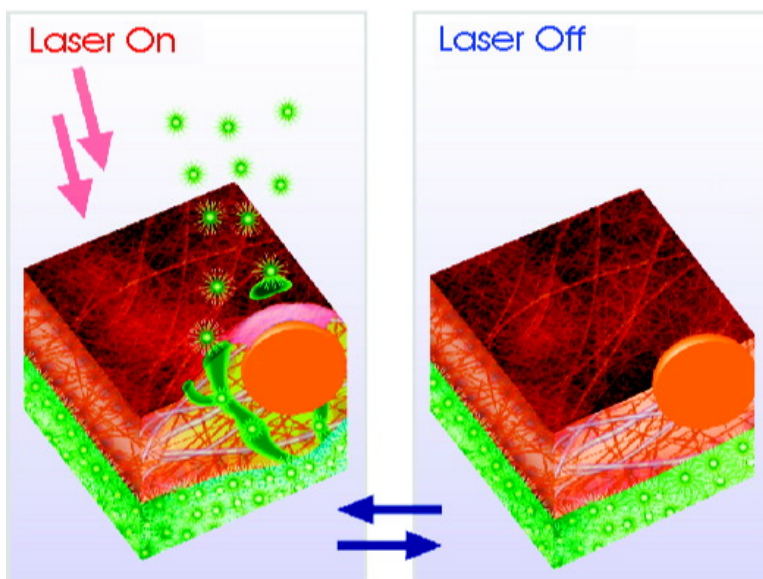


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Reversibly Permeable Nanomembranes of Polymeric Microcapsules

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Nanoparticles (NPs) and nanomaterials, the key building blocks of nanotechnology,¹ find increasing applications.² Noble metal NPs are attractive candidates to functionalize thin membranes³ because of unique optical and electronic properties. In this work polymeric nanomembranes are implemented using NPs and polyelectrolytes as building blocks. Control over the permeability of nanomembranes is attained by laser-nanoparticle interaction, whose mechanism relies on surface plasmon resonance absorption⁴ and subsequent temperature rise on NPs upon exposure to laser light. For this reason metallic NPs have been used to induce the release of encapsulated material by generating enough heat that the capsules' shells were deformed.^{5,6} In this work we show how near-infrared (IR) illumination can be tuned to achieve a desired release reversibly, while preserving the capsules' integrity. A particularly interesting application of such nanomembranes is remote initiation and manipulation of intracellular activity.^{7,8}

IR light is particularly important in biotechnology due to low absorption of biological materials in that spectral window. Aggregates of gold NPs absorb IR and produce heat with the potential to affect materials around them (Supporting Information).⁵ On the other hand, aggregates allow for relatively low laser intensities to be used since the heat generated by NPs is localized to a smaller volume. Polymeric microcapsules are ideal model systems to study the laser-NP effect on membrane permeability because of the high degree of control over their volume, surface area, and membrane thickness.

Figure 1A illustrates the schematics of a section of polyelectrolyte/NPs composite nanomembrane as would be found in a microcapsule with encapsulated material within its cavity. Upon IR laser illumination the NPs' aggregate generate heat and the encapsulated material (green) can diffuse through the membrane. By using aggregates of NPs the membrane becomes sensitive enough to IR irradiation, that it is possible not only to avoid destructive heat generation, but also to reversibly control membrane permeability. The magnified wall region on the right shows how this is possible. When the infrared laser is on, the NP absorbs light and converts it to heat, which dissipates to the polyelectrolyte network around it. When heated, the crystalline polymeric network becomes fluidlike allowing the release of encapsulated molecules through the membrane. If the irradiation is arrested, the NP stops producing heat and the polymeric complex around the NP rapidly cools, returning to its impermeable crystalline state.

Figure 1B presents experimental evidence of reversibly permeable nanomembranes. Two capsules doped with aggregated gold NPs and filled with a fluorescent polymer can be seen. Fluorescence profiles are plotted from the green line for each image (inset). The upper microcapsule was exposed to the laser beam, whence its fluorescence decreased. Upon a second exposure, the fluorescence

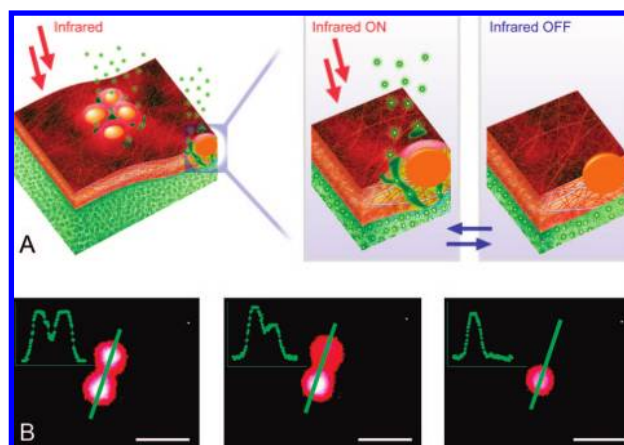


Figure 1. Remote release from microcapsules: (A) schematics of nanoparticle functionalized polymeric nanomembranes opening channels upon laser illumination; (B) a polymeric microcapsule shell acts as a reversible nanomembrane. Upon laser light illumination the microcapsule (left image) partially releases encapsulated polymers and reseals (middle). After the second illumination the microcapsule completely releases its content (right). Profiles in the left upper corner are drawn along the green line. Scale bars correspond to 5 μm .

emitted by the capsule vanished, while the unexposed microcapsule below retained its original fluorescence intensity. Control experiments using microcapsules that lacked NPs showed no photobleaching. No change in fluorescence intensity occurred between the first and second laser exposure supporting that the membrane sealed itself after the laser was turned off and that the permeability changes observed after illumination are reversible.

Polymeric microcapsules with gold NPs were fabricated according to the previous work.⁸ Briefly, 4.78 μm SiO₂ templates were alternatively coated by poly(diallyldimethylammonium chloride) (PDADMAC) (2 mg/mL, 0.5 M NaCl), 20 nm colloidal gold and poly(styrenesulfonate) (PSS, 2 mg/mL, 0.5 M NaCl). Gold NPs do not possess near-IR absorption, but a near-IR absorption peak can be formed by aggregating them by, for example, adding salt ions.⁹ The color of the gold solution changes from red to blue-gray within seconds after adding salt resulting in the apparition of a near-IR absorption peak¹⁰ between 700 and 900 nm. To build shells containing aggregated gold NPs, equal volumes of colloidal gold solution and 0.1 M NaCl were gently mixed for 60 s and added to a solution containing the capsules templates. The full assembly and core dissolution procedures were described in other work.⁸ The final capsules composition was (PDADMAC/Au/PSS)₄. Electron microscopy revealed the presence of meshlike aggregates containing up to 100 gold NPs within the capsules wall (Supporting Information). The encapsulation of Alexa Fluor 555 dextran (10 kDa) was achieved by heating a mixture of capsules and dextran (0.1 mg/ml) at 54 °C for 20 min. Remote release experiments were

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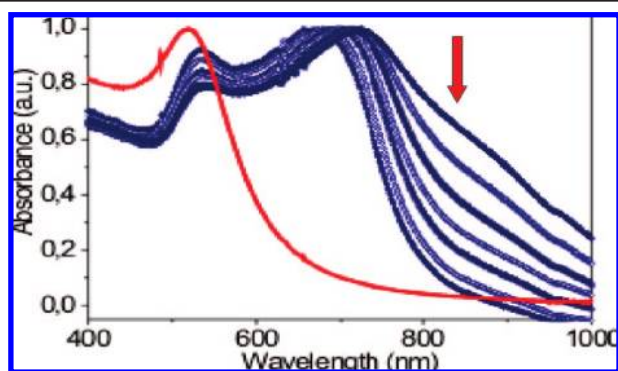


Figure 2. Normalized absorption spectrum of gold nanoparticles (red trace) with a single surface plasmon resonance peak at 520 nm and spectra of nanoparticle aggregates (blue traces). The spectra for aggregates were collected with three minutes intervals. The arrow indicates the wavelength of IR light used.

conducted using an IR laser as reported previously (Supporting Information).⁵

Irradiating the capsules for 5 s or more was enough time to allow the entire capsule content to diffuse out. The minimum laser power required to remotely open capsules containing aggregated gold NPs was found to be 10 milliwatts. At 60 mW, 100% of the capsules had lost their load. In addition, the laser-induced release of material from the shell was never accompanied by deformation or “explosion” of the microcontainers. As it was mentioned earlier, the light absorbed by metal NPs is converted into thermal energy. In this regard, the spectral features of aggregates of gold NPs are reminiscent of nanorod-like structures.¹¹ Figure 2 presents absorption spectra of gold NPs (red curve) and aggregates of these NPs (blue curves). It can be seen from these data that NPs possess a single surface plasmon resonance peak situated around 520 nm and weak near-IR absorption. During salt induced NPs aggregation a second peak is formed in the IR region, and this second peak moves with time toward higher wavelengths. In this sense, the spectral features of aggregates of NPs are less versatile than those of nanorods but the preparation of aggregates is simpler and does not require specific surface-active compounds. Also, according to Figure 2 the position of the near-IR absorption peak can be controlled via the time elapsed from the initial aggregation till adsorption.

The mechanism for controlling the permeability of nanomembranes can be understood by conducting an analysis of the interaction of laser light with NPs. Upon illumination, the temperature on the NPs rises because light energy is converted into heat. More efficient heat production can be obtained by controlling the distribution of NPs embedded within polymeric nanomembranes.¹² Furthermore, to implement reversibility one needs to locally raise temperature on the nanomembrane just above the glass transition temperature (T_g) of the polyelectrolyte complex.¹³ A mean T_g as low as 40 °C was measured for this system¹³ with a high temperature phase distinguished by high elasticity and high permeability.¹⁴ The relatively low T_g of this polymeric system has major implications for in vivo studies as typical cell experiments are

conducted at 37 °C. Therefore, in the presence of living cells one needs a rise in temperature of only 3 °C to affect the permeability of such a polymeric shell. Gold NPs heated with an infrared laser beam can easily fulfill this requirement.

In conclusion, we implemented nanomembranes with controllable permeability using polymeric microcapsules as a model system. The incorporation of aggregates of gold NPs in polyelectrolyte shells resulted in a near-IR absorption peak inexistent in single particles. The microcapsules’ permeability could be reversibly changed to partially release encapsulated material upon IR laser light illumination. The shells’ permeability was immediately decreased after the laser was turned off and subsequently increased when the laser was turned on. The heat produced by the absorbing NPs transiently melts the polymeric network around the NPs, locally increasing the membrane permeability. Switching off the laser brings the temperature of the molten polyelectrolytes below T_g , forcing the nanomembrane to seal itself back. Further applications of controllable membranes¹⁵ are envisioned in separation sciences, as well as in remote intracellular signaling.⁸

Supporting Information Available: TEM image shows aggregates of gold nanoparticles in a dried microshell. A LSCM image shows the release of fluorescent dextran from four capsules after irradiation with an infrared laser. Additional details of the encapsulation and release procedures as well as capsule assembly and characterization are also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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