J Therm Anal Calorim (2017) 127:895–904
DOI 10.1007/s10973-016-5798-7

Temperature rise around nanoparticles

Applications for polyelectrolyte multilayer capsules

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Received: 25 November 2015 / Accepted: 27 August 2016 / Published online: 19 September 2016

Abstract Nanoscale heating governs a multitude of processes relevant to molecular states and biomolecular functionality. In this mini-review, we describe application of localized laser–nanoparticle heating for polymeric polyelectrolyte capsules and layers, covering the principles governing the nanoscale laser-induced heat generation, synthesis of nanoparticles and their adsorption on polyelectrolyte multilayer membrane and different applications of these effects. Release of encapsulated materials is considered as one of the methods of release, while its further application is linked, among others, with intracellular delivery and release of encapsulated peptides, remotely controlled reactors, polymeric surface properties and corrosion protection.

Keywords Temperature · Thermal · Nanoparticles · Laser · Polymers

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Introduction and background: nanoparticle functionalized polyelectrolyte multilayer capsules

Heat generation around nanoparticles is of interest for uncovering fundamental processes at the nanoscale [1]. Molecular interactions, manipulation of molecular properties as well as such practical applications as release of encapsulated materials, remote permeability control, corrosion protection, etc. benefit from and utilize the nanoscale heat generation.

In this mini-review, we describe theoretical background of nanoparticle heating, discuss nanoparticle synthesis and adsorption on polyelectrolyte multilayers and further highlight application of localized heating around nanoparticles on polymeric capsules. Polyelectrolyte multilayer capsules are drug delivery carriers available in addition to other carrier types [2–9]. They are produced by consecutive application of oppositely charged polyelectrolyte polymers on sacrificial templates [10–12]. The fact that the charge-connected or charge-assembled polymers still retain their properties after washing out the solvent may not be obvious, at least at the first thought, but indeed the solvents, which are added for a relatively short time (minutes to tens of minutes), are washed away, and they do not affect the electrostatic interaction of polymers. Which solvents are used to dissolve and remove the template? That depends on the template itself. There are a large number of templates, also referred to as cores, available for microcapsule fabrication, with porous, smooth ones with sizes ranging from nano- to micrometers [13]. Once the core is chosen, the process of polyelectrolyte multilayer adsorption starts, and that represents the first step of capsule preparation. The whole series of steps of making the capsules are shown in Fig. 1, together with their real confocal fluorescence microscopy images (the bottom row).

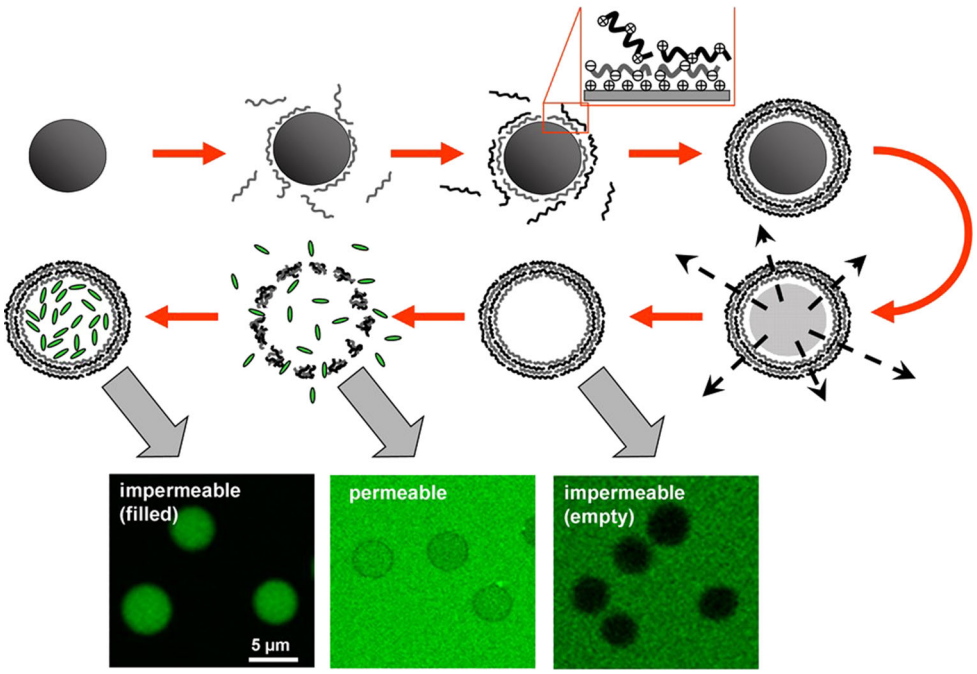

Fig. 1 Schematics showing production of LbL microcapsules and encapsulation of molecules. Reproduced from O. Kreft and A. Skirtach, Nanotechnology in Drug Delivery

It should be pointed out that during the microcapsule assembly, different molecules, particles and nanoparticles can be added in the shell, providing their multifunctionality. One such functionality—light responsiveness of polyelectrolyte multilayer assemblies [14]—has been used for drug delivery [15] and controlled release applications [16, 17]. In these applications, nanoparticles adsorbed in the shell of polyelectrolyte multilayer capsules perform the function of active absorbing centers, which absorb light and convert it to heat. Both silver [18] and gold [19–21] nanoparticles are very popular types of nanoparticles.

Heat generation around nanoparticles

Theoretical background

The nanoparticles of such metals as gold and silver can effectively generate heat under laser excitation. The heat generation is due to the laser electric field strong driving electrons within the nanocrystals, while the energy received by the carrier is converted into heat. Then, the heat diffuses from the nanocrystal increasing the temperature of the ambient medium [22]. In the case of semiconductor nanoparticles, the heat release rate is much weaker because heat is generated through the interband absorption process with the creation of a mobile electron and a hole (exciton).

In the absence of phase transitions, the temperature distribution in the surrounding medium can be written as follows [20, 23, 24]. The temperature distribution on a nanoparticle and around it in the surrounding medium can be calculated by considering the model of uniformly heated homogeneous spheres placed in an infinite homogeneous medium, for which an exact analytical solution of the heat equation with the boundary conditions exists [23].

Control of the surface plasmon resonance: control of the heating

Optical plasmon resonance is discussed in a number of reviews and books [25–27]. Red sols of gold nanoparticles due to the surface plasmon resonance are associated with a broad absorption band in the visible region at a wavelength of about 520 nm. It represents the collective oscillations of the electron gas on the surface of nanoparticles under the influence of the electromagnetic field of the incident light wave. The theory of surface plasmon resonance for spherical metal particles has been established by Mie in the quasi-static approximation (particle size is much smaller than the wavelength of light). The displacement of electrons in an electric field results in the polarization of the sphere, so that there is a linear restoring force, which reaches the maximum at the surface plasmon resonance. Thus, a free electron in the spherical particles is a vibrational system, in contrast to the bulk material. There is an infinite number of plasmon modes of different symmetry (dipole, quadrupole and so on).

The optical properties of nanoparticles are characterized by absorption cross section and scattering cross section: σ_{abs} σ_{sca}. The cross section of extinction $\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$. It is related to the extinction coefficient $\gamma_{ext} = N\sigma_{ext}$,

where N—number of nanoparticles per unit volume. In the quasi-static approximation, the cross section of the extinction of the frequency of light is given by the Mie equation:

$$\sigma_{\text{ext}}(\omega) = 9\frac{\omega}{c}\varepsilon_{\text{m}}^{3/2}V_0\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_{\text{m}}]^2+\varepsilon_2(\omega)^2} \quad (1)$$

Here, $V_0 = (4\pi/3)\ R^3$—the amount of particles, ε_{m}—the dielectric constant of the surrounding material and $\varepsilon_1\ (\omega)$ and $\varepsilon_2\ (\omega)$—the real and imaginary parts of the dielectric constant of the metal.

The surface plasmon resonance peak of small spherical particles is shifted to longer wavelengths with increasing particle size and dielectric constant. Small spherical bilayer nanoshells also have a response that is shifted to longer wavelengths with increasing particle size, the permeability of the core and the dielectric environment, and reducing the ratio of shell thickness to core size [28].

Morphology of nanoparticles is another important factor. Small nanorods have two resonances corresponding to transverse and longitudinal dimensions in regard with the polarization of light. The transverse resonance is usually of lesser interest, while the longitudinal resonance axial ratio is easily customizable and has a high Q-factor. Nanorods were shown to serve as wavelength-controllable activation centers, i.e., in this case the release depends on the wavelength of laser light [29]. Furthermore, optical properties of metal nanoparticles depend on the dielectric properties of the surrounding matrix, which, in the case of nanorods, is limited to surfactants used for stabilization of the nanorods growth.

Optical properties of aggregates of NP

NP adsorbed on polyelectrolyte multilayers have been the subject of early research. The interaction of gold nanoparticles, stabilized by a positively charged dimethylaminopyridine, with different polyelectrolytes was studied [30]. Here, the plasmon absorption band of nanoparticles broadens and shifts to the red part of the spectrum (longer wavelengths) with the addition of PSS, PEI and PAH. This was ascribed to the fact that the PSS electrostatically binds to gold nanoparticles and PEI and PAH form weak covalent bonds. Addition of PDADMAC to the sol does not affect the absorption band, suggesting that the polyelectrolyte does not interact with the nanoparticles. Another study focused on the optical properties of polyelectrolyte films obtained by polyionic assembly comprising of 12-nm gold nanoparticles [31]. The nanoparticles were incorporated into the film by adsorption of the sol. All films had a peak at 510–550 nm, corresponding to the red-shifted (due to the dielectric environment) peak of individual plasmon resonances. By increasing the particles surface density (decrease of the distance between the particles), the peak position of the surface plasmon resonance shifted to the red part of spectrum, accompanied by an increase of its height.

The interaction of nanoparticles affects the optical properties of the system, wherein the sum of the external field and fields generated by other particles plays an important role. When the distance between the particles is less than approximately the diameter of the particles, a change in the absorption spectrum is seen [32]. The excitation of the surface plasmons in pairs of gold nanoparticles obtained using electron beam lithography was studied [33]. A two-dimensional structure on the substrate with different distances between nanoparticles with a diameter of 150 nm was obtained. It was observed that as the distance between the nanoparticles decreases, the peak of the surface plasmon resonance is shifted toward longer wavelengths from 780 to 870 nm, when the polarization of light is parallel to the axis of the particle pair, and toward lower wavelengths up to 760 nm, when the polarization is perpendicular to that axis. This was assigned to due to dipole–dipole interaction between neighboring particles.

Measurement of temperature rise upon laser illumination

We note that other materials, for example, laser absorbing dyes [18], shape-switchable azobenzene [34], photosensitive porphyrins [35, 36], carbon nanotubes [37], graphene oxide [38] and photochemically activated polycations [39], can also be used for generation of heat upon laser illumination. Peculiar is the fact that IR-sensitive dye IR-806 (the maximum absorption at 806 nm), although having much smaller absorption cross section than metal nanoparticles, was still found suitable for remote activation by laser light. These experiments were conducted using a laser diode (intensity of 60 mW) focused through a 100×/NA 1.25 microscope objective.

Nanoparticles possess a higher absorption cross section than organic dyes. The mechanism of heat generation on nanoparticles is the conversion of the laser field generated energy driving electrons within nanoparticles into heat. The heat dissipates from nanoparticles into the environment. Production of heat is particularly strong if the excitation takes place into the nanoparticle surface plasmon resonance band, in which case the collective motion of a large number of electrons is most pronounced. It can be noted that for semiconductor nanoparticles, the heat release rate is much weaker because heat occurs through the interband absorption process with the creation of a mobile electron and a hole (exciton). Prevention of aggregation relies on the surface stabilization of nanoparticles—the functionality, which can also be used for targeting of nanoparticles [40].

Numerical simulation and analytical calculations revealed that that aggregates produce a higher temperature rise than stand-alone nanoparticles [41], and different aggregation states can be obtained [41, 42]. Methods of measuring the temperature distribution around polyelectrolyte multilayer capsules were proposed earlier [10], where a suspension of capsules was immersed in the solution containing Tris buffer containing a temperature-sensitive dye (BCECF, Molecular Probes). Subsequently, the change in fluorescence intensity of the dye was assigned (by calibration) to the temperature change around the capsule. The temperature rise around nanoparticles incorporated into the capsule shell is proportional not only to the intensity of the incident radiation, but also to the size of the nanoparticles, as well as their concentration in the capsule shell or, in other words, their filling factor [40]. It can be noted that Raman Stokes/anti-Stokes signals [43] as well as rare-earth upconversion systems [44] have been recently reported to be alternative methods for temperature measurements.

Control of the direction of heat propagation

Phenomena considered here are not directly related to the main subject of the permeability of polyelectrolyte multilayer control, but they can be used for modifying nanoparticles and for affecting polyelectrolyte multilayers. Further extension of the surface modification by laser–nanoparticle interaction was demonstrated by controllable embedding of nanoparticles into the polymeric layers [45].

Upon heating a metal nanoparticle by a laser, the generated heat symmetrically spreads around. The easiest way to control the flow of the heat propagation is to place nanoparticles at the interface between two different media with two different thermal conductivities/diffusivities. A classic example in this case would be the water–air interface, which is particularly interesting for directing heat into water in this case. Figure 2 demonstrates a situation when the temperature rise stimulates heating of the water (and not air, which is a good isolator). This principle was applied to embed nanoparticles into a polymeric coating [45].

Synthesis and adsorption of metal nanoparticles on polyelectrolyte multilayers

In a large number of applications, nanoparticles have been used to control heating in the shell of microcapsules, as shown in Fig. 3. Here, they (nanoparticles) have a dual function: a) They serve as active centers absorbing light and converting it to heat, and b) they can be used for strengthening and improving mechanical properties of microcapsules [46]. Laser–nanoparticles interaction is one of the main applications considered in this mini-review, and that is why this functionality is analyzed in details here. Control over the laser–nanoparticle interaction can be performed by intensity of incident light, the ambient medium and the size as well as the distribution of nanoparticles.

The adsorption of pre-synthesized nanoparticles

In regard to polyelectrolyte multilayer capsules, metal nanoparticles can also be incorporated into their walls [7–11] by means of adsorption from a pre-synthesized sol. Stabilized nanoparticles are adsorbed on the oppositely charged polyelectrolyte layer by electrostatic interaction. Chemical reduction (e.g., using the method of Turkevich) is one of the popular methods used for the preparation of colloidal solution of metal particles. Recovery of metal salts is carried out by various reducing agents in the presence of stabilizers. The system's capability to maintain a degree of dispersion of nanoparticles, due to the same

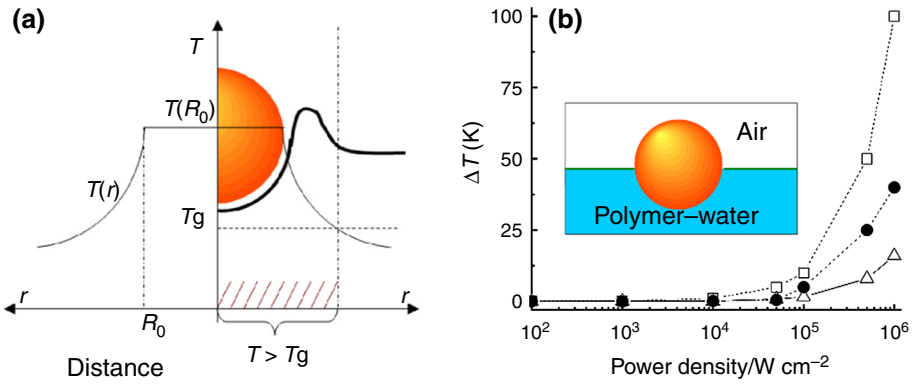

Fig. 2 **a** Temperature rise in nanoparticles: temperature as a function of distance (*left-hand side of the graph*); schematics showing that the polymeric network is modified in the area where $T > Tg$ (*right-hand side of the graph*). **b** Temperature rise in a 20-nm nanoparticle as a function of the incident power density in air (*hollow squares*), polymer–water (*hollow triangles*) medium and that for polymer–water–air systems (*solid circles*). Reproduced from [45] with permission of the American Institute of Physics

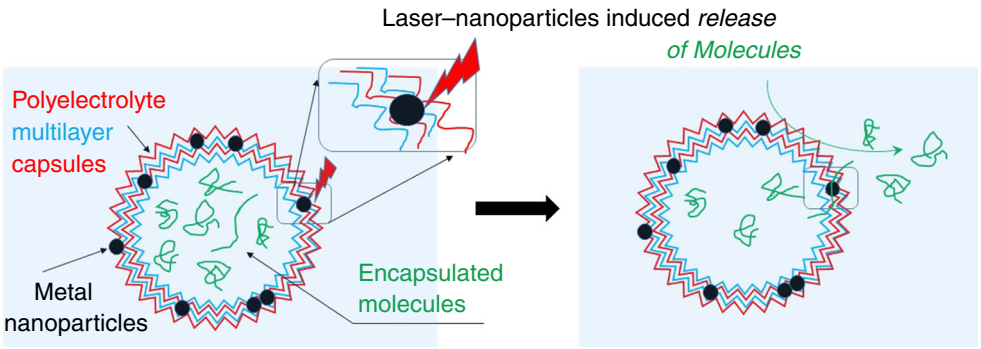

Fig. 3 Schematics of the laser-induced release from polyelectrolyte multilayer capsules

charge, prevents the aggregation. The appearance of such charges is connected with a high capacity of nanoparticles to adsorb ions from a solution. To prevent the aggregation of metal nanoparticles, stabilization can be also performed by the solvent transfer.

The methods of synthesizing nanoparticles in the capsule shell

Alternatively to the adsorption of pre-synthesized nanoparticles on polyelectrolyte multilayers, they can be directly synthesized on the polymeric surface. For the formation of nanoparticles directly in the shell or within capsules, a chemical or photocatalytic reduction can be used. Such polyanions as PSS or polyaniline can act as electron donors for photocatalysis of silver recovery. Low light intensity irradiation is used at centimolar concentration of silver ions in the surrounding volume to proceed with the photoreduction of silver, while an increase in light intensity accelerates the duration of the reaction.

One effective way to obtain silver nanoparticles in the polyelectrolyte shell is recovery of silver ions by means of the silver mirror reaction. It can be noted that the polyelectrolyte shell also acts as a stabilizer for the formed particles. The silver mirror reaction is the process of the chemical reduction of silver by the oxidation of acetaldehyde [42, 47]:

$$AgNO_3 + NH_4OH = AgOH + NH_4NO_3$$

$$AgOH + 2NH_4OH = \left[Ag(NH_3)^2\right]OH + 2H_2O$$

$$2\left[Ag(NH_3)^2\right]OH + CH_3CHO = CH_3COONH_4 2Ag^+ + 3NH_3 + H_2O$$

The variation of the reaction conditions offers extensive possibilities to control the nanoparticle growth [48]. Prepared by this method, nanoparticles may exist in the form of a slurry in water or as a coating on the microspheres of silica and polystyrene. According to transmission electron microscopy analysis, the formation of nanoparticles includes three steps: (1) nucleation, (2) growth and aggregation and (3) conversion into discrete particles. It was shown that the growth of the nanoparticles depends on the temperature at which the reaction takes place: the size of the resulting nanoparticles increases with increasing temperature. This is due to the higher frequency of collisions between the particles at elevated temperature.

The first reaction of a silver mirror for silver nanoparticles in polyelectrolyte capsule shell was applied by Antipov [47]. A certain amount of polymer deposited layers was placed in a solution of [Ag $(NH_3)_2$] OH with the addition of acetaldehyde. The positively charged Ag^+ ions adsorbed on the outer negatively charged polyelectrolyte layer are further reduced resulting in the formation of silver nanoparticles. Using different sequences of polyelectrolyte layers and silver nanoparticles, structures with different properties and stability were obtained [49].

Controlling the aggregation state of nanoparticles in polyelectrolyte multilayers

Controlling the aggregation state of nanoparticles has been performed for gold and silver nanoparticles. In the case of nanoparticles, it is essential to control their distribution on the surface, and two factors can be considered here: the surface density of particles and their aggregation state. It has been shown that the increase in the surface density results in a shift of the absorption band toward longer wavelengths. Controlling the distribution of nanoparticles can be performed by polymers simultaneously adsorbed with nanoparticles or relative concentrations of nanoparticles versus capsules on which they are to be deposited [41].

The aggregation state of silver nanoparticles and their size have been performed by controlling the rate of the silver mirror reaction, which was widely used to produce silver particles [42].

The influence of morphology of nanoparticles: nanoparticles, nanorods, nanocages

The shape of both gold and silver nanoparticles can also be controlled. In the former case, the addition of CTAB

molecules results in fabrication of elongated gold nanorods [50]. Nanorods enable the wavelength selective permeability control of microcapsules and other drug delivery vesicles [29, 51, 52], which is viewed to be particularly important for theranostics [53]. Some other geometries include gold nanostars produced by the group of Liz-Marzan [54], which appear to be effective light absorbers.

In the case of silver nanoparticles, the conversion of small colloidal silver nanoparticles (diameter <10 nm) into larger nanoparticle of different shapes can be carried out by conducting a silver mirror reaction also in the presence of CTAB (n-hexadecyltrimethylammonium bromide) at a temperature of 120 °C. The resulting particles were obtained in the form of cubes, triangles, filaments and rods. The shape and size of the nanoparticles depends on the concentration of surfactants and reactants, temperature and time of the synthesis. Increasing the concentration of CTAB can be used to control the shape of nanoparticles: spherical, cubic and filamentous were obtained. Increasing the concentration of $[Ag(NH_3)_2]^+$ leads to an increase in the average size, and then the appearance of particles with triangular shapes. Cubic particles are monodisperse and monocrystalline and have strictly cubic shape with facets 200. In the course of the reaction CTAB stabilized, small, silver colloid particles were initially formed. They are unstable because of the large value of the surface energy and due to the thermal motion of the particles collected in the larger spherical shape. This is due to the fact that the growth is faster in directions 111 and 110 than in 200, assigned to a stronger bond of CTAB with silver crystal planes 111 and 110. The formation of one-dimensional chains of colloidal silver particles with a diameter of about 4-nm CTAB micelles as well as nanowires along these chains was also observed.

Selected applications

Remote permeability control of polyelectrolyte shells with the laser radiation

Encapsulation [55] and release [56] of molecules using polyelectrolyte multilayer microcapsules, prepared on different cores [13], is a promising method for the controlled storage and transport of compounds. Two distinct ways of controlling the permeability [57] of capsules and thus release of encapsulated cargo by laser light are possible: a release with explosion [18] and a non-disruptive release [58, 59]. In the former case, excessive energy accumulation around a microcapsule results in its explosion, while in the latter case, the energy is concentrated only at the discrete heating centers generating the permeability change in the polymeric membrane, Fig. 4. It was shown that intracellular operation of such capsules can lead to cell death in the former case, while maintaining viability of cells in the latter case [60]. The higher energies and temperatures can be used for laser-induced processing or deposition of nanoparticles on other metals [61].

Release of the encapsulated material takes place only if the shell is heated so that its disruption occurs. Another interesting effect is fusion of microcapsules, which was realized first by salt [62] and then by remote laser action [63].

Intracellular delivery of peptides: study relevant for immune system response

Remote release of encapsulated material within living cells was first shown by a cw laser [64], where polymeric capsules with a model system molecule, AF-488 (Alexa Fluorophore)-labeled dextran, were released at a desired point in time and at a desired location [65]. Gold nanoparticles were incorporated into the shell of capsules. Subsequently, the same principles were applied to release small peptides inside living cells. In these studies, relevant for immune system response, the surface presentation of small peptides was observed on the cell surface upon intracellular release. Although such concept was proposed earlier, intracellular release of peptide had a special place in that area as this represented an unambiguous and "clean" way of verifying such a hypothesis. Direction-specific release [66] and specific delivery into cytosol are point to future developments in this area conducted by capsules [67].

Nanoparticles on polymeric layers

Thermal properties of polyelectrolyte multilayers [68, 69] have been the subject of particular interest. Not only capsules, but also films [70] benefit from plasmonic nanoparticles. In such applications, nanoparticles are adsorbed on the surface of films. Activation of such films by laser light results in release of adsorbed molecules from the surface of the films [71] or by microcapsules embedded directly into the films [72]. Subsequently, these released molecules should be capable of reaching cells grown on the surface of the films. The coatings in the form of fibers can also serve as an effective surface for adsorption of nanoparticles [73], wherein utilization of sensing properties [74] can be explored.

On the one hand, that enables to study the surface properties of materials in comparison with bulk properties, while on the other hand such an approach is relevant for controlling the patchiness [75] of non-symmetric (Janus, for example) particle modification.

Further application of nanoparticles on the surfaces and coatings includes laser-guided cell displacement and detachment [76, 77]. Here, heat also plays an important

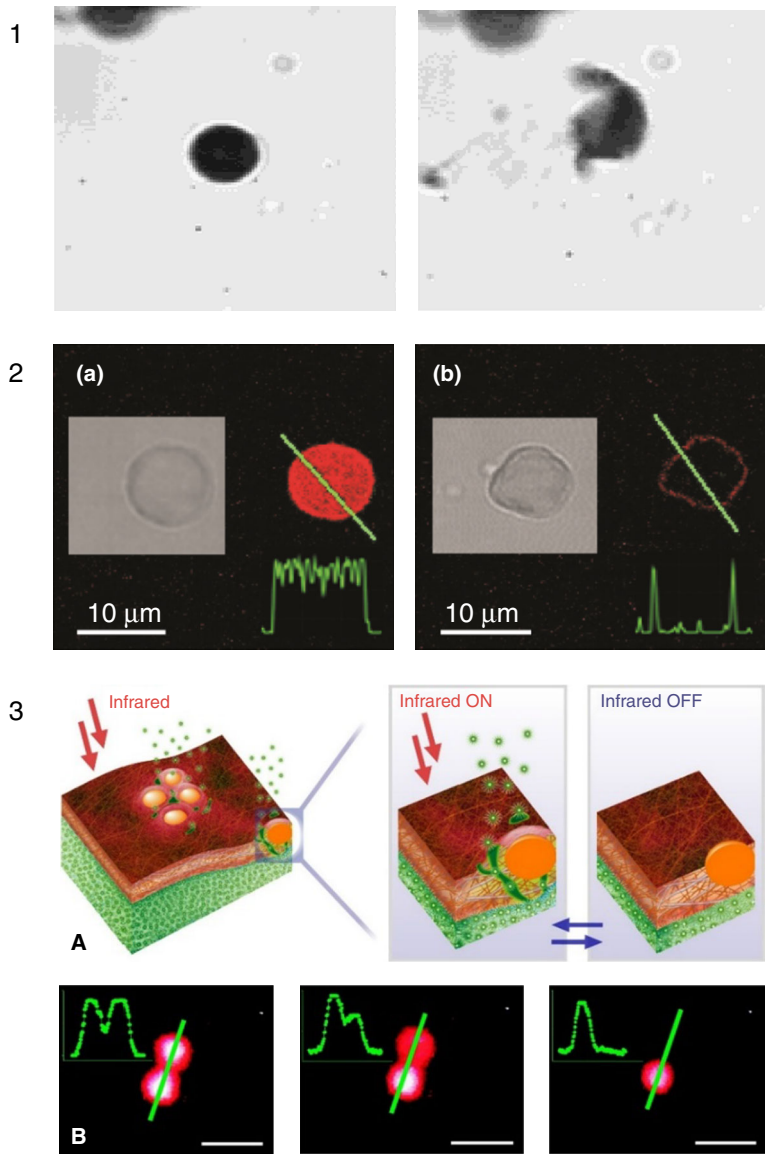

Fig. 4 Remote release from microcapsules by laser light: (1) destructive capsule break-up realized under conditions similar to those reported earlier [18]; (2) nondestructive release by creating transient pores in the microcapsule shell. Reproduced from [59] with the permission of ACS

role in facilitating the disruption of cell surface interaction and eventual detachment of cells. It can be noted that such a disruption can be also directly used for biomolecule delivery [78, 79].

From polymeric to lipid membranes and red blood cells

Not only polymeric, but also lipid membranes could be modulated by plasmonic nanoparticles. It was shown by different groups and under different conditions that nanoparticle functionalized liposomes can release encapsulated materials from its interior [80–86]. Optical trapping was used to guide nanoparticles through lipid membranes [87], while in another example, nanoparticles adsorbed on the lipid membrane enabled modulation of the lipid membrane [88]. The above studies were conducted with a cw (continuous wave) laser, although pulsed laser sources could also be used for affecting the cell membrane [38]. Further extension of this work was carried out by encapsulating and releasing two very different (small <1 kD and large >50 kD) molecules inside red blood cells (RBC). Using developed for microcapsules methods of depositing nanoparticles on the surface of RBC and applying laser light, simultaneous release of both molecules was demonstrated [89].

On-demand corrosion protection and release from multicompartment capsules

Corrosion protection is seen as an important application area. In this area, capsules were incorporated into the

coatings and were subsequently activated by laser light enabling release of corrosion inhibitors [90], thus complementing self-healing [91, 92] coatings [93].

Release from microcompartment [94] capsules, particularly those possessing anisotropic functionality [95], is essential for different applications and can lead to creation of sophisticated multireactors [96].

Outlook and conclusions

In this mini-review, we have described the heat generation on nanoparticles and its application to control the polymers at the nanoscale. Theoretical description of the mechanism of heat generation is highlighted together with the methods of synthesis of nanoparticles in solution or directly on the polymeric shells. Nanoparticle synthesis is also considered in regard with the aggregation state of nanoparticles, revealing the importance of non-aggregated versus aggregated states of nanoparticles. A number of phenomena, including intracellular release, polymeric coating modification, membrane permeability modulation and corrosion protection are considered as potentially important, relevant areas of applications. In future, investigation of physicochemical properties (for example phase transitions [97]) is viewed in conjunction with further development, especially biological, applications.

Acknowledgements We thank the EU-IRSES Mari-Curie project "DINaMIT", FWO (Flemish Research Council) and BOF (University of Ghent) for support of this work. BVP is an FWO fellow.

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