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Near-infrared photochemistry at interfaces based on upconverting nanoparticles

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Near-infrared (NIR) light is better suited than ultraviolet (UV) light for biomedical applications because it penetrates deeper into tissue and causes less photodamage to biological systems. The use of NIR light to control biointerfaces has attracted increasing interest. Here, we review NIR photoreactions at interfaces based on upconverting nanoparticles (UCNPs). UCNPs can convert NIR light to UV or visible light, which can then induce photoreactions of photosensitive compounds. This process is referred to as UCNP-assisted photochemistry. Recently, we and others demonstrated UCNP-assisted photochemistry at interfaces to control interfacial properties of nano-carriers, implants, emulsions, and cells. We introduce the fundamentals of UCNP-assisted photochemistry at interfaces, highlight its potential applications, and discuss remaining challenges.

1. Introduction

Interfacial properties of materials are important for diverse applications in our daily lives, fundamental research, and industry. Light provides a non-contact way to control interfacial properties with high spatiotemporal resolution. The development of photosensitive interfaces has attracted a lot of attention (Fig. 1).^{1–8} Grafting photosensitive compounds on a substrate can prepare photosensitive surfaces (Fig. 1a). Photoreactions such as photoisomerization, photopolymerization, photolysis, and

photo-coupling on a substrate can control surface properties and functions.^{1,2,4–10} These surface photoreactions have been used for controlling wettability,^{2,4,6,11,12} preparing coatings and patterns,^{7,13–15} controlling motions of objectives on a surface,^{2,4} regulating adhesion,^{16,17} and switching electromagnetic devices.^{18,19} A topic under intense investigation is photosensitive surfaces of nanoparticles (NPs) (Fig. 1b). NPs have large surface areas; their stability, properties and functions are strongly influenced by their surface properties. Inducing photoreactions at NP surfaces is an elegant way to manipulate NPs.^{20–23} A topic related to photoreactions at surfaces is photoreactions at other interfaces (Fig. 1c). Photosensitive surfactants, amphiphiles, lipids, and colloids are usually used for interfacial

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light can induce photoreactions of photosensitive compounds. This process is referred to as UCNP-assisted photochemistry. Compared with NIR photochemistry based on two-photon absorption, UCNP-assisted photoreactions are more efficient. The excitation intensity for UCNP-assisted photochemistry is several orders of magnitude lower than that for two-photon absorption.³⁹ UCNP-assisted photoreactions are induced by inexpensive NIR laser diodes and do not require high-intensity, expensive femtosecond lasers.³⁹ Additionally, it has been demonstrated that NIR light can induce UCNP-assisted photoreactions after passing through tissue with a thickness of a few millimeters.³⁹ Moreover, UCNP are highly stable under laser excitation.

We will not introduce the mechanism of photon upconversion and the synthesis of UCNP in this perspective because there are comprehensive and very good reviews.^{49–53} Photodynamic therapy and NIR light-sensitive materials based on UCNP have also been reviewed.^{39,54,55} In the current perspective article, we concentrate on UCNP-assisted photochemistry at interfaces, highlight some potential applications, and discuss future challenges.

2. General concept of UCNP-assisted photochemistry

In UCNP-assisted photochemistry, UCNP convert NIR light to UV or visible light (Fig. 3). Two typical UCNP, NaYF₄:Yb/Tm UCNP (β-phase NaYF₄ doped with Yb³⁺ and Tm³⁺) and NaYF₄:Yb/Er UCNP (β-phase NaYF₄ doped with Yb³⁺ and Er³⁺) are shown in Fig. 3b and c. In these UCNP, Yb³⁺ is the sensitizer which can harvest NIR light and transfer energy to Tm³⁺ or Er³⁺. The energy transfer process from Yb³⁺ to Tm³⁺ or Er³⁺ may occur for several times so that Tm³⁺ or Er³⁺ can be excited to a higher excited state. Tm³⁺ is a UV/blue emitter; Er³⁺ is a green/red emitter.

The second important component for UCNP-assisted photochemistry is the photosensitive substance. Conventional photosensitive compounds are usually sensitive to UV or visible light but are not sensitive to NIR light because of their short absorption wavelengths. To make them NIR photosensitive, they are combined with UCNP. The upconverted UV or visible light from UCNP can induce photoreactions of conventional photosensitive compounds (Fig. 3a). A requirement for UCNP-assisted photochemistry is that the emission wavelengths of UCNP should overlap with the absorption wavelengths of photosensitive compounds. If photosensitive compounds are very close to UCNP, energy transfer from excited UCNP to photosensitive compounds may occur. Usually, photosensitive compounds re-absorb upconverted light which induces photoreactions.

UCNP have assisted different types of photoreactions such as photoisomerization,^{47,56–65} photopolymerization,^{66–70} photolysis,^{71–91} and photo-coupling⁹² (Fig. 3a). (1) UCNP-assisted photoisomerization can be triggered reversibly using NIR light in the presence of UCNP and photoswitchable compounds such as azobenzene derivatives,^{59,63} spiropyran derivatives,^{64,93} and dithienylethene derivatives.^{47,56} (2) UCNP-assisted photopolymerization is useful to cure thick samples

(up to 13.7 cm).⁷⁰ Different monomers have been polymerized under NIR light irradiation in the presence of photoinitiators and UCNP.⁶⁷ (3) UCNP-assisted photolysis is conducted by combining UCNP with photolytic compounds including *o*-nitrobenzyl derivatives,^{72,73} coumarin derivatives,^{80,82} Ru complexes,^{81–84,91} and other photocaged compounds.^{85–88} UCNP-assisted photolysis has been extensively studied because of its wide applications such as drug delivery,⁷² activation of sensors,⁷⁴ and controlling protein adsorption and cell adhesion.^{81,90} (4) UCNP-assisted photo-coupling is a new type of UCNP-assisted photoreactions, which was demonstrated by us and our collaborators very recently.⁹² These UCNP-assisted photoreactions at different interfaces will be discussed in the next sections.

3. UCNP-assisted photochemistry at nanoparticle surfaces

NIR light can trigger reactions of photosensitive compounds grafted on UCNP (Fig. 4). Upon NIR irradiation, the grafted photosensitive compounds may absorb the upconverted light that induces photoreactions. The short distance between the grafted photosensitive compounds and UCNP may allow non-radiative energy transfer from the excited UCNP to the photosensitive compounds. Therefore, UCNP-assisted photoreactions at UCNP surfaces are usually more efficient than UCNP-assisted photoreactions in solution, where photosensitive compounds are far away from UCNP.

The first UCNP-assisted photoreaction at UCNP surfaces was reported by Branda and co-workers.⁷¹ UCNP were grafted with 3',5'-di(carboxymethoxy)benzoic cage **1a** (Fig. 5). UCNP converted 980 nm NIR light into 290 nm UV light, which induced the release of the caged species on the UCNP surface. This work opened up the avenue of using UCNP for NIR-controlled drug delivery, surface modification, and activation of sensors, prodrugs and targeting groups.

NIR light-induced release of caged species was used to activate cell targeting groups on UCNP surfaces (Fig. 6).⁷⁷ To achieve phototargeting, the tumor-homing agent folate was caged with a photolytic *o*-nitrobenzyl group and grafted onto UCNP. Upon NIR irradiation, the upconverted UV light uncaged the *o*-nitrobenzyl

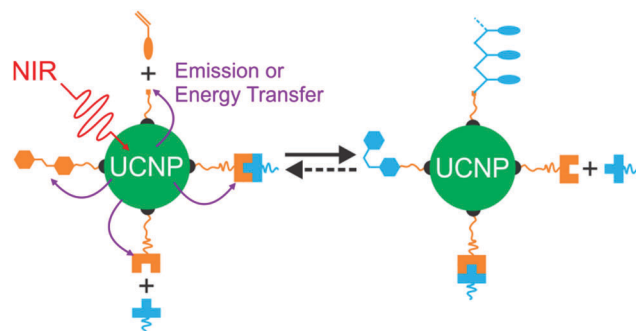


Fig. 4 Schematic illustration of UCNP-assisted photochemistry at NP surfaces.



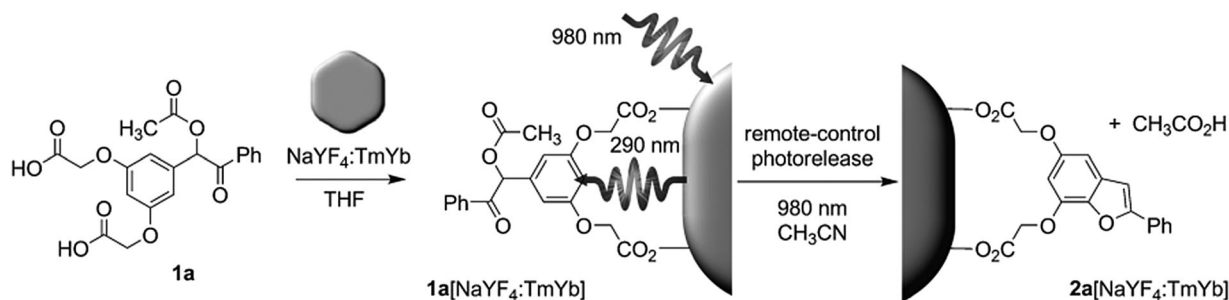


Fig. 5 UCNP-assisted photolysis at surfaces of UCNPs. Decoration of UCNPs with 3',5'-di(carboxymethoxy)benzoin cage **1a** produces the remote-control release system (**1a[NaYF₄:TmYb]**), which can be triggered by indirect irradiation with NIR light to generate **2a[NaYF₄:TmYb]** and release a carboxylic acid. Reproduced with permission.⁷¹ Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

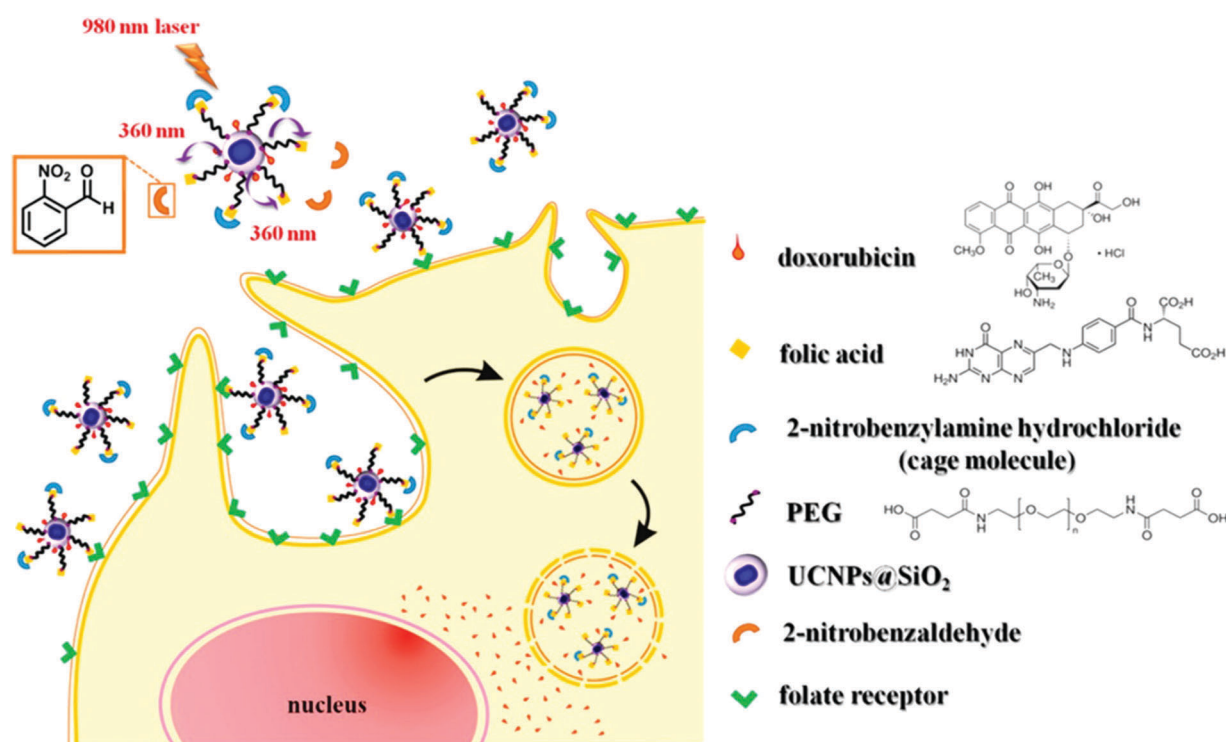


Fig. 6 Illustration of NIR-light-controlled targeting of cancer cells via UCNP-assisted photochemistry. Targeting of cancer cells can be achieved by the activation of the photocaged folic acids on the surfaces of the UCNPs using NIR light. Reproduced with permission.⁷⁷ Copyright 2013, American Chemical Society.

group and allowed folate-conjugated UCNPs to target cancer cells. After the UCNPs were taken up by cancer cells, the antitumor drug doxorubicin grafted on the surface of UCNPs *via* a disulfide bond was cleaved by lysosomal enzymes within the cancer cells. The released doxorubicin inhibited the growth of cancer cells. The photocaged UCNPs can serve as a platform for the improvement of selective targeting and reduction of side effects in cancer therapy.

Another application for UCNP-assisted photochemistry at NP surfaces is activation of fluorescent dyes for bioimaging (Fig. 7).⁷⁴ Yang *et al.* demonstrated *in vitro* and *in vivo* uncaging and bioluminescence imaging based on photocaged UCNPs. A photocaged *D*-luciferin was conjugated to UCNPs. UCNPs unconverted NIR light into UV light, which uncaged the

o-nitrobenzyl group from *D*-luciferin. As a result, the released *D*-luciferin effectively conferred enhanced fluorescence and bioluminescence signals. Shen *et al.* also used NIR light to activate a fluorescent dye grafted on UCNPs.⁷⁶ Caged fluorescein, which can recover fluorescence upon removing the photolytic *o*-nitrobenzyl group, was grafted on UCNPs. UCNPs converted NIR light into UV light to uncage fluorescein in live cells. NIR photoactivation for enhanced bioimaging is an important technique that may offer new possibilities for analyzing cell lineages, probing cellular protein dynamics, and monitoring the dynamic functions of cells.

Several groups have constructed NIR-controlled drug delivery systems based on UCNP-assisted photochemistry at NP surfaces.^{60,62,79,83,85,86} For example, we coated UCNPs with a



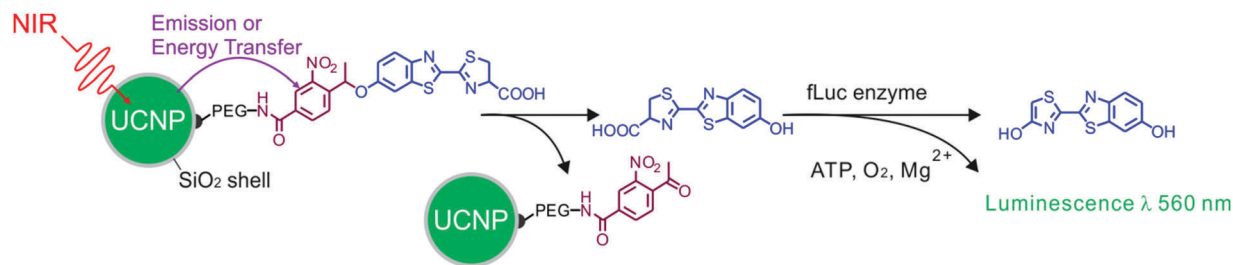


Fig. 7 UCNP-assisted photochemistry at surfaces of core/shell UCNPs for bioimaging. NIR light induced uncaging of *D*-luciferin and subsequent bioluminescence. Adapted with permission.⁷⁴ Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA.

mesoporous silica shell, loaded the anticancer drug doxorubicin in the pores, and grafted photocleavable Ru complexes onto the NP surfaces (Fig. 8a).⁸³ The Ru complexes acted as molecular valves, which prevented drug leakage. Upon NIR irradiation, the upconverted blue light induces cleavage of Ru complexes

that releases the drug which inhibited cancer cells growth. The advantage of this system is that drug release was triggered by 974 nm light with an intensity as low as 0.35 W cm^{-2} . Such a low light intensity minimized overheating problems and prevented photodamage to the biological system.

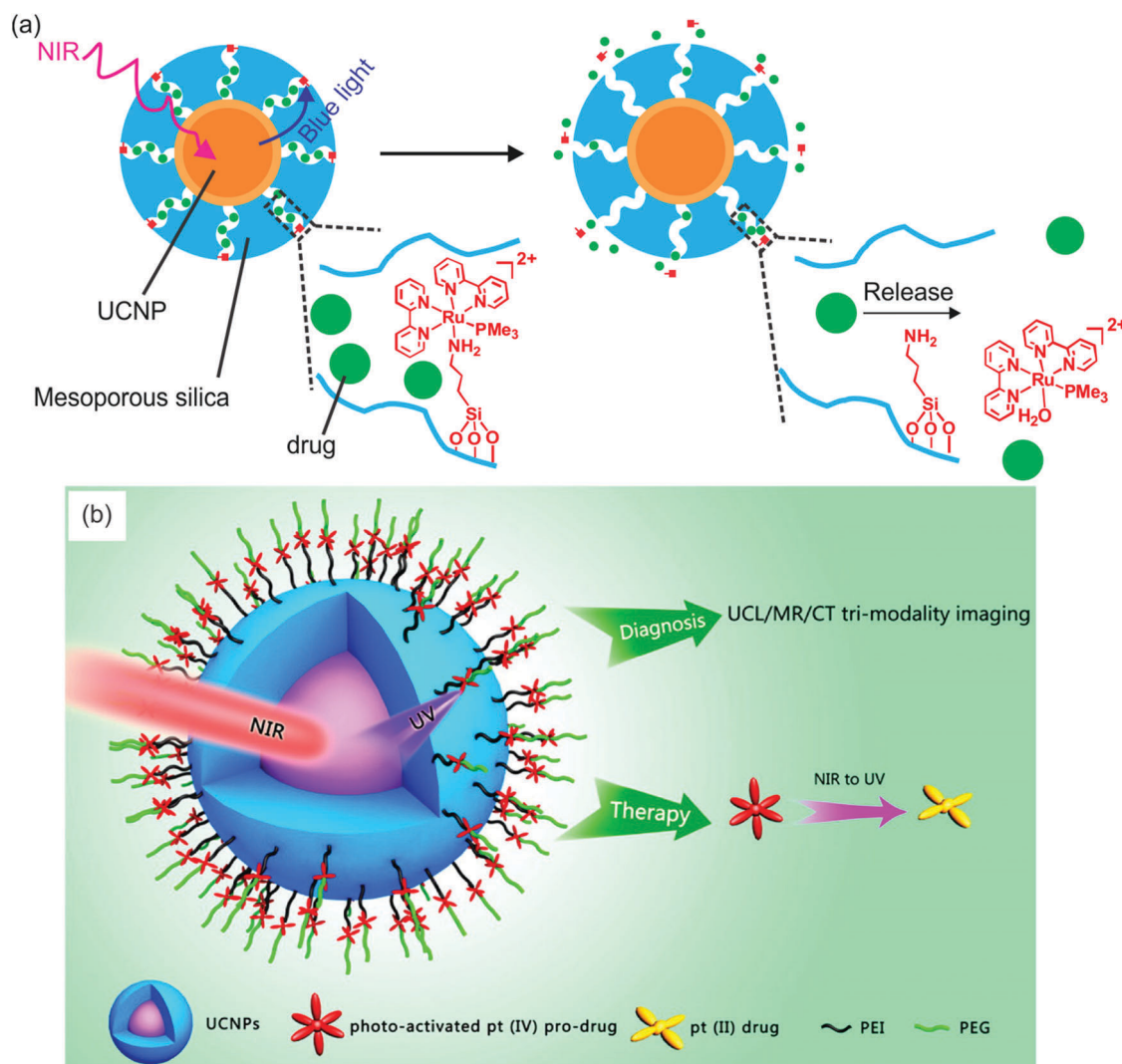


Fig. 8 UCNP-assisted photochemistry at NP surfaces for drug delivery. (a) NIR light-induced drug release using UCNP/mesoporous silica core/shell NPs functionalized with photocleavable Ru complexes. Under NIR excitation, the upconverted blue light triggers cleavage of the Ru complexes and release of the drug doxorubicin (green balls). (b) Schematic illustration of UCNPs functionalized with a photoactivated Pt(IV) prodrug. Panel (a) adapted with permission.⁸³ Copyright 2015, Royal Society of Chemistry. Panel (b) reproduced with permission.⁸⁵ Copyright 2013, American Chemical Society.



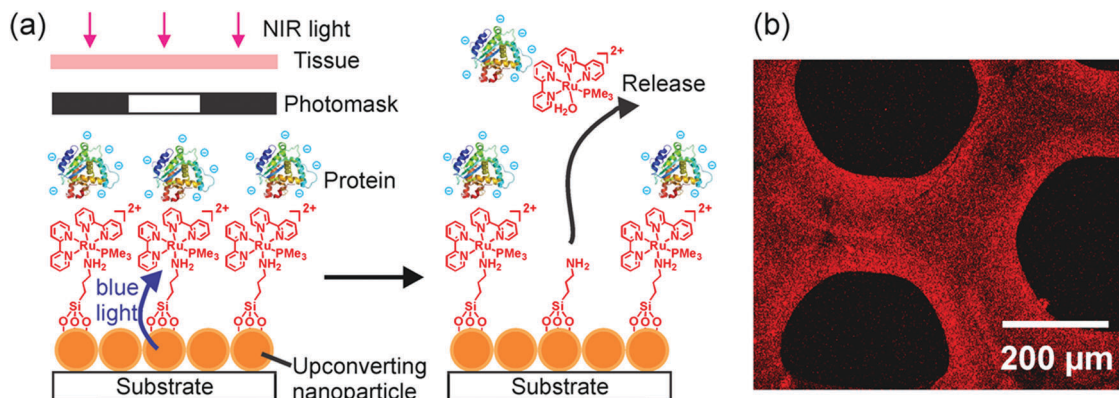


Fig. 11 (a) Schematic of photon upconversion lithography for the patterning of proteins. Polyethylene glycol, which is co-grafted with Ru complexes on the UCNPs, is not shown for clarity. (b) Confocal laser scanning microscopy image of a protein pattern fabricated using photon upconversion lithography. Adapted with permission.⁸¹ Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA.

UV light and merocyanine-to-spiropyran back isomerization is induced using green light. Qu and co-workers synthesized $\text{NaYF}_4:\text{Tm}/\text{Yb}@\text{NaYF}_4@\text{NaYF}_4:\text{Er}/\text{Yb}@\text{NaYF}_4$ core-shell-shell UCNPs, which emit more UV light under the excitation of high-intensity 980 nm light (e.g., 8 W cm^{-2}) and emit more green light under the excitation of low-intensity 980 nm light (e.g., 0.5 W cm^{-2}).⁶⁵ Thus, the two-way isomerization of spiropyran on the UCNPs merely depends on the excitation intensity. At a high intensity, the spiropyran-to-merocyanine isomerization was prominent, whereas its reverse isomerization occurred upon irradiation by the same laser but with a lower intensity. Such NIR-controlled reversible isomerization made the interactions between surface-grafted spiropyran and cell surface protein fibronectin switchable, thus leading to reversible cell adhesion and detachment. Moreover, efficient adhesion-and-detachment of cells was realized even after 10 cycles. NIR light showed little damage toward cells and could

control cell adhesion after passing through 4 mm-thick tissue. This approach is promising for *in vivo* dynamically manipulating cell-molecule interactions and biological processes.

5. UCNP-assisted photochemistry at liquid/liquid interfaces

NIR light can also trigger UCNP-assisted photoreactions at liquid/liquid interfaces. Recently, Chen *et al.* demonstrated UCNP-assisted photoisomerization at water/oil interfaces (Fig. 13).⁹⁵ UCNPs conjugated with photoswitchable spiropyran was hydrophobic. Light can reversibly control hydrophobicity/hydrophilicity of the NPs (Fig. 13d). UCNPs converted NIR light to UV light, which induced spiropyran-to-merocyanine isomerization and hydrophobic-to-hydrophilic transition. Subsequently, visible light induced the reverse merocyanine-to-spiropyran

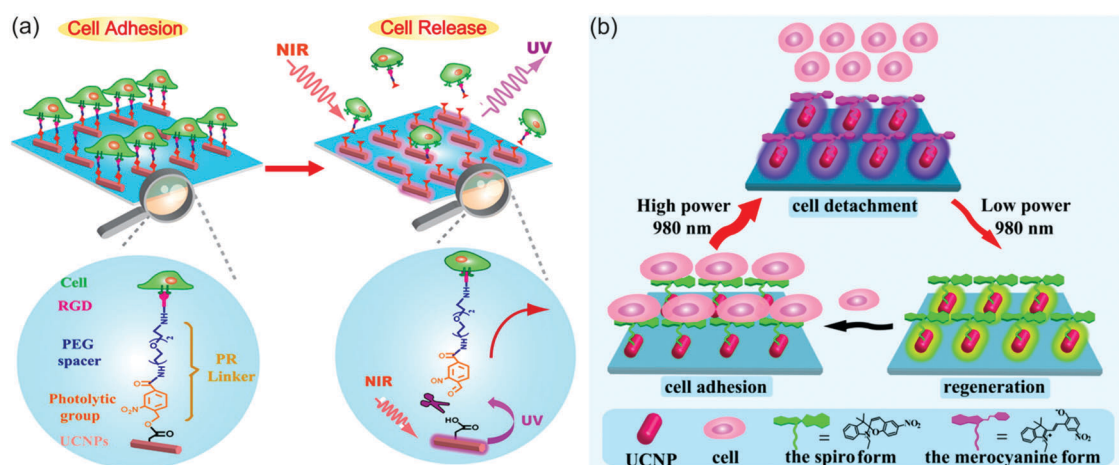


Fig. 12 (a) Irreversible control of cell adhesion using NIR light based on UCNPs. Upon 980 nm light excitation, the UCNPs emit UV photons, which cleave the photolytic linker. As a result, the cells dissociate from the substrate. (b) Reversible control of cell adhesion/detachment using NIR light with different intensities based on UCNPs. At a high intensity (8 W cm^{-2}), the UCNPs emit UV photons and activate the isomerization from the spiropyran form to the merocyanine form, resulting in the cell detachment. Conversely, when exposed to a low intensity (0.5 W cm^{-2}), the same UCNPs can emit visible light to drive the merocyanine form back to the spiropyran form, leading to cell adhesion again. Panel (a) reproduced with permission.⁹⁰ Copyright 2014, American Chemical Society. Panel (b) reproduced with permission.⁶⁵ Copyright 2015, American Chemical Society.



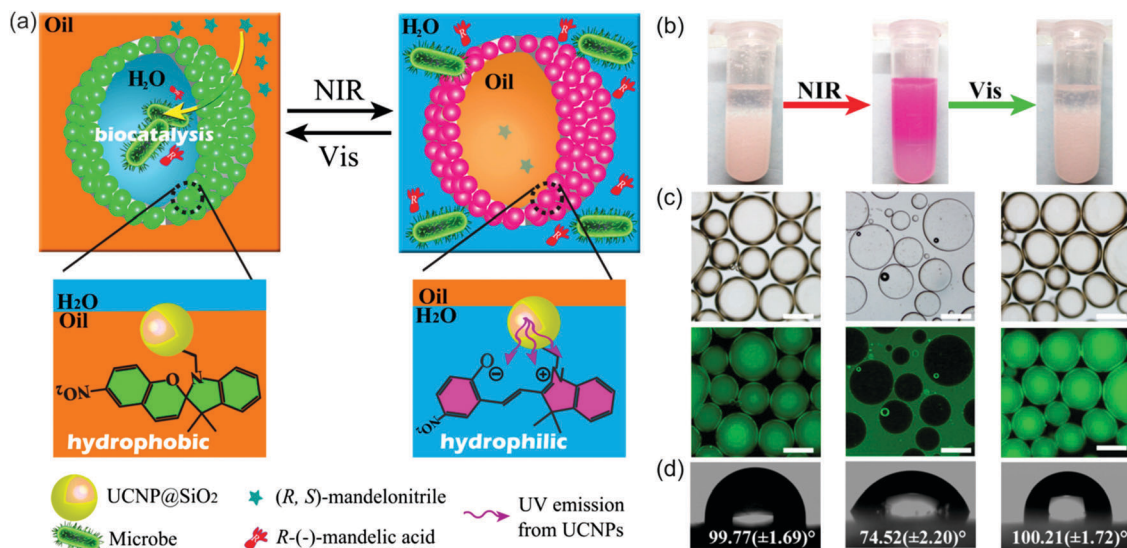


Fig. 13 (a) Schematic illustration of the NIR light-responsive Pickering emulsions with reversible inversion ability for biphasic enantioselective biocatalysis. (b) Photograph of Pickering emulsions stabilized by spiropyran-conjugated UCNPs: w/o (left), o/w (middle), and w/o (right) before and after the irradiation of light with different wavelengths. (c) Fluorescence microscopy images of the corresponding Pickering emulsions shown in (b) (scale bar: 200 μm). (d) Water contact angles on a filter paper deposited with spiropyran-conjugated UCNPs irradiated using light with wavelengths. Reproduced with permission.⁹⁵ Copyright 2014, American Chemical Society.

isomerization and hydrophilic-to-hydrophobic transition. Similar to other colloids,^{96,97} the spiropyran-conjugated UCNPs with interfacial activity are suitable to prepare Pickering emulsions. The Pickering emulsions stabilized by spiropyran-conjugated UCNPs can be inverted under light irradiation (Fig. 13b and c). Spiropyran-conjugated UCNPs can stabilize water-in-oil (w/o) emulsions at the bottom of the sample and prevent sedimentation (Fig. 13b, left). Upon NIR irradiation and homogenization, spiropyran-conjugated UCNPs transferred to the upper layer and oil-in-water (o/w) emulsions were formed (Fig. 13b, middle). Spiropyran-conjugated UCNPs could transfer back to the bottom layer after exposing to visible light and shaking (Fig. 13b, right). A model enantioselective biocatalytic active bacterium was loaded in the aqueous phase (Fig. 13a). The Pickering emulsion enhanced the catalytic performance. In addition, product recovery, and biocatalysts and colloid emulsifiers recycling could be easily realized based on the light-controlled inversion of the Pickering emulsion. Importantly, the utilization of NIR/visible light to perform the reversible inversion without any chemical auxiliaries showed little damage toward the biocatalysts, which was highlighted by the high catalytic efficiency and high enantioselectivity even after 10 cycles. NIR/visible light controlled Pickering emulsions showed promising potential for biocatalysis in biphasic systems.

Another example of UCNP-assisted photochemistry at interfaces is NIR light-induced photoisomerization in the bilayer membranes of vesicles (Fig. 14).⁹⁸ Phospholipid modified UCNPs and the anticancer drug DOX were encapsulated in azobenzene-doped liposomes. NIR light can be converted into UV and visible light to trigger photoisomerization of azobenzene amphiphiles, which resulted in drug release. The release amount and rate of the anticancer drug can be well

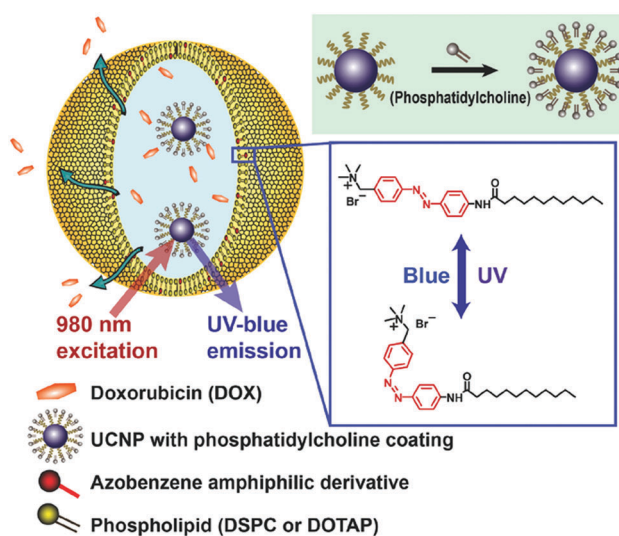


Fig. 14 Schematic illustration of the NIR-triggered azobenzene-liposome/UCNP hybrid vesicles for controlled drug delivery. The phosphatidylcholine coated UCNPs and the anticancer drug DOX are loaded together within the hydrophilic compartment of the liposome. The amphiphilic azobenzene derivatives are embedded in the liposome bilayers consisting of phospholipids (DSPC/DOTAP). Reproduced with permission.⁹⁸ Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA.

controlled by tuning the intensity and duration of the NIR laser. The NIR light-triggered drug release ability makes this novel drug delivery system an effective chemotherapy to overcome multidrug resistance by spatiotemporal control. This drug delivery system provides great values in the advancement of clinical NIR light-regulated precise drug release and drug-resistant tumor treatment.



6. Outlook

From the chemistry point of view, it is interesting to develop new NIR photoreactions at interfaces based on UCNP. UCNP-assisted photoisomerization, photolysis, and photopolymerization at interfaces have been extensively studied and some potential applications have been demonstrated. In contrast, UCNP-assisted photo-coupling reactions have been reported by us and our collaborators only recently;⁹² this type of reactions has not been widely investigated (Fig. 15). We envision the use of UCNP-assisted photo-coupling reactions to modify biointerfaces. A possible application is NIR light-induced NP coupling, which can result in NP aggregates with enhanced therapeutic effects due to the size effect.⁹⁹ Another possible application of UCNP-assisted photo-coupling reactions at interfaces is to glue biological tissues with NIR light.¹⁰⁰

Improving spatial resolution of photon upconversion lithography for the patterning of biomaterials is still a challenge. Two-photon lithography is a standard technique in some labs and in industry to fabricate patterns with a feature size of a few hundred nanometers. However, the smallest feature size fabricated by photon upconversion lithography is only $\sim 15 \mu\text{m}$.⁸¹ It is too large for some studies on interactions between patterned biomolecules and cells.¹⁰¹ It is highly desirable to improve the spatial resolution of photon upconversion lithography. We and our collaborators have shown that the spatial resolution of upconversion can be improved using pulsed excitation because pulsed excitation can avoid saturation in the upconversion process.¹⁰² This technique has been adapted to high-resolution photopatterning by us, which will be reported in due course.

NIR-controlled cell adhesion based on UCNP has been demonstrated and is promising for *in vivo* applications. The next step in this direction would be guide cell migration and stem cell fate. Currently, light-guided cell migration and stem cell fate are based on UV photopatterning or two-photon lithography.^{38,103} Photon upconversion lithography with the spatial resolution of tens of μm should be suitable for these applications.

UCNP-assisted photochemistry at interfaces still faces some problems that may hinder its applications. A big problem for UCNP-assisted photochemistry is photothermal overheating. The quantum yield of UCNP is usually less than 1%.¹⁰⁴ To obtain sufficient UV or visible light for photoreactions, UCNP are excited by high-intensity NIR light; typical excitation

intensities at 980 nm are $0.35\text{--}560 \text{ W cm}^{-2}$.³⁹ Because the maximum permissible exposure for skin at 980 nm is $\sim 0.726 \text{ W cm}^{-2}$,^{105,106} high-intensity 980 nm light can overheat and damage biological systems.⁸² We and others partially addressed the overheating problem using Ru complexes as photosensitive compounds,^{82,83} high-efficient UCNP,⁷⁶ and UCNP that can be excited by 808 nm light.^{107–112} Although NIR light at 980 nm is better suited than UV light for biomedical applications, NIR light at 808 nm is even better because the penetration depth of 808 nm light in bovine tissue is 54% deeper than that of 980 nm light.⁴¹ The development of highly efficient UCNP, which can be excited with 808 nm light, is currently a topic of intense investigation. At the moment, different strategies are under investigation to enhance the efficiency of upconversion.¹¹³ In particular, enhancing upconversion using surface plasmons and photonic structures is a topic under intense investigation because of the potential to achieve large enhancement.^{114–119} Different strategies might be combined in a system to optimize upconversion efficiency and minimize the overheating problem for deep-tissue applications.

Another interesting application of UCNP-assisted photochemistry at interfaces is photovoltaics such as solar cells.^{120–123} The incorporation of UCNP into dye-sensitized solar cells enables the use of the NIR region of the solar spectrum.^{120–123} This design requires the development of highly efficient UCNP that can be excited by broadband NIR light.

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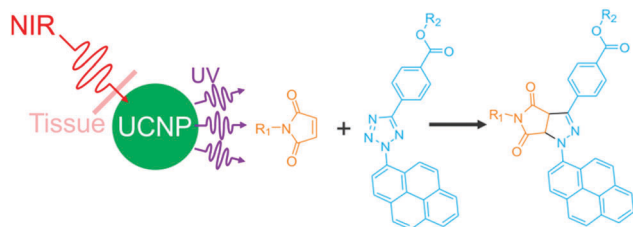


Fig. 15 NIR photo-coupling reaction based on nitrile imine-mediated tetrazole-ene cycloadditions in the presence of UCNP. This type of photoreaction at interfaces still awaits exploration.



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