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Signal-Induced Release of Guests from a Photolabile Metal–Phenolic Supramolecular Cage and Its Hybrid Assemblies

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Dedicated to Professor Chulhee Kim on the occasion of his 60th birthday

Abstract: The coordination chemistry of plant polyphenols and metal ions can be used for coating various substrates and for creating modular superstructures. We herein explored this chemistry for the controlled release of guests from mesoporous silica nanoparticles (MSNs). The selective adsorption of tannic acids (TAs) on MSN silica walls opens the MSN mesoporous channels without disturbing mass transport. The channel may be closed by the coordination of TA with Cu^{II} ions. Upon exposure to light, photolysis of Trojan horse guests (photoacid generators, PAGs) leads to acid generation, which enables the release of payloads by decomposing the outer coordination shell consisting of TA and Cu^{II} . We also fabricated a modular assembly of MSNs on glass substrates. The photoresponsive release characteristics of the resulting film are similar to those of the individual MSNs. This method is a fast and facile strategy for producing photoresponsive nanocontainers by non-covalent engineering of MSN surfaces that should be suitable for various applications in materials science.

Controlled response to a signaling cascade is critical in signal transduction as it enables controlled vital activity.^[1] In particular, channel proteins can selectively gate mass transport in response to certain stimuli generated by complex chemical communication.^[2,3] Creating nanovehicles with a precise response to a signaling cascade on demand would allow the development of complex action systems such as nanorobots.^[4–6] As they can exhibit clear, controlled, on-demand release, mesoporous silica nanoparticles (MSNs) with responsive gatekeepers have been extensively investigated.^[7–14] Owing to the complex chemical communication pathways occurring under physiological conditions, the development of nanomachines that work in a certain way when triggered by complex stimuli is a formidable challenge in

various fields, ranging from nanomedicine to materials science.^[15–19]

Stimuli-responsive nanovalves on the surface of MSNs have attracted much attention as controlled nanomachines for biomaterials science^[7–17,20–24] owing to their clear on-demand performance and good stability against unexpected leakage. Many synthetic versions of such nanovalves for MSNs have been realized to date based on complicated processes. Recently, Yang and co-workers developed smart gating systems by judiciously selecting responsive polymer networks as gatekeepers, and also demonstrated that other porous nanostructures, such as metal–organic frameworks, are good nanocontainers instead of MSNs.^[25–27] Coordination complexes are robust, efficient, and sensitive to their environment; however, owing to their dynamic nature, they have not been heavily investigated for the stabilization of the stimuli-responsive layers of mesoporous silica nanocontainers.

Caruso and co-workers recently showed that the coordination of tannic acid (TA) with metals enables the synthesis of a variety of nanoscale and bulk substrates by simple wet chemistry.^[28–33] This strategy has been employed for the synthesis of various types of multifunctional nanocapsules and combinatorial nanostructures. In contrast, Messersmith and co-workers suggested that plant polyphenols (including TA) can envelop various substrates without the need for coordination when employed as the sole coating precursor.^[34] However, owing to a lack of functionality, such systems have not been considered as photoresponsive systems to date even though such systems can be used to control various properties in both time and space.

Herein, we report a facile strategy to render bare MSNs photoresponsive without making use of covalent modification steps. This approach is based on the simple combination of plant polyphenol–metal coordination and a photoacid generator (PAG) to decompose the coordination complexes upon light exposure. Densely packed MSNs capped with TA–metal complexes were fabricated on a glass substrate by coordination-induced adhesion. This simple strategy was further applied to obtain complex hybrid materials by fabricating both a nanoparticle thin film with photoresponsive release characteristics and a photodegradable hydrogel.

To examine the feasibility of employing TA–metal complexes as responsive gatekeepers on MSNs, molecular dynamics (MD) simulations were first performed on the interaction of TA and TA– Cu^{II} complexes with an MSN surface (pore diameter ≈ 2.5 nm; Figure 1a). Subsequent

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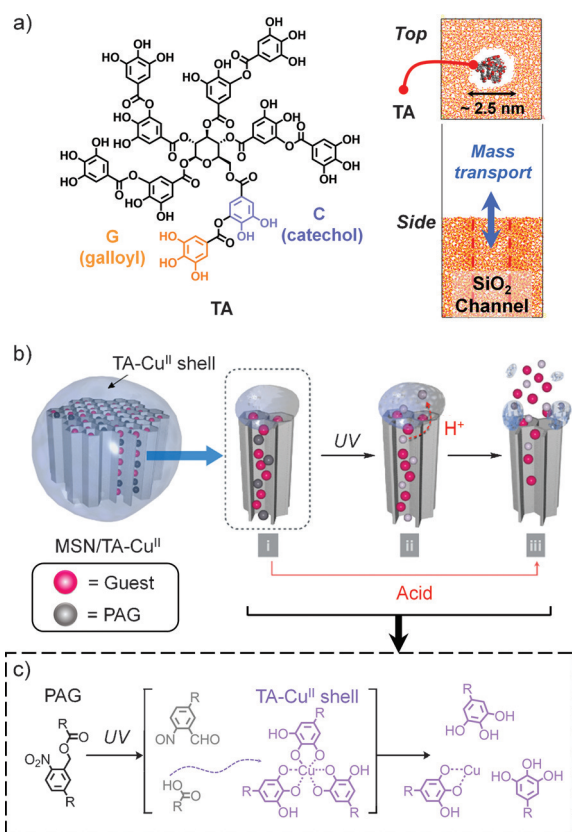


Figure 1. Gating activity and adhesion of TA and TA-Cu^{II} complexes on mesoporous silica surfaces. a) Chemical structure of TA (major axis ca. 2.2 nm) and mesoporous SiO₂. b) Typical gating of MSNs bearing bulky responsive polyphenol-metal complexes on their outer surface. c) Decomposition of TA-Cu^{II} complexes by a PAG.

adhesion of the galloyl (G) and catechol (C) units of TA onto the MSN silica surface took place without bridging over the pore, thereby keeping the pore open (see the Supporting Information, Figure S1).^[35] On the other hand, TA coordination complexes consisting of twelve TA molecules and only five Cu^{II} ions (12 TA/5 Cu^{II}) induced the closure of the MSN pores (Figure S1). Under ideal conditions, owing to the three-dimensional coordination network, the pore would be efficiently blocked by other ions as well as the TA molecules. Notably, according to the MD simulations, the suggested coordination network of 12 TA/5 Cu^{II} complexes is based on a partially cross-linked network.

We therefore devised non-covalently tailored MSNs covered with a pH-sensitive TA-Cu^{II} shell where the MSN porous channels were filled with rhodamine B (RB) and PAGs (2-nitrophenyl acetate) as Trojan horses (Figure 2a). We first prepared bare MSNs (MSN-0) with hexagonally ordered pores by template condensation of tetraethyl orthosilicate (TEOS) in the presence of a micellar solution of cetyltrimethylammonium bromide (CTAB).^[35] The X-ray diffraction (XRD) pattern for MSN-0 revealed a lattice constant of 46.8 Å (Figure S2). The spherical shape of MSN-0 (diameter = 50 nm) was corroborated by field emission scanning electron microscopy (FE-SEM, Figure S3). The N₂ adsorption-desorption isotherm of MSN-0 further revealed

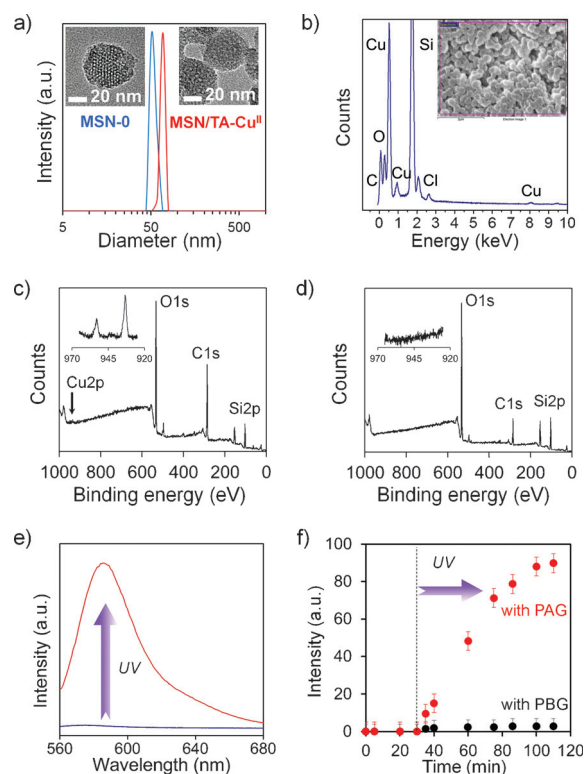


Figure 2. a) DLS analysis and TEM images of MSN-0 and MSN/TA-Cu^{II}. b) EDX profile of MSN/TA-Cu^{II}. c, d) Survey scan XPS spectra of MSN/TA-Cu^{II} before (c) and after (d) UV irradiation ($\lambda = 365$ nm). e) Fluorescence spectra of RB released from MSN/TA-Cu^{II} before (blue) and after (red) UV irradiation. f) Release of RB guests from MSN/TA-Cu^{II} with PAG (red) and PBG (black) before and after UV irradiation ($\lambda = 365$ nm).

a Brunauer-Emmett-Teller (BET) isotherm that is typical of an MCM-41 structure (type IV, BET surface area = 670.27 m² g⁻¹) and a narrow Barrett-Joyner-Halenda (BJH) pore size distribution (average pore diameter = 2.35 nm, Figure S4). The hexagonally ordered porous structure was also observed by transmission electron microscopy (TEM; Figures 2a and S5). The hydrodynamic diameter (53.2 nm) of MSN-0 was determined by dynamic light scattering (DLS; Figure 2a).

The porous channels of MSN-0 were used to soak up a dimethylformamide (DMF) solution of RB (10 mg mL⁻¹). After removal of excess dye, the surface was subsequently covered with the TA-Cu^{II} shell. The resulting particles were centrifuged and thoroughly washed with water to remove excess dyes, ligands, and ions. TEM analysis illustrated the weak contrast between MSN/TA-Cu^{II} and MSN-0, indicating that the particles are filled with payloads and covered with a thin layer of TA-Cu^{II} complexes (Figures 2a and S5). The hydrodynamic diameter of MSN/TA-Cu^{II} determined by DLS is 67.4 nm, which is greater than that of MSN-0, indicating full coverage of the particle surface with TA molecules (Figure 2a). Energy-dispersive X-ray spectroscopy supported our assumption that the surface of the MSN/TA-Cu^{II} system had been covered with TA-Cu^{II} complexes (Figure 2b). XRD analysis revealed that the hexagonally

ordered structure of MSN/TA-Cu^{II} was maintained during this procedure (Figure S6). The presence of the TA-Cu^{II} coordination complexes was further corroborated by X-ray photoelectron spectroscopy (XPS; Figures 2c and S6). A peak attributable to the HO-C group was not observed in the O 1s spectrum, indicating electron transfer from TA to the metals (Figure S6).^[29]

The BET surface area (25.78 m² g⁻¹) of the MSN/TA-Cu^{II} particles was smaller than that (670.27 m² g⁻¹) of MSN-0 (Figure S6). The MSN/TA-Cu^{II} system was stable without payload leakage for the first 30 min in the absence of a light stimulus (Figure 2e,f). However, when the MSN/TA-Cu^{II} particles were exposed to UV light ($\lambda = 365$ nm), we observed a remarkable release of entrapped RB molecules from MSN/TA-Cu^{II} (Figure 2e,f). XPS analysis revealed the disappearance of the Cu ions (Figure 2d) after UV exposure. In sharp contrast, we could not observe significant leakage of RB molecules from MSN/TA-Cu^{II} when the PAG was replaced with a photobase generator (PBG, 2-nitrobenzyl cyclohexylcarbamate; Figure 2f), indicating the critical role of the PAG for the gating of the TA-Cu^{II} shells.

We then decided to determine the local pH change in the MSNs caused by the photogenerated acid. For better visualization, we prepared mesoporous silica microparticles (MSMs, diameter ≈ 1 μm , $d_{100} = 33.4$ \AA by XRD, BET surface area = 1292.18 cm² g⁻¹) with hexagonally ordered pores (Figure S7).^[36] The MSM pores were filled with PAGs and acridine orange (AO). This dye emits green fluorescence under neutral conditions and red fluorescence under acidic conditions. Subsequent coating of the MSMs with the TA-Cu^{II} complexes afforded MSM/TA-Cu^{II}, which exhibited green fluorescence when visualized by confocal laser scanning microscopy (CLSM) in the absence of UV light (Figure 3a).

Interestingly, upon UV irradiation, we observed the appearance of red fluorescence not only within the inner part but also in the outer environment of the MSMs (Figure 3a). This observation indicates that the PAGs play two roles, namely in the protonation of the AO dyes as well as in the gating of the TA-Cu^{II} shell. In sharp contrast, when a PBG was used as the Trojan horse instead of a PAG under the same conditions, we did not observe any fluorescence changes or release of AO dyes (Figure 3b). These results clearly support our hypothesis that the acids generated from the PAGs gradually degrade the TA-Cu^{II} complex shell and induce the subsequent release of guests from the MSM channels. We believe that the method developed here can be further applied to design a strategy for the release of only activated guest molecules via a photoinduced reaction inside the MSN vessels.

To further demonstrate the versatility of our approach, we also fabricated a stimuli-responsive thin film that can release guest molecules on demand as a proof of concept. Stimuli-responsive films with the ability of releasing loaded guest molecules on request are especially attractive for biological and self-healing applications.^[37–39] In particular, the use of MSN containers instead of soft containers (e.g., micelles or dendrimers) would provide an alternative strategy for biological applications. Owing to the versatile coating capability of TA with metal ions, we successfully fabricated a film (ca.

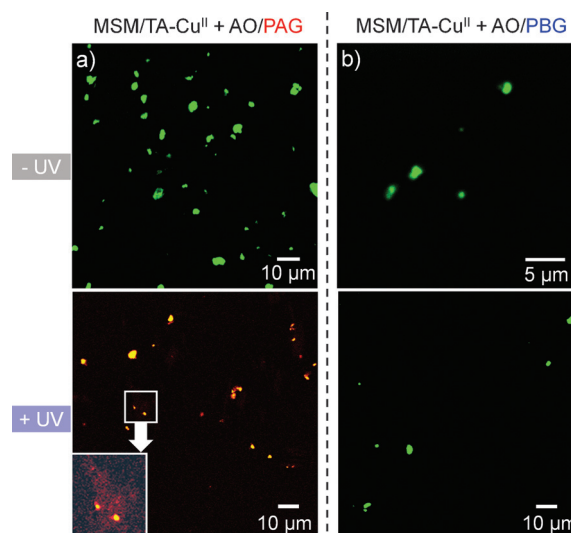


Figure 3. Visualization of the photoinduced acid generation and subsequent release of guest molecules from mesoporous containers. Confocal laser scanning microscopy (CLSM) images of MSM/TA-Cu^{II} particles showing a) the activity of the PAG and b) the ineffectiveness of the PBG. The inset shows the release of AO dyes.

200 nm thickness) composed of MSN/TA-Cu^{II} on a glass substrate (Figure 4a). First, a glass substrate was coated with TA-Cu^{II} coordination complexes as an adlayer (AdL; Figure 4a). The substrate was then coated by MSN/TA-Cu^{II} loading with RB guests via coordination between the AdL and the surface of the particles to afford AdL + MSN/TA-Cu^{II}. The adhesion was corroborated by electronic absorption spectroscopy (Figure 4b). The FE-SEM image in Figure 4c further reveals the dense arrangement of the MSN/TA-Cu^{II} particles as a multilayer on the glass substrate. XPS analysis demonstrated the presence of TA-Cu^{II} complexes (Figure 4e). In sharp contrast, a glass substrate without the TA-Cu^{II} coating (glass + MSN/TA-Cu^{II}) did not afford MSN/TA-Cu^{II} particles (Figure S8). This indicates that the coordination chemistry specifically allows the formation of MSN/TA-Cu^{II} particles. The film released nearly 90% of its guest molecules within only 1 h of UV irradiation (UV-AdL + MSN/TA-Cu^{II}; Figure 4b), and the color clearly faded when compared to the TA-Cu^{II} complex. Interestingly, FE-SEM revealed that the MSN/TA-Cu^{II} particles were still packed on the substrate after light exposure; this was employed to decompose the metal complex (Figure 4d). We assume that the stickiness of the TA molecules enables them to retain not only the MSNs but also the glass substrate, even after leaching of the metals has occurred. This might allow them to keep their original arrangement. Judging from the stickiness of TA as described by Messersmith and co-workers, residual TA molecules may adhere to the SiO₂ surface and act as a bridge to other MSNs, thereby remaining on the substrate.^[34] XPS analysis (Figure 4f) revealed the presence of TA molecules even after significant degradation of the TA-Cu^{II} complexes. The disappearance of the Cu 2p peak also indicates degradation. Upon dipping the films (AdL + MSN/TA-Cu^{II} and UV-AdL + MSN/TA-Cu^{II}) into aqueous AgNO₃ solution, we observed the appearance of a brown metallic silver film on

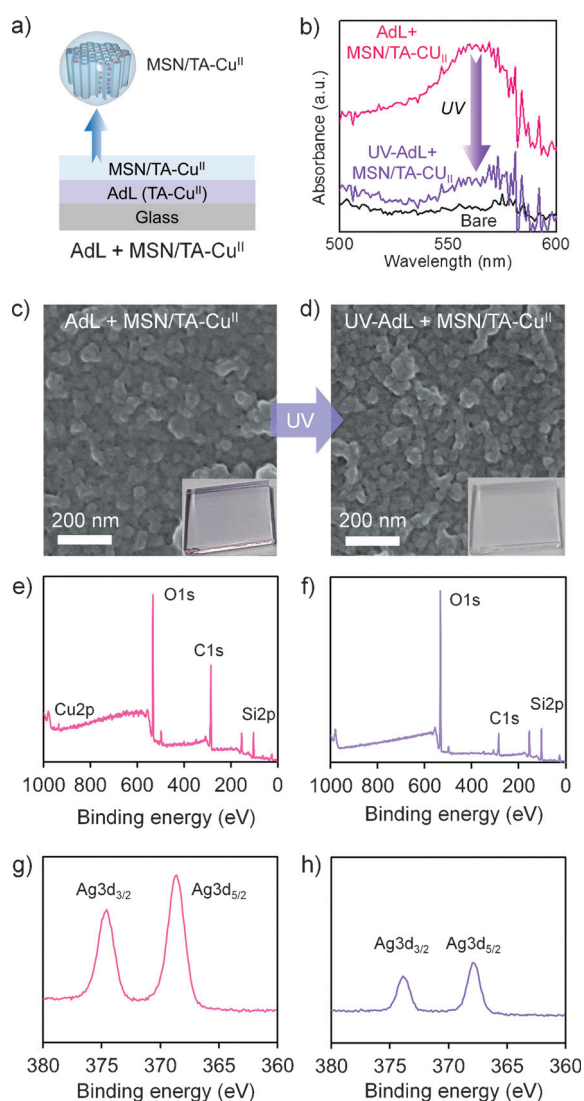


Figure 4. a) Schematic illustration of the AdL + MSN/TA-Cu^{II} film. b) Electronic absorption spectra of AdL + MSN/TA-Cu^{II} before and after UV irradiation. c, d) FE-SEM images and e, f) survey scan spectra (XPS) of the AdL + MSN/TA-Cu^{II} film (c, e) and the UV-AdL + MSN/TA-Cu^{II} film (d, f). g, h) XPS analysis of the AdL + MSN/TA-Cu^{II} film (g) and the UV-AdL + MSN/TA-Cu^{II} film (h) after treatment with aqueous silver solution.

the surface, indicating the presence of TA molecules as revealed by Messersmith and co-workers (Figures 4 g, h).^[34]

We also investigated the potential use of our approach for the synthesis of adaptive composites or responsive soft devices.^[18, 19, 37–42] The cascade reaction system based on MSN/TA-Cu^{II} was further coupled with an acid-degradable hydrogel consisting of polyvinyl alcohol (PVA) and borax. Upon exposure to light, the PAGs triggered the decomposition of the TA-Cu^{II} complexes as well as the gel network, resulting in a significant release of RB molecules and accelerated decomposition of the hydrogel in distilled water (Figure 5). In sharp contrast, without light irradiation, the PVA gel with MSN/TA-Cu^{II} (PVA/MSN/TA-Cu^{II}) did not exhibit significant degradation for the first 25 min. This result

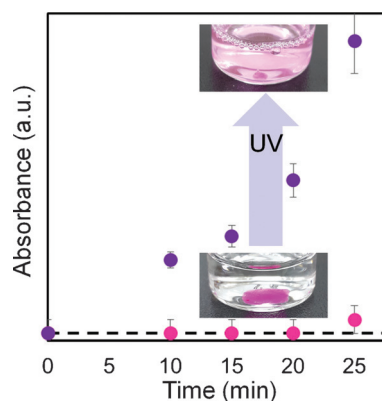


Figure 5. Accelerated release of RB guests from PVA/MSN/TA-Cu^{II} particles by photoinduced decomposition of both the PVA gel network and the TA-Cu^{II} complex shell (purple: with UV irradiation, pink: without UV irradiation).

clearly indicates that these cascade reactions can be efficiently guided by controlled light activation.

In conclusion, we have demonstrated that the Trojan horse strategy to gate MSN nanochannels via chemical communication is an efficient and versatile approach for various applications. The system is facile to construct and exhibits clear responsiveness for on-demand payload release. One might also consider near-infrared-responsive PAGs instead of UV-responsive ones for biological applications.^[43] Owing to the possibility to further functionalize TA with thiols, we believe that it should be possible to form functionalized nanocontainers from our nanocontainers in the future. According to the strategy described herein, judicious combinations of functionalities and materials will lead to advances in adaptive composites and materials science.^[18, 19, 37–42]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: controlled release · hybrid assemblies · mesoporous silica nanoparticles · signaling cascades · tannic acid

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