

Shape-dependent Thermo-plasmonic Effect of Nanoporous gold at the Nanoscale for Ultrasensitive Heat-mediated Remote Actuation

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Nanoporous gold (NPG) promises efficient light-to-heat transformation, yet suffers limited photothermal conversion efficiency owing to the difficulty in controlling their morphology for direct modulation of thermo-plasmonic properties. Herein, we showcase a series of shape-controlled NPG nanoparticles with distinct bowl- (NPG-B), tube- (NPG-T) and plate-like (NPG-P) structures for quantitative temperature regulation up to 140 °C in < 1 s using laser irradiation. Notably, NPG-B exhibits a highest photothermal efficiency of 68% which is >12 and 39 percentage points better than other NPG shapes (NPG-T, 56%; NPG-P, 49%) and Au nanoparticles (29%), respectively. We attribute NPG-B's superior photothermal performance to its >13% enhanced light absorption cross section compared to other Au nanostructures. We further realize an ultrasensitive heat-mediated light-to-mechanical "kill switch" by integrating NPG-B with a heat-responsive shape-memory polymer (SMP/NPG-B). This SMP/NPG-B hybrid is analogous to a photo-triggered mechanical arm, and can be activated swiftly in <4 s simply via remote laser irradiation. Achieving remotely-activated "kill switch" is critical in the case of emergency such as gas leaks where physical access is usually prohibited or dangerous. Our work offers valuable insights on the structural design of NPG for optimal light-to-heat conversion, and create opportunities to formulate next-generation smart materials for on-demand and multi-directional responsiveness.

Introduction

Nanoporous gold (NPG) are highly porous structures comprising dense three-dimensional networks of interconnected and highly-curved nanoscale ligaments.¹ This unique nanoscale architecture endows NPG with remarkable specific surface areas, high-indexed catalytically-active facets, and excellent electrical/thermal conductivity.²⁻⁴ More importantly, NPG exhibits impressive photothermal capabilities. As a plasmonic material, gold (Au) ligaments in NPG support localized surface plasmon resonances (LSPRs) upon light irradiation. Subsequent non-radiative decay of the surface plasmons generates substantial heat,⁵ which has been widely utilized for applications in light-/heat-gated controlled molecular release, in-vivo photothermal therapy, plasmonic- and thermo-catalysis.⁶⁻¹² However, current NPGs suffer from relatively low light-to-heat conversion efficiency of < 60 %. This limitation primarily

arises from the use of dealloying technique to generate two-dimensional NPG sheets that lack morphological control.¹³ We hypothesize that attaining morphological control over NPG is critical in achieving breakthroughs in the photothermal performance of NPGs.⁵ This is because such morphological control will enable modulation of both LSPRs of NPGs and the light-matter interactions between nanoscale ligaments and overall NPG morphology.¹⁴ Morphological control of NPG structures is therefore key to allow heat generation at high efficiency, even at low laser irradiation powers. This capability is critical for efficient light harvesting and ultrasensitive heat-mediated actuation.

Herein, we present the first series of shape-controlled free-standing NPG nanoparticles, evaluate their morphology-dependent NPG photothermal capability, and demonstrate the use of NPG as an efficient heat-responsive 'kill switch'. Using a seed-templated wet-chemical approach, we first synthesize three different shape-controlled NPG nanoparticles in high yields, including nanoporous gold bowls (NPG-B), nanoporous gold tubes (NPG-T), and nanoporous gold hexagonal plates (NPG-P). Next, we unravel the relationship between NPG morphology and their photothermal effect using an infrared (IR) camera, which enables spatially-resolved and real-time temperature readout. We establish NPG-B as the best-performing morphology with a light-to-heat conversion efficiency approaching 70 %. As a proof-of-concept application, we integrate

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NPG-B with a heat-responsive polymer to create a remote heat-mediated light-to-mechanical “kill switch” with swift responsiveness. This device serves as a potential early-warning/trigger system, especially in situations where physical access is prohibited. Our insights on NPG’s shape-dependent photothermal effects establishes the importance of NPG structural design for optimal light-to-heat conversion, as well as paves the way for the formulation of next-generation, multi-stimuli-responsive smart materials for spatially-precise actuation.

Experimental

Materials.

Silver nitrate (AgNO_3 ; $\geq 99\%$), hydroquinone (Hq; $\geq 99\%$), gold (III) chloride trihydrate (HAuCl_4 ; $\geq 99.9\%$), ethylene glycol (EG) and poly(vinylpyrrolidone) (PVP, average $M_w = 1300000$) were purchased from Sigma Aldrich. Potassium hydroxide and hydrochloric acid (37%) were purchased from Schedelco. Nitric acid (69%) was purchased from Honeywell. Ammonium hydroxide (25% in water) was purchased from Merck. Ethanol and N,N-dimethylmethanamide (DMF) were purchased from Fisher Chemical. Polyurethane shape memory polymer (SMP MM-3520) was purchased from SMP Technologies Inc. The chemicals were used without further purification. Milli-Q water (18.2 $\text{M}\Omega/\text{cm}$) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgCl nanocubes, AgCl nanowires and AgBr nanoplates.

AgCl nanocubes were prepared using the following method. 0.4 g PVP and 0.4 g AgNO_3 were dissolved in 30 mL and 20 mL of cold EG correspondingly. After mixing PVP solution and AgNO_3 solution in flask for 1 min at 500 rpm at room temperature, 1.23 mL of 37% HCl was added into the solution and kept stirring for 1 min. Then the solution was heated to 150 °C and kept stirring at 500 rpm for 20 min. After the reaction, the solution was naturally cooled down. 40 mL acetone was added to 10 mL resulting solution for sedimentation and centrifuged at 5000 rpm. After washing with water twice, the product was dispersed in 10 mL water to give a white suspension. This white suspension was used for future reactions. AgCl nanowires were synthesized using the method reported by Bi et al.¹⁵ AgBr hexagonal nanoplates were prepared using the method reported by Wang et al.¹⁶

Synthesis of nanoporous gold (NPG).

0.35 g PVP was dissolved in 50 mL water. 300 mg Hq was dissolved in 10 mL water. HAuCl_4 was also dissolved in water to get 0.5 M solution. AgCl nanocube solution (containing 51 mg AgCl) was first mixed with 45 mL PVP solution at 1300 rpm in RBF. After mixing for 1 min, 780 μL Hq solution was added followed by addition of 323 μL HAuCl_4 solution. After reaction for 1 min at 1300 rpm at room temperature, AgCl/NPG-B hybrid was obtained. The solution was centrifuged at 3000 rpm for 3 min and washed twice with water. The product could be re-dispersed in water. After mixing AgCl/NPG-B hybrid solution with 10 mL ammonia, the solution was centrifuged at 3000 rpm for 3 min and washed with water twice. As-synthesized

nanoporous gold bowl (NPG-B) were then re-dispersed in water. The concentration of NPG-B solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Nanoporous gold tubes (NPG-Ts) and nanoporous gold plates (NPG-P) were synthesized using similar method, except for AgCl nanowires and AgBr nanoplates were used as sacrificial templates.

Synthesis of Au NPs, smooth Au plates, Ag nanocubes and Ag octahedral.

Au NPs with same size as NPG ligaments were prepared by following the synthetic strategy reported by Sivaraman et al.¹⁷ Smooth Au plates were prepared using the method reported by Jiu et al.¹⁸ Ag nanocubes and Ag octahedral were prepared by following the experimental procedures reported by Yang et al. and Lee et al.^{19,20}

Photothermal temperature characterization.

Using NPG-B as an example, we manually dropcast its colloidal solution onto a thin layer chromatography (TLC) plate to form a particle cluster with a regulated area density of $\sim 7.55 \mu\text{g}/\text{mm}^2$ (diameter ~ 4 mm). Other NPG samples were prepared at the same area density. The actual area density of all NPG particles dropcast on substrate were confirmed by ICP-OES. Photothermal temperature under 532 nm laser irradiation (25 to 90 mW, power tuned by ND filters) was evaluated using FLIR SC7000 infrared (IR) camera to track real-time and spatially-resolved photothermal temperature profiles.

Preparation of shape memory polymer (SMP) / NPG-B.

Typically, 500 mg of SMP pellets were dissolved in 15 mL DMF at 90 °C. The solution was poured into a glass petri dish. The solvent was slowly evaporated at 70 °C for 24 h to get SMP film. SMP was cut into 5×2 mm strips with thickness of 0.05 mm and NPG-B was dropcast onto SMP. The area density of NPG-B on SMP was controlled to be the same as those previously prepared on TLC substrates.

Materials Characterization.

Nanoparticles were dropcast onto a clean silicon substrate for scanning electron microscopy (SEM) observation. SEM imaging was performed using a JEOL JSM 7600F microscope. Voltage was set at 5 kV. X-Ray photoelectron spectroscopy (XPS) spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. 284.5 eV for C 1s binding energy peak was used for XPS calibration. Composition and concentration analysis of the obtained nanoparticle suspension were conducted using a Thermo Scientific iCAP 6500 model ICP-OES. Nanoparticle suspension was mixed with Aqua Regia, and then diluted with water prior to ICP-OES measurement. X-z Raman imaging was acquired using Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan) with an excitation wavelength of 532 nm. A 532 nm laser (power density of $6.25 \text{ mW}/\text{mm}^2$) attached in uRaman microscope is used for controlling the movement of SMP/NPG-B. The movement of SMP/NPG-B was recorded in the form of video and frames at pre-defined timings were analyzed using ImageJ software.

Results and discussion

Shape-controlled synthesis of NPG offers a great opportunity to tailor its shape-dependent thermo-plasmonic properties essential for enhanced photothermal performance (Figure 1A). To achieve this, we employ a two-step template-assisted method that involves an initial growth of NPG on shape-controlled Ag halide-based sacrificial templates (including AgCl nanocubes, AgCl wires and AgBr nanoplates; Figure S1).²¹ This is followed by the ammonia-based etching of Ag halide sacrificial templates to yield uniform NPG with bowl-, tube-, and plate-like shapes that are denoted as NPG-B, NPG-T and NPG-P, respectively (Figure 1B - D; Figure S1). All NPG structures comprise uniform interconnected ligaments with size of $\sim 18 \pm 2$ nm, and small pores with sizes ranging from 4 - 30 nm, (Figure S2). More importantly, the morphologies of all as-synthesized NPG structures are distinct and predominantly defined by the shapes of their respective sacrificial templates. NPG-B features a hemispherical bowl-like shape with an open cavity of (0.7 ± 0.1) μm in diameter (Figure 1B). NPG-T has a hollow tube-like structure (length, 6.1 ± 2.3 μm) with open ends on both sides and an inner diameter of 0.2 ± 0.1 μm (Figure 1C; Figure S3A). NPG-P displays a hexagonal and hollow plate-like structure with close ends on all sides (edge length, 2.0 ± 0.5 μm) and an average thickness of 0.5 ± 0.1 μm (Figure 1D; Figure S3B). We attribute the presence of open cavity and hollow structure in our NPGs to the removal of the inner Ag-based sacrificial templates after the growth of NPG on these templates.

Chemical composition analyses on NPGs using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) demonstrate the successful reduction of Au(III) to Au(0), as well as the significant removal ($\geq 94\%$) of Ag-based sacrificial template (Figure S4, S5). Further quantitative elemental analysis using inductively-coupled plasma optical emission spectrometry (ICP-OES) affirms negligible residual Ag present ($< 6\%$) in all three NPG morphologies (Table S1). We also note that all NPGs exhibit broadband extinction spectrum between 400 - 1000 nm, whereas 18 nm-Au nanoparticles (comparable to NPGs' ligament sizes) exhibit LSPR only at 520 nm (Figure S6, S7). The differences in the extinction spectra are attributed to the strong plasmonic coupling between interconnected Au nanoparticles within the nanoporous framework architecture.^{22, 23} Collectively, these results highlight the first synthesis of shape-controlled NPG structures, which are crucial for subsequent investigation into their shape-dependent photothermal performances.

We evaluate the remote and on-demand photothermal heating of NPG (532 nm, 90 mW) by employing infrared (IR) camera to monitor its real-time and spatially-resolved temperature profiles during laser irradiation (Figure 2A). Using NPG-B as an example, we deposit the particles onto a thin layer chromatography (TLC) plate to form a particle cluster with a constant area density of ~ 7.55 $\mu\text{g}/\text{mm}^2$ (diameter ~ 4 mm) and a thickness estimated at ~ 17 layers of NPG-B (Figure S8, S9). NPG-B cluster exhibits a homogenous surface temperature of 25 °C prior to laser illumination (Figure 2B, 0 s). Upon laser irradiation, the surface temperature of NPG-B at the central

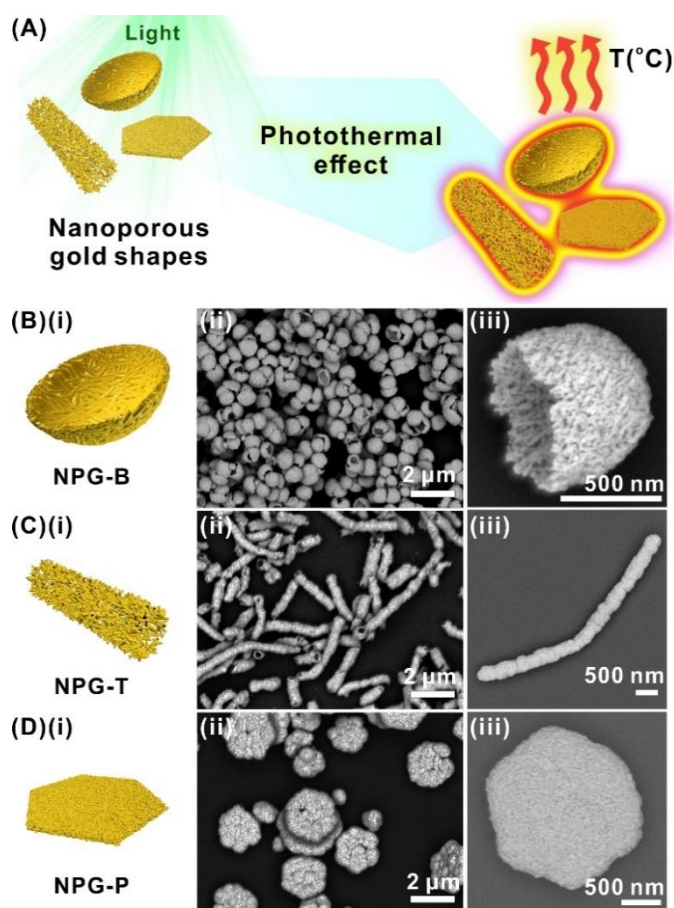


Figure 1. Characterization of as-synthesized nanoporous gold (NPG) nanoparticles with various shapes. (A) Scheme depicting the use of various shape-controlled NPGs for light-to-heat conversion. (B - D) As-synthesized nanoporous gold bowl (NPG-B), nanoporous gold tube (NPG-T) and nanoporous gold plate (NPG-P), respectively. (i) Schemes, (ii) SEM images and (iii) magnified SEM images of respective NPG particles.

irradiation zone (distance from irradiation center, $x = 0$ mm) rapidly increases to ~ 122 °C at a maximum heating rate ($(dT/dt)_{\text{max}}$) of ~ 364 °C/s (Figure S10), which eventually plateaus at ~ 138 °C beyond 10 s. (Figure 2C, 2D). The spatial-temperature plots exhibit Gaussian-like profiles, indicating localized photothermal heating due to the use of Gaussian laser beam. The temporal temperature profile indicates that the photothermal heating of NPG-B occurs in two sequential steps.²⁴ First, there is an initial surge in surface temperature at the central irradiated zone due to the instantaneous photothermalization of light by NPG-B. A gradual temperature increment to a steady state follows this initial surge, indicating that a thermal equilibrium is achieved between photothermal heat generation and heat dissipation to the entire NPG-B cluster (even the non-irradiated zone), underlying silica layer, as well as the surrounding air environment. Similarly, we also observe a two-step cooling process when the laser irradiation is switched off, whereby the surface temperature rapidly decreases from 138 to 33 °C within 1 s and later equilibrates at ~ 25 °C within 25 s (Figure S11). More

importantly, NPG-B exhibits > 2-fold higher maximum equilibrium temperature and heating rate as compared to a control platform comprising 18 nm-Au nanoparticles (similar to NPG-B's ligament sizes, surface temperature, 68 °C; maximum heating rate, 140 °C/s; Figure S12). This highlights the importance of constructing interconnected Au ligaments in a NPG architecture to attain photothermal heating beyond conventional randomly-aggregated Au nanoparticle platforms (to be discussed later).

Next, we demonstrate the shape-dependence of NPG's photothermal effect by comparing the light-to-heat conversion efficiencies of various NPG shapes (NPG-B, NPG-T and NPG-P) under identical experimental conditions. Similar to NPG-B, both NPG-T and NPG-P display a two-step photothermal heating phenomenon where surface temperature first surges and eventually reaches a thermal equilibrium (Figure 2D). Notably, the maximum surface temperature attained for NPG-T (125 °C) and NPG-P (112 °C) are at least 13 °C lower than NPG-B (138 °C; Figure 2D, 2E; Figure S13). The $(dT/dt)_{\max}$ of NPG-T and NPG-P are ~ 343 °C/s and 301 °C/s, respectively, which are at least 21 °C/s slower than NPG-B's (Figure S14A). More importantly, NPG-B exhibits the highest photothermal efficiency – defined as the ratio of heat energy output and laser energy input – of $\sim 68\%$ (Figure 2E) and is at least 12 % higher than NPG-T (56%) and NPG-P (49%; Supporting Notes 1; Figure S15; Table S2). We also affirm the importance of NPG's unique framework to achieve better light-to-heat conversion by comparing against their smooth counterparts and Au nanoparticles. Using nanoplates as an example, NPG-P exhibits ~ 5 -fold and 2-fold better photothermal conversion efficiency than smooth Au nanoplates (49% vs 10%; Figure S16) and randomly-aggregated Au nanoparticles (29 %; Figure S17), respectively. Collectively, NPG-B's superior photothermal efficiency, maximum achievable equilibrium temperature and its heating rate over NPG-T and NPG-P platforms clearly underscore the impact of NPG's morphology on their corresponding photothermal performances.

We attribute the superior photothermal performance of NPG-B to its highest absorption cross section (C_{abs} ; mm^2/g) as compared to NPG-T and NPG-P. The C_{abs} is associated with the heat generation ability of plasmonic nanoparticles (Figure 2F; refer to Supporting Notes 2; Figure S18).²⁵ From the photothermal heat generated, we calculate the absorption cross section of various shape-controlled NPG particles using the following equation:²⁵

$$C_{abs} = Q / (d \times N \times P \times \Delta t) \quad (1)$$

where Q is heat generated from photothermal conversion (J), d is the penetration depth of laser into the particle cluster (mm), N is the apparent density of NPG (g/mm^3), P is the laser power (W), and Δt is the duration of laser irradiation (t). Notably, this method gives a more accurate estimation on the C_{abs} because our NPG particles deviate from typical Mie and Beer-Lambert Law due to the presence of scattering particles and particle-particle (ligament-ligament) interactions.^{26, 27}

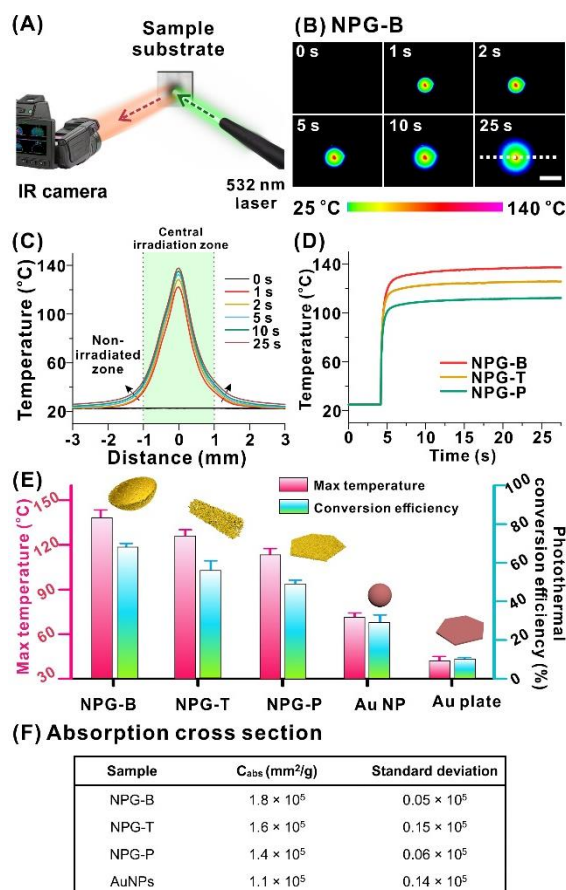


Figure 2. Photothermal effect of various shape-controlled NPGs. (A) Scheme of photothermal experimental setup composing of a laser beam irradiating on NPG surface and an IR camera to record the spatial temperature profile of the irradiated NPG in real-time. (B) Thermogram of NPG-B upon laser irradiation. Laser power = 90 mW. Scale bar, 4 mm. (C) Spatial temperature profiles of NPG-B as indicated in (B). (D) Time-temperature profiles of various NPG shapes upon laser irradiation. (E) Maximum equilibrium temperature and photothermal conversion efficiency of various metal nanostructures. Au NP denotes gold nanoparticle. (F) Absorption cross section of NPG-B, NPG-T, NPG-P, and AuNPs.

NPG-B exhibits the highest C_{abs} of $\sim 1.8 \times 10^5 \text{ mm}^2/\text{g}$ (Figure 2F), which is > 13 %, 29 % and 64 % higher than those of NPG-T ($1.6 \times 10^5 \text{ mm}^2/\text{g}$), NPG-P ($1.4 \times 10^5 \text{ mm}^2/\text{g}$) and Au nanoparticles ($1.1 \times 10^5 \text{ mm}^2/\text{g}$), respectively. We normalize C_{abs} against Au mass because it quantitatively compares and highlights the enhanced photothermal effect arising solely from NPG's geometry, especially when all NPGs possess similar ligament size in our experiments. We also validate the C_{abs} of Au nanoparticles in this work with theoretical prediction and experimental results from previous literature (refer to Supporting Notes 2).²⁵ Considering that all NPGs possess similarly-sized Au ligaments (~ 18 nm), we then assume that the absorption property of individual Au ligament is similar and any differences in NPGs' absorption cross sections are mainly attributed to the variation in their morphologies. Consequently, NPG-B's enhanced absorption cross section likely stems from its symmetry-broken bowl-shape

geometry, which allows strong plasmonic coupling between dipolar plasmons from the cavity (the aperture hole) and the dipolar/quadrupolar plasmons from the NPG's shell.^{28, 29} Such plasmon hybridization has been reported to induce significant charge accumulation at the bowl edges for immense and spatially-localized electric field enhancement.³⁰ Hence, our results clearly indicate the combination of geometry-induced optical phenomenon through the synthesis of shape-controlled NPG structures and the extensive plasmonic coupling between ligaments within the unique 3D bowl-like structure are critical in enhancing the light harvesting effects. As for the other NPGs (NPG-T and NPG-P), we note that NPG-T has higher C_{abs} and photothermal efficiency compared to NPG-P, which are likely ascribed to the plasmonic coupling across the intraparticle gap within the hollow tube-like structure. Collectively, our findings emphasize the importance of NPG's morphological design to attain efficient light-to-heat transformation. This is in turn critical to realize drastic and instantaneous temperature changes even at low laser irradiation power, which is essential for photothermal applications such as *in vivo* photothermal therapy, light-to-heat harvesting as well as heat-mediated actuation.

Using our best-performing NPG-B, we further demonstrate its photothermal capability to achieve quantitative and rapid temperature control. By controlling the laser power between 25 to 90 mW, we systematically elevate the surface temperature of NPG-B from 33 to 138 °C (Figure 3A), respectively, with a similar two-step heating profile. Switching off the laser leads to a decrease in the surface temperatures of all NPG-B to the pre-heated state of ~ 25 °C (Figure 3B). Correspondingly, regulating laser power from 25 mW to 90 mW allows a dynamic modulation of both the maximum heating speed and cooling speed from 31 °C/s to > 350 °C/s (Figure 3C, 3D; Figure S19). The change in surface temperature (ΔT) in both heating and cooling process are proportional to laser power (Figure 3E), indicating that NPG's surface temperature can be precisely programmed simply via the laser power applied. Moreover, NPG-B also demonstrates timely and reproducible photothermal heating where its surface temperature alternates precisely between 25 °C and 138 °C over five cycles of successive photothermal heating/cooling (laser power = 90 mW; Figure 3F). This ability to achieve on-demand and programmable temperature control suggests the potential application of NPG-B in diverse thermal mechanical applications.

By integrating NPG-B's superior photothermal performance with a thermo-responsive shape-memory polymer (SMP; Figure 4A), we further create a photo-triggered mechanical arm as a fast-response and remote "kill-switch". This proof-of-concept application exploits the photothermal heat generated from NPG to trigger polymer chain movement to relieve the stress accumulated in a pre-deformed SMP,³¹ thus reverting the heat-responsive material to its original shape. In a typical set-up, one side of a SMP strip is first loaded with NPG-B particles via repeated drop-casting. The SMP/NPG-B ensemble is subsequently folded at an angle of ~ 30° using a reported

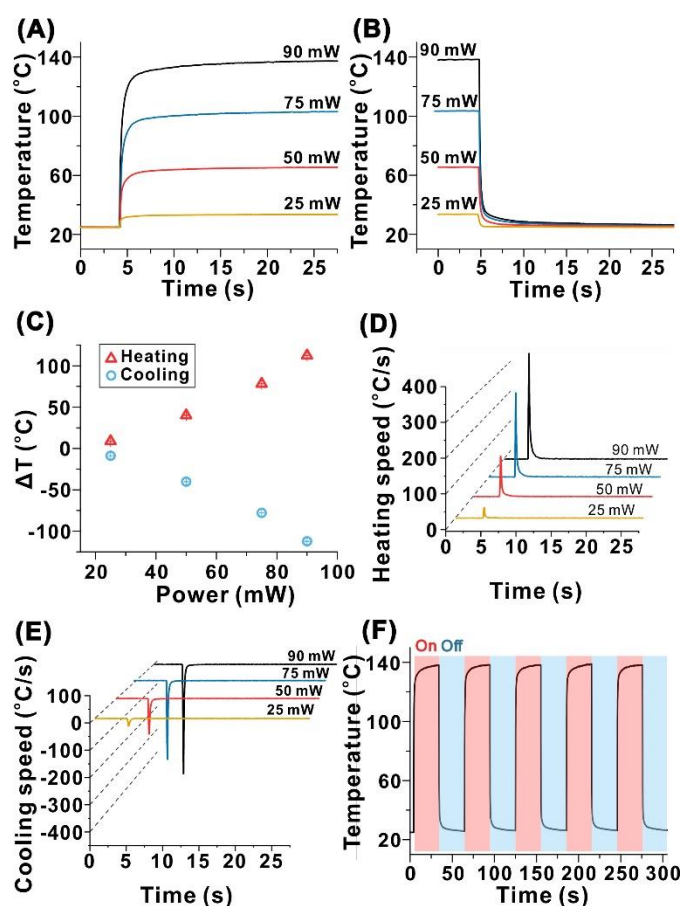


Figure 3. Laser power-dependent photothermal properties of NPG-B. (A, B) Temperature-time profiles of NPG-B when the laser irradiation is switched on and off, respectively. The applied laser power is controlled between 25 and 90 mW. (C) Heating and (D) cooling speed of NPG-B upon irradiation with different laser powers. (E) Changes in the surface temperature of NPG-B as a function of laser power during heating and cooling. (F) Heat-cool cycling test on NPG-B (laser power = 90 mW).

protocol to instill the memory of the polymer at a temperature lower than its glass transition temperature (T_g , 35 °C).

Illuminating the pre-folded region (laser power = 100 mW) rapidly reverts the SMP/NPG-B strip to its original position by opening up with an angle change from 32° to 169° within a short duration of 4 s (Figure 4B, 4C). In contrast, SMP strip without NPG-B exhibits negligible movement (< 2°) upon laser irradiation, affirming that the drastic movement in SMP/NPG-B is caused by photothermal heating and not due to laser-induced processes and/or potential heating arising solely from the laser source. We also note that SMP/NPG-B strip did not completely revert to its initial state (180°) possibly due to partial disruption of the cross-linking points present in the original SMP during intense photothermal heating.³¹ Furthermore, we observe that the heat-induced mechanical behavior in SMP/NPG-B (≤ 4 s) is slightly sluggish compared to the photothermal heating in NPG-B (≤ 1 s). This is due to the relatively slower heat-triggered recovery

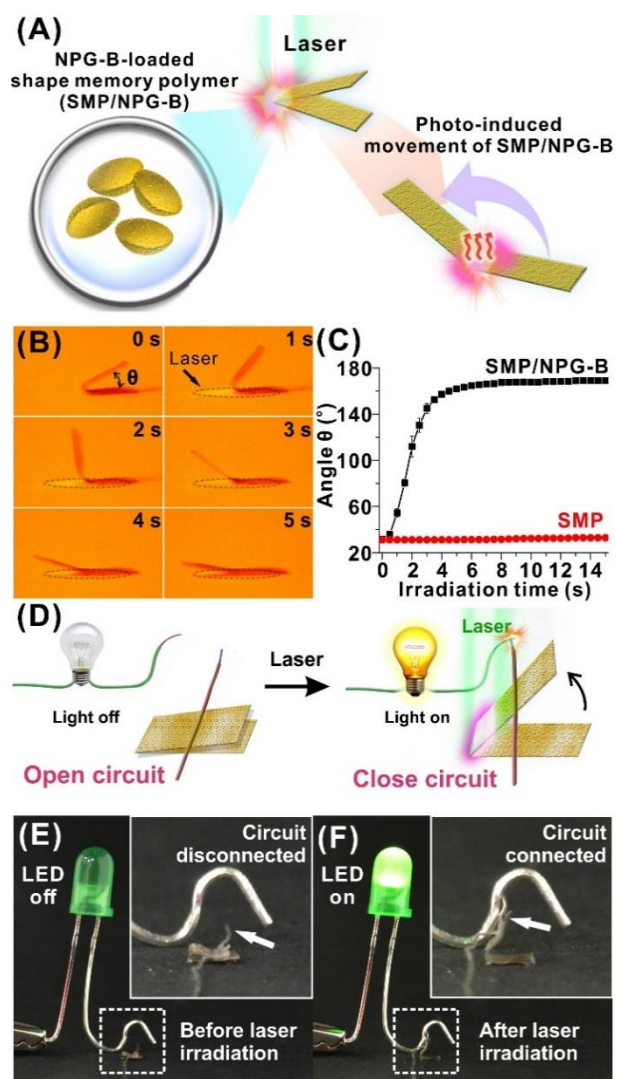


Figure 4. Integration of NPG with shape memory polymer (SMP/NPG-B) for application as heat-mediated light-to-motion transducer. (A) Scheme illustrating remote heat-mediated light-to-motion conversion using shape-memory polymer (SMP) strip that is decorated with NPG-B. (B) Photographic images displaying the time-dependent movement of SMP/NPG-B strip upon laser irradiation. The black circles indicates the area under laser irradiation. θ represents the opening angle of folded SMP. (C) Plots of the opening angle of folded SMP/NPG-B against laser irradiation time. SMP strip in the absence of NPG-B coatings under laser irradiation is also included for comparison. (D) Scheme depicting the integration of SMP/NPG-B with an electrical circuit for the realization of an efficient remote laser-controlled “kill switch” to activate the LED light which mimics an alarm/early-response system. (E, F) Experimental realization of a light-triggered, heat-mediated “kill switch” using SMP/NPG-B before and after laser irradiation, respectively. Insets contain the corresponding zoom-in images on the SMP/NPG-B “kill switch” installed in the system.

of SMP, which typically occurs in a time-scale between seconds to minutes.³² Nevertheless, the response time in our SMP/NPG-B is > 40-fold faster compared to similar SMP system such as 3D printed

polyurethane.³¹ We attribute this phenomenon to NPG-B’s intense and localized photothermal heating which enables timely and spatially-controlled mechanical movement directly at the point of interest. This effectively overcomes the slow responses and energy wastage commonly encountered in traditional heating methods (such as oven or heat-plate), where the latter requires gradual ramping to target temperature and is unable to achieve localized and remote heating. It is also noteworthy that our free-standing NPGs allows seamless integration with thermo-sensitive SMP as well as transfer onto arbitrary surfaces, whereas conventional NPG platforms involve 2D or surface-bound particles that cannot be easily transferred.³³

Building on our SMP/NPG-B system, we further devise a highly responsive photo-triggered switch to serve as an alarm device and/or “kill-switch” with potential application in the remote enforcement of automated safety countermeasures. This is important in the event of an emergency, especially when access to safety controls are dangerous or restricted. As a proof-of-concept, we integrate our SMP/NPG-B as a photo-responsive mechanical switch to remotely activate a LED light which mimics an alarm system (Figure 4D). Prior to laser irradiation, the angle of the strip is 0° and the LED light is off because the electrical circuit is open (Figure 4E). When we direct the laser irradiation onto the SMP/NPG-B strip, the photo-triggered switch rapidly turns on (opening angle = 60°; Figure 4F) and activates the LED-based “alarming system” within 2 s of laser irradiation. These results jointly demonstrate SMP/NPG-B as an ideal strategy to design an ultrasensitive mechanical switch energized by light-to-heat-to-motion conversion. This strategy is highly relevant in situations requiring swift and remote control and where physical access is prohibited such as in confined spaces with gas leakage. The ensemble of benefits offered in our design also create new possibilities in the development of next-generation hybrid smart materials to achieve multi-stimuli-responsive and multi-directional actuation that can be remotely directed simply using laser irradiation.

Conclusions

In this work, we develop three distinct NPG nanoparticles with bowl-, tube- and plate-like structures to enable highly sensitive and quantitative temperature control up to 140 °C in < 1 s. Direct evaluation on the photothermal conversion efficiencies unveils bowl-like NPG (NPG-B; 68 %) as the best performing NPG, which is at least 2-fold superior than conventional Au nanoparticles. These results highlight the importance of constructing the NPG framework and modulating NPG’s shape-dependent thermo-plasmonic effect at the nanoscale in achieving efficient light-to-heat conversion. By integrating NPG-B with a heat-responsive polymer, we further devise a heat-mediated light-to-mechanical “kill switch” that can be remotely and swiftly activated in < 4 s using laser irradiation. This kill switch will be especially crucial in emergency situations such as during gas leaks or natural disasters, where physical access to conventional alert system is typically prohibited or hazardous. Our work offers valuable

insights on the structural design of NPG for optimal light-to-heat conversion, as well as create immense opportunities in the formulation of next-generation smart materials for on-demand and multi-directional responsiveness.

Conflicts of interest

There are no conflicts to declare.

Author Contributions

Z. Y., X.H., H.K.L. and X.Y.L. conceived and designed the research. Z.Y., X.H., G.C.P.Q., C.S.L.K., C.L.L., and I.Y.P. carried out the experiments. Z.Y., X.H., H.K.L., Y.H.L., Y.M., I.Y.P. and X.Y. L. analysed the results and wrote the manuscript in consultation with T.L. All authors provided critical feedback and helped shape the manuscript. T.L., I.Y.P., and X.Y.L. supervised the project.

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