Electronic Supporting Information

Light-driven Pickering interfacial catalysis for oxidation of alkenes at near-room temperature

Yaoyao Feng,^a Jean-François Dechezelles,^a Quentin D'Acremont,^b Emmanuel Courtade,^b Vincent De Waele,^c Marc Pera-Titus^{d,*} and Véronique Nardello Rataj^{a,*}

^{*a*} Université de Lille, CNRS, Centrale Lille, Université Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

^b Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France

^c Univ. Lille, CNRS, UMR 8516, LASIRe - Laboratoire Avancé de Spectroscopie pour les Intéractions la Réactivité et l'Environnement, F-59000 Lille, France

^{*d*} Cardiff Catalysis Institute, School of Chemistry, Main Building, Cardiff University, Park Place, Cardiff CF10 3AT, UK

*Corresponding authors: veronique.rataj-nardello@univ-lille.fr, peratitusm@cardiff.ac.uk

FIGURE CAPTIONS

Figure S1. Evolution of the zeta potential as a function of the pH for dispersions of SiO_2-C_3 and Au/SiO_2-C_3 NPs in water at 25 °C (IEP = isoelectric point). pH adjusted using different concentration of HCl and NaOH (1 to 10^{-4} M) aqueous solution. (a) 0.1 wt% SiO_2-C_3 dispersion in deionized water; (b) 0.1 wt% Au/SiO_2-C_3 dispersion at variable Au loading.

Figure S2. XPS spectrum of the Au 4f core level of Au/SiO₂-C₃ NPs.

Figure S3. UV-vis spectra of Au, Au/SiO₂-C₃, $H_3PW_{12}O_{40}$ and $[C_{12}]_3[PW_{12}O_{40}]$ dispersion. The spectra were measured using deionized water for Au NPs, $H_3PW_{12}O_{40}$ and $[C_{12}]_3[PW_{12}O_{40}]$, and SiO₂-C₃ for Au/SiO₂-C₃ NPs, respectively, which were used as references.

Figure S4. TG profiles of SiO₂, SiO₂-C₃ and Au/SiO₂-C₃ NPs. Experimental conditions: 10-20 mg samples for each analysis, 10 °C/min from 30 to 900 °C and N₂ as atmosphere.

Figure S5. FT-IR spectra (transmittance mode) of SiO_2 , SiO_2-C_3 and Au/SiO_2-C_3 NPs. (a) Complete spectra. (b) and (c) Magnification of the spectra.

Figure S6. Photographs of water droplets deposited on compressed NPs and corresponding contact angles measured with water.

Figure S7. Photographs (a-d) and emulsion volume fractions (e) of water/toluene Pickering emulsion stabilized by $Au/SiO_2-C_3 NPs$, $[C_{12}]_3[PW_{12}O_{40}] NPs$, and a 40/60 wt% combination of $Au/SiO_2-C_3 NPs + POM NPs$ at 60 °C. Emulsification conditions: 1.5 mL toluene, 1.5 mL water, 80 mg (2.8 wt%) NPs, 11,500 rpm for 2 min.

Figure S8. Backscattering (Δ BS) and transmission (Δ T) signals *vs.* sample height and time at 60 °C for water/toluene (1:1 v/v) Pickering emulsions stabilized by [C₁₂]₃[PW₁₂O₄₀] NPs (a and a'), Au/SiO₂-C₃ NPs (b and b'), and a 40/60 wt% combination of SiO₂-C₃ NPs + [C₁₂]₃[PW₁₂O₄₀] NPs (c and c') and Au/SiO₂-C₃ NPs + [C₁₂]₃[PW₁₂O₄₀] NPs (d and d') from 0 h (blue curve) to 6 h (red curve). Emulsification conditions: 1.5 mL water, 1.5 mL toluene, 80 mg NPs, emulsification at 11,500 rpm for 2 min.

Figure S9. Backscattering (Δ BS) and transmission (Δ T) signals *vs.* sample height and time at 60 °C for water/toluene (containing substrate or product) emulsions stabilized by a 40/60 wt% combination of Au/SiO₂-C₃ NPs and [C₁₂]₃[PW₁₂O₄₀] NPs from 0 h (blue curve) to 6 h (red curve). Emulsification conditions: 80 mg NPs, 50/50 v/v,

emulsified at 11500 rpm for 2 min, (a and a') using 2 mol/L cyclooctene (substrate) in toluene as oil phase and (b and b') using 2 mol/L cyclooctene oxide (product) in toluene as oil phase.

Figure S10. Photothermal profiles of Au NPs dispersion and Au/SiO₂-C₃-stabilized emulsion. (a) Temperature profiles of Au NPs dispersion with different power density as a function of light irradiation time using 13 μ g Au NPs (1 mL dispersion). (b) Temperature profiles of Au/SiO₂-C₃-stabilized emulsion with different power density as a function of light irradiation time using 13 μ g Au NPs (1 mL dispersion). (b) Temperature profiles of Au/SiO₂-C₃-stabilized emulsion with different power density as a function of light irradiation time using 13 μ g Au NPs (1 mL emulsion).

Figure S11. a) Yield of cyclooctene oxide against the weight ratio of $[C_{12}]_3[PW_{12}O_{40}]$ using a combination of $[C_{12}]_3[PW_{12}O_{40}]$ and Au/SiO₂-C₃ NPs (80 mg). b) Yield of cyclooctene oxide with/without stirring under light irradiation and heating (47 °C) with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg). c) Yield of cyclooctene oxide against the water/toluene ratio under light irradiation and heating (47 °C) with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg). d) Results for cyclooctene oxidation over $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 or 15 mg) under pulsed laser irradiation and heating. All the results are based on ¹H NMR.

Figure S12. Optical images of the emulsion, optical micrographs of the emulsion droplets and droplet size distribution for emulsions stabilized by: a) 1.0 wt% $SiO_2-C_3 + 1.8$ wt% $H_3PW_{12}O_{40}$ and b) 1.0 wt% $SiO_2-C_3 + 1.8$ wt% $[C_{12}]_3[PW_{12}O_{40}]$.

Figure S13. Results for cyclooctene oxidation using different types of POMs and combinations with Au/SiO₂-C₃ NPs: only 50 mg $H_3PW_{12}O_{40}$, only 50 mg $[C_{12}]_3[PW_{12}O_{40}]$ NPs, or combination of 50 mg $H_3PW_{12}O_{40} + 30$ mg Au/SiO₂-C₃ NPs, and 50 mg $[C_{12}]_3[PW_{12}O_{40}] + 30$ mg Au/SiO₂-C₃ NPs under light irradiation, room temperature and external heating. Results based on ¹H NMR.

Figure S14. Results for cyclooctene oxidation with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg) under light or laser irradiation and heating. Photothermal profiles of Au/SiO₂-C₃ + $[C_{12}]_3[PW_{12}O_{40}]$ -stabilized emulsion under light irradiation (1000 mW/cm²) and pulsed laser (100 mW/cm²).

Figure S15. (a) and (b) HR-TEM micrographs of recovered Au@SiO₂-C₃ NPs after the fifth run (red circles indicate Au NPs). (c) Particle size distribution of Au NPs in Au/SiO₂-C₃ NPs. (d) Optical micrographs of emulsion droplets (the inset shows a photograph of the emulsion).

Experimental Section

Materials

Reagent-grade HAuCl₄· $3H_2O$ (99.9%), sodium citrate (99%), NaBH₄ (98%), (3-aminopropyl) triethoxysilane (APTES, 99%), sodium hydroxide (NaOH, 99%) and trimethoxy(propyl)silane (97%) were purchased from Aldrich (USA). Aerosil®200 was a generous gift from Evonik Industries AG (Germany). Hydrogen peroxide (50%) was supplied by VWR International (France). Cyclooctene (95%) was procured from TCI (Japan). Toluene (99%) and heptane (99%) were supplied by Sigma-Aldrich. CDCl₃ (99.8%) was purchased from Euriso-top (France). All the aqueous solutions were prepared using Millipore water produced by a water purification system with a water resistivity higher than 18.2 M Ω .cm (Barnstead, Thermo Scientific, USA).

Methods

Synthesis of amphiphilic silica NPs (SiO_2 - C_3)

In a typical procedure, a suspension of Aerosil[®]200 was prepared by adding 0.5 g Aerosil[®]200 in 200 mL water/ethanol solution (1/1 v/v, pH = 9.8). Then, 0.91 mL (5 mmol) of trimethoxy(propyl)silane (C₃) was slowly added into the suspension under vigorous stirring. Furthermore, 0.105 mL (0.5 mmol) of APTES was added to the suspension. The reaction mixture was stirred at room temperature for 1 h, followed by heating at 80 °C for 1 h. The NPs were collected by centrifugation, and were washed with water and ethanol six times. Ultimately, the amphiphilic SiO₂-C₃ NPs were dried at 80 °C overnight.

Synthesis of Au NPs

Au NPs were obtained using the protocol reported by Turkevich *et al.*^{S1} In brief, 95 mL of an aqueous solution of HAuCl₄·3H₂O (1 wt%) was prepared, and then 2 mL of an aqueous solution of sodium citrate (38.8 mM) was added under vigorous stirring. After 1 min, 1 mL of a freshly prepared NaBH₄ aqueous solution (10 mM) was added to the mixture which took a reddish colour. The Au dispersion was stored under darkness at 4 °C.

Synthesis of Au-loaded amphiphilic silica NPs (Au/SiO₂-C₃)

Au NPs were immobilized on the surface of amphiphilic SiO_2-C_3 NPs by self-assembly method.⁵² Firstly, 3 mL of a Au NPs dispersion (obtained in section 2.3) were added to 3 mL of an ethanolic dispersion of SiO_2-C_3 NPs (1.5 wt%) under vigorous stirring. The Au/SiO₂-C₃ NPs was collected by centrifugation and washed with deionized water three times. The NPs were collected and then dried in an oven at 80 °C overnight.

Synthesis of amphiphilic POM NPs [C₁₂]₃[PW₁₂O₄₀])

Amphiphilic POM NPs were prepared by the protocol described in ref.⁵³ Briefly, 100 mL of an aqueous solution of dodecyltrimethylammonium bromide $[C_{12}][Br]$ (0.2 M) was eluted on a hydroxide ion exchange resin to obtain an aqueous solution of $[C_{12}][OH]$. An aqueous solution of $H_3PW_{12}O_{40}$ (around 6.5 mmol, 10⁻⁴ M) was added dropwise to the aqueous $[C_{12}][OH]$ solution (0.3 mM) until pH 7 at 25 °C under dry Ar and vigorous magnetic stirring (1,500 rpm). The colourless precipitate of tri(dodecyltrimethylammonium) phosphotungstate was obtained after a few minutes. The resulting $[C_{12}]_3[PW_{12}O_{40}]$ NPs were collected and washed with water to remove impurities, and then lyophilized.

Physicochemical characterization of NPs

The Au and Au/SiO_2-C_3 NPs were visualized by high-resolution transmission electron microscopy (HRTEM) using a JEOL JSM-6360LV microscope at a voltage of 200 kV. Two drops of NPs suspension were deposited on a carbon-

copper grid (CF200-Cu, Electron Microscopy Sciences, USA).

The UV-Vis spectra of Au and Au/SiO₂-C₃ NPs were recorded with a Nano Photometer N60 spectrometer (IMPLEN, Germany).

The nanoparticle size distribution and zeta potential of the different particle dispersions were obtained using Zetasizer (Nano ZS ZEN 3600, Malvern, UK) equipped with a He-Ne laser at 632.8 nm, using 0.1 wt% particles dispersed in water at room temperature (a few drop of ethanol was for hydrophobic NPs). The pH of the solutions was controlled using aqueous HCl and NaOH solutions (from 10⁻⁴ mol.L⁻¹ to 1 mol.L⁻¹).

Fourier transform infrared spectroscopy (FT-IR) was performed using a Nicolet 380 FTIR Spectrometer equipped with an attenuated total reflector (Thermo Electron, USA).

Thermogravimetric analyses (TGA) were performed on a Q500 (TA Instruments, USA). In a typical test, at least 10 mg of sample was heated from 30 to 900 °C at a rate of 10 °C/min under nitrogen atmosphere (60 mL (STP)/min).

Contact angle measurement was performed by the sessile drop method (DSA 100 Krüss GmbH, Germany) by deposing a small drop of 4 μ L of water onto the pellet with 100 mg NPs compressed at 1800 bar during 10 min.

The Au loading in the Au/SiO₂-C₃ NPs was quantified by Agilent 5110 vertical dual view inductively coupled plasma optical emission spectrometer (ICP-OES) equipped with an OneNeb nebulizer, a quartz double pass spray chamber and a quartz torch (Agilent). In a typical test, 50 mg samples were weighed and 1mL HF/1mL HCl/1mL HNO₃ were added and heated at 110 °C in closed Teflon tubes for 24 h. Then, 30 ml of ultrapure water were added. The cleared solutions were filtered at 0.45 μ m and diluted for the ICP-OES analysis.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD spectrometer using a monochromatic Al Ka radiation (1486.6 eV) operating at 225 W (15 mA, 15kV). High-resolution spectra were collected using an analysis area of \approx 300 µm × 700 µm and a 20 eV pass energy.

Preparation and characterization of emulsions

Typically, 1.0 wt% Au/SiO₂-C₃ and 1.8 wt% $[C_{12}]_3[PW_{12}O_{40}]$ were dispersed in 1.5 mL of oil phase and ultrasound for 5 min, followed by the addition of 1.5 mL of water in a 5 mL glass vial. Emulsions were formed using Ultraturrax T10 basic (IKA, Germany) at room temperature and 11,500 rpm for 2 min.

Optical micrographs were taken using a VHX-900 F digital microscope equipped with a VH-Z100UR/W/T lens (Keyence, France). The emulsions were diluted with the continuous phase before observation, and photographs from different locations of the emulsion drop were taken to represent the general view of the emulsion droplets. The images were analysed using ImageJ software (National Institutes of Health, USA) to measure the droplet diameter. The log-normal distribution function was obtained after statistical analysis of the micrographs using OriginPro 8[®] (OriginLab, USA).

The emulsion stability was characterized at 60 °C by static multiple light scattering (SMLS) using a Turbiscan Lab (Formulaction, France) operating with a near-infrared light source (λ = 880 nm). Transmission mode was used to analyse from clear to turbid dispersions while backscattering mode was used to analyse opaque and concentrated dispersions.⁵⁴

The light intensity of emulsion usually changes slightly, indicating a low change of droplet concentration and higher stability. More specifically, the Δ BS intensity decreases for larger particle sizes (coalescence and flocculation) or at lower particle concentrations (sedimentation and creaming) when the particle size is larger than the incident wavelength. The decrease in Δ BS at the top layer of an emulsion indicates a decrease in the top concentration and clarification of upper layer. In contrast, an increase of Δ T at the top layer reflects the clarification process. Moreover, the backscattering light is more sensitive for detecting emulsion droplets because

they have high obscuration which can reflect the backscattering light.⁵⁵ Meanwhile, transmission light is suitable to evaluate the diluted emulsion phase.⁵⁶ Although gravitational separation can sometimes happen due to the difference in the density of the two immiscible phases, coalescence involving collision of two or more small droplets to form a single larger droplet can be considered as the parent instability mechanism.⁵⁷

Photothermal conversion measurements

The photothermal conversion experiments were carried out under light irradiation using a Hg-Xe lamp (LightningCure LC8, Hamamatsu, Japan) incorporating a filter (A9616-09) inside to select the irradiation light. A thermal insulation was made with PS foam at the outside of the cuvette to limit heat dissipation. A 495-nm long-pass filter was placed between the sample and the light source. The UV light irradiance distribution was dependent on the distance from the light output end to the target surface. The longer the distance from the light source to the target sample, the lower the power density and the larger beam size can be obtained. The light source was placed at 2 cm from the surface of the cuvette rendering a maximum power of 355 mW measured using an 843-R optical power meter (Newport Corporation). The beam size focused to around 6.7 mm with the maximum power density of 1 W/cm². The temperature change of the solution was recorded using a data logger thermometer YC-727U (Maximum Electronic Co., LTD). The thermometer was kept outside the irradiation area to avoid photoheating of the iron-made probe. A magnetic stirrer was used for gentle stirring. In the photothermal conversion test, 1 mL of Au NPs dispersion or Au/SiO₂-C₃ emulsion were irradiated with light. The temperature change of the prepared sample was recorded every 20 s.

Catalytic tests

In a typical catalytic test, 1.5 mL of toluene containing cyclooctene (2 mol/L) and 1.5 mL of water containing 1.2 equiv. H_2O_2 (50%) were added to a 5-mL glass vial, followed by $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) and Au/SiO₂-C₃ (30 mg) at room temperature. The final dispersion was emulsified using an Ultraturrax at 11,500 rpm for 2 min. Then, 1 mL of the obtained emulsion was added into a 2-mL cuvette, and it was gently stirred at 120 rpm under light irradiation (495 nm wavelength) at a given power density for the desired period of time. The temperature change inside the emulsion was recorded every 20 s.

The laser-driven catalytic experiments were carried out with the same setup and identical catalytic reaction conditions, but changing the light source. For pulsed laser tests, a 532 nm pulsed laser Surelite II (Continuum, USA) operating in 10 Hz repetition rate and 10 ns pulse width was employed to investigate the plasmon-assisted oxidation of olefins in emulsion. The average power is set to around 500 mW and the beam size of the laser focused to around 10 mm, while the average power density of the pulsed laser is around 100 mW/cm².

For control experiments, the catalytic reaction was performed at the same emulsification and reaction conditions described above, but under heating in an oil bath (IKA, RCT standard, heat output 600 W), and the temperature was set as the corresponding maximum temperature reached with the light-driven experiment. Another catalytic reaction was carried out at identical conditions at room temperature in a dark environment, *i.e.* without light irradiation.

The cyclooctene conversion and cyclooctene oxide yield were calculated by ¹H NMR using $C_2Cl_4H_2$ as internal standard as follows

$$Cyclooctene\ conversion(t) = 1 - \frac{n_{cyclooctene}(t)}{n_{cyclooctene}} x100$$
(S1)

$$Cyclooctene \ oxide \ yield(t) = \frac{n_{cyclooctene \ oxide}(t)}{n_{cyclooctene}} x100$$
(S2)

where $n_{cyclooctene}^{0}$ and $n_{cyclooctene}^{(t)}$ refer to the mole number of cyclooctene at time = 0 and time = t, respectively, and $n_{cyclooctene oxide}$ (t) is the mole number of cyclooctene oxide at time = t.

The turnover number (TON) and turnover frequency (TOF) with respect to cyclooctene oxide formation were computed as follows

$$TON(t) = \frac{n_{cyclooctene\ oxide\ (t)}}{n_{catalyst}}$$
(S3)

$$TOF = \frac{n_{cyclooctene oxide (t)}}{n_{catalyst}} \frac{1}{t}$$
(S4)

where $n_{catalyst}$ refers to the moles number of $[C_{12}]_3[PW_{12}O_{40}]$ (mol), t is the reaction time (h).

After the reaction, the system was demulsified by centrifugation, the upper oil phase was separated by decantation, and it was dissolved in $CDCl_3$, whereas $C_2Cl_4H_2$ was used as internal standard for analysis. Then, 50 μ L of the oil phase, 50 μ L (0.5 mol/L) of the internal standard solution and 400 μ L of deuterated CDCl₃ were added in an NMR tube. The yield was measured by ¹H NMR on an Advance 300 Bruker spectrometer at 300.12 MHz. Mass balance errors were within 5-15% for all catalytic tests.

Catalyst reusability test

For catalyst reuse experiments, the mixed NPs were collected by centrifugation and dried at 80 °C. The emulsification protocol described above was repeated and the subsequent catalytic run was carried out. This protocol limited the loss of particles loss during centrifugation and washing. To limit their loss, NPs were collected and dried after each catalytic reaction followed by centrifugation.



Figure S1. Evolution of the zeta potential as a function of the pH for dispersions of SiO_2-C_3 and Au/SiO_2-C_3 NPs in water at 25 °C (IEP = isoelectric point). pH adjusted using different concentration of HCl and NaOH (1 to 10⁻⁴ M) aqueous solution. (a) 0.1 wt% SiO_2-C_3 dispersion in deionized water; (b) 0.1 wt% Au/SiO_2-C_3 dispersion at variable Au loading.



Figure S2. XPS spectrum of the Au 4f core level of Au/SiO₂-C₃ NPs.



Figure S3. UV-vis spectra of Au, Au/SiO₂-C₃, H₃PW₁₂O₄₀ and $[C_{12}]_3[PW_{12}O_{40}]$ dispersion. The spectra were measured using deionized water for Au NPs, H₃PW₁₂O₄₀ and $[C_{12}]_3[PW_{12}O_{40}]$, and SiO₂-C₃ for Au/SiO₂-C₃ NPs, respectively, which were used as references.



Figure S4. TG profiles of SiO₂, SiO₂-C₃ and Au/SiO₂-C₃ NPs. Experimental conditions: 10-20 mg samples for each analysis, 10 °C/min from 30 to 900 °C and N₂ as atmosphere.



Figure S5. FT-IR spectra (transmittance mode) of SiO₂, SiO₂-C₃ and Au/SiO₂-C₃ NPs. (a) Complete spectra. (b) and (c) Magnification of the spectra.

Figure S6. Photographs of water droplets deposited on compressed NPs and corresponding contact angles measured with water.

Figure S7. Photographs (a-d) and emulsion volume fractions (e) of water/toluene Pickering emulsion stabilized by $Au/SiO_2-C_3 NPs$, $[C_{12}]_3[PW_{12}O_{40}] NPs$, and a 40/60 wt% combination of $Au/SiO_2-C_3 NPs + POM NPs$ at 60 °C. Emulsification conditions: 1.5 mL toluene, 1.5 mL water, 80 mg (2.8 wt%) NPs, 11,500 rpm for 2 min.

Figure S8. Backscattering (Δ BS) and transmission (Δ T) signals *vs.* sample height and time at 60 °C for water/toluene (1:1 v/v) Pickering emulsions stabilized by [C₁₂]₃[PW₁₂O₄₀] NPs (a and a'), Au/SiO₂-C₃ NPs (b and b'), and a 40/60 wt% combination of SiO₂-C₃ NPs + [C₁₂]₃[PW₁₂O₄₀] NPs (c and c') and Au/SiO₂-C₃ NPs + [C₁₂]₃[PW₁₂O₄₀] NPs (d and d') from 0 h (blue curve) to 6 h (red curve). Emulsification conditions: 1.5 mL water, 1.5 mL toluene, 80 mg NPs, emulsification at 11,500 rpm for 2 min.

Figure S9. Backscattering (Δ BS) and transmission (Δ T) signals *vs.* sample height and time at 60 °C for water/toluene (containing substrate or product) emulsions stabilized by a 40/60 wt% combination of Au/SiO₂-C₃ NPs and [C₁₂]₃[PW₁₂O₄₀] NPs from 0 h (blue curve) to 6 h (red curve). Emulsification conditions: 80 mg NPs, 50/50 v/v, emulsified at 11500 rpm for 2 min, (a and a') using 2 mol/L cyclooctene (substrate) in toluene as oil phase and (b and b') using 2 mol/L cyclooctene oxide (product) in toluene as oil phase.

Figure S10. Photothermal profiles of Au NPs dispersion and Au/SiO₂-C₃-stabilized emulsion. (a) Temperature profiles of Au NPs dispersion with different power density as a function of light irradiation time using 13 μ g Au NPs (1 mL dispersion). (b) Temperature profiles of Au/SiO₂-C₃-stabilized emulsion with different power density as a function of light irradiation time using 13 μ g Au NPs (1 mL emulsion).

Figure S11. a) Yield of cyclooctene oxide against the weight ratio of $[C_{12}]_3[PW_{12}O_{40}]$ using a combination of $[C_{12}]_3[PW_{12}O_{40}]$ and Au/SiO₂-C₃ NPs (80 mg). b) Yield of cyclooctene oxide with/without stirring under light irradiation and heating (47 °C) with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg). c) Yield of cyclooctene oxide against the water/toluene ratio under light irradiation and heating (47 °C) with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg). c) Yield of cyclooctene oxide against the water/toluene ratio under light irradiation and heating (47 °C) with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg). d) Results for cyclooctene oxidation over $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 or 15 mg) under pulsed laser irradiation and heating. All the results are based on ¹H NMR.

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Figure S13. Results for cyclooctene oxidation using different types of POMs and combinations with Au/SiO₂-C₃ NPs: only 50 mg $H_3PW_{12}O_{40}$, only 50 mg $[C_{12}]_3[PW_{12}O_{40}]$ NPs, or combination of 50 mg $H_3PW_{12}O_{40} + 30$ mg Au/SiO₂-C₃ NPs, and 50 mg $[C_{12}]_3[PW_{12}O_{40}] + 30$ mg Au/SiO₂-C₃ NPs under light irradiation, room temperature and external heating. Results based on ¹H NMR.

Figure S14. Results for cyclooctene oxidation with $[C_{12}]_3[PW_{12}O_{40}]$ (50 mg) + Au/SiO₂-C₃ NPs (30 mg) under light or laser irradiation and heating. Photothermal profiles of Au/SiO₂-C₃ + $[C_{12}]_3[PW_{12}O_{40}]$ -stabilized emulsion under light irradiation (1000 mW/cm²) and pulsed laser (100 mW/cm²).

Figure S15. (a) and (b) HR-TEM micrographs of recovered NPs after the fifth run (red circles indicate Au NPs). (c) Particle size distribution of Au NPs in Au/SiO₂-C₃ NPs. (d) Optical micrographs of emulsion droplets (the inset shows a photograph of the emulsion).

Calculation of energy consumption

Thermal reactor

 $\circ~$ Energy supplied for heating the reaction mixture from room temperature to 47 °C

$$Q_{TH-heating} = mc_P \Delta T = (m_w c_{PW} + m_T c_{PT}) \Delta T = (V_W \rho_W c_{PW} + V_T \rho_T c_{PT}) \Delta T = Q_{TH-heating} = 624 J$$
(S1)

where m_w and m_T represent the mass of water and toluene (g), respectively; c_{PW} and c_{PT} represent the specific heat capacity of water and toluene, respectively (Jg⁻¹°C⁻¹); ΔT is the temperature change observed for the reaction.

 \circ Energy supplied for cooling reaction mixture from 47 °C to room temperature

$$Q_{TH-cooling} = Q_{TH-heating} = 624 J \tag{S2}$$

 \circ $\,$ Total energy supplied for conventional thermal heating method $\,$

$$Q_{TH} = Q_{TH-heating} + Q_{TH-cooling} = 1248 J$$
(S3)

Photoreactor

• Energy supplied during light irradiation (260 mW/cm², 1 h)

$$Q_L = P_{avg} \Delta t = P_{density} S_{beam} \Delta t = P_{density} \pi (r^2) \Delta t = 0.09 W/h = 0.09 \times 3600 = 324 J$$
(S4)

where $P_{density}$ is the power density of the lamp (260 mW/cm²), S_{beam} is the light beam area (0.35 cm²) and r is light beam radius (3.3 mm).

Energy saving (photo- vs. thermal reactor)

$$\eta = \frac{(Q_{TH} - Q_L)}{Q_{TH}} = 74\%$$
(S5)

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