Supplementary Information

Scattering-mediated Photothermal Heating in Plasmonic PES/Au Membranes for Heterogeneous Catalysis

Chang Hyeon Song,[†] Maulida Zakia,[†] Geon Seok Lee and Seong Il Yoo*

Department of Polymer Engineering, Pukyong National University, Busan, 48513, Republic of Korea
Email: siyoo@pknu.ac.kr

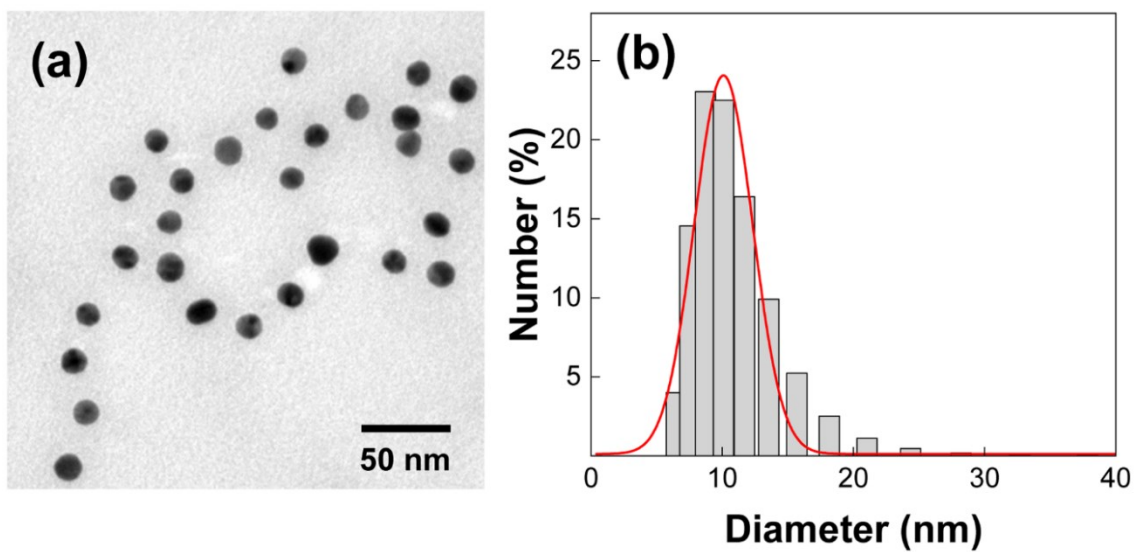[†]These authors contributed equally to this work.

Fig. S1 (a) TEM image and (b) dynamic light scattering results of Au NPs. The red line in Fig. S1b corresponds to a Gaussian fitting of the result.
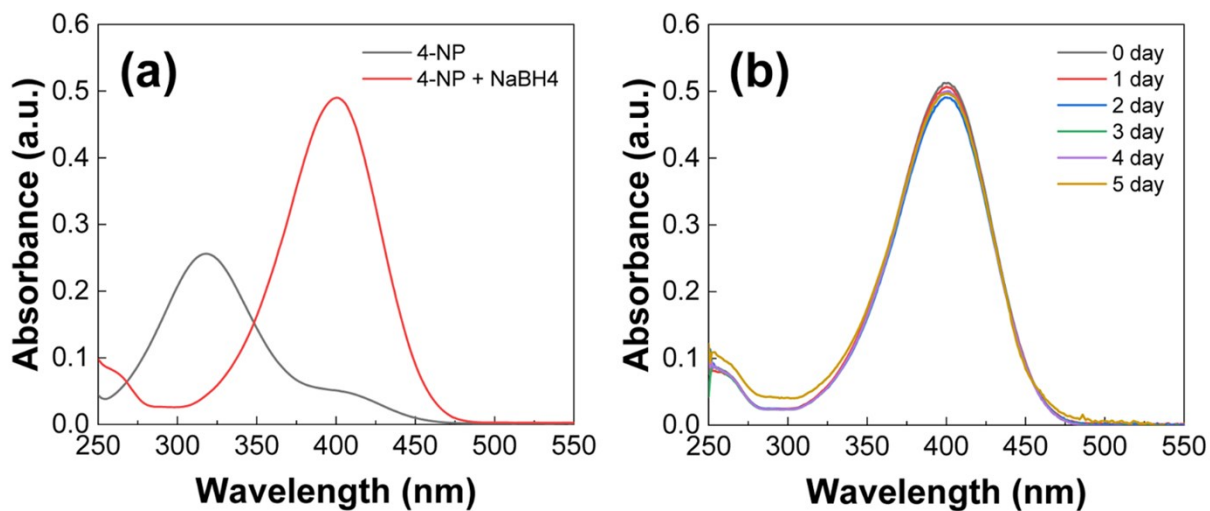
Fig. S2 (a) UV–Vis spectra of 4-nitrophenol before (black) and after (red) the addition of NaBH$_4$. (b) Time-dependent UV–Vis spectra of 4-nitrophenol after the addition of NaBH$_4$ in the absence of PES/Au membrane.

The direction conversion of 4-nitrophenolate to 4-aminophenol can be confirmed by the presence of isosbestic points and the comparison between the rate constants of 4-nitrophenol consumption and 4-aminophenol formation.

At isosbestic points, the molar extinction coefficients of 4-nitrophenolate (Nip) and 4-aminophenol (Amp) are identical ($\epsilon_{NiP} = \epsilon_{AmP} = \epsilon$); hence, the total absorbance can be expressed as $A_{tot} = A_{Nip} + A_{Amp} = \epsilon \cdot L \cdot ([Nip] + [Amp])$ by Beer-Lamber law. For the case of direct one-to-one conversion of 4-nitrophenolate to 4-aminophenol, the sum of molar concentration $[Nip] + [Amp]$ remains the same during the entire course of reaction. On the other hand, if side products were formed, $[Nip] + [Amp]$ varies with the extent of reaction. Hence, the appearance of isosbestic points at 251 nm, 275 nm and 315 nm indicates that $[Nip] + [Amp]$ remains the same, and therefore proves the direction conversion of 4-nitrophenolate to 4-aminophenol without the formation of side products.

For the case of direct one-to-one conversion, the consumption rate of 4-nitrophenolate and the formation rate of 4-aminophenol can be expressed as $[Nip] = [Nip]_0 e^{-kt}$ and $[Amp] = [Nip]_0 (1 - e^{-k't})$, respectively, at which the subscript 0 indicates the initial concentration. To extract rate constants of the consumption (k) and the formation (k'), the time-dependent absorbance in Fig. 2a and 2b (main text) were converted to time-dependent molar concentrations in Fig. S3. By fitting the converted molar concentrations with the exponential rate equations, the corresponding rate constants were evaluated under dark and illuminated conditions, which were summarized in Table S1. In comparing the result, one needs to note that the UV-Vis spectrum of 4-aminophenol more or less overlaps with that of 4-nitrophenolate (Fig. 2 in the main text). Therefore, absorbance value of 4-aminophenol at 297 nm contained minor contribution from 4-nitrophenolate, which would reduce the accuracy of the evaluated rate constants. Nevertheless, the rates of 4-nitrophenolate consumption (k) and 4-aminophenol formation (k') were still quite comparable with each other. This result additionally supports the direct conversion of 4-nitrophenolate to 4-aminophenol beyond the presence of isosbestic points.
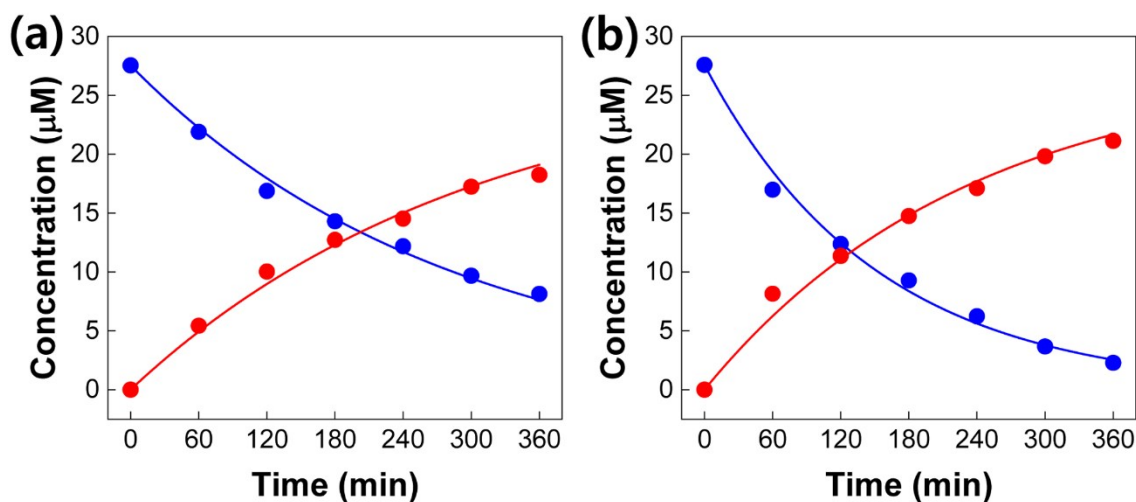
Fig. S3 Time-dependent concentration of 4-nitrophenolate (blue) and 4-aminophenol (red) from the reaction mixture under (a) dark and (b) illuminated conditions. The solid lines were obtained by fitting the time-dependent concentrations with the exponential equations. Molar extinction coefficients of $19.1 \times 10^3 \, M^{-1} \, cm^{-1}$ and $2.08 \times 10^3 \, M^{-1} \, cm^{-1}$ were utilized for 4-nitrophenolate and 4-aminophenol, respectively.

Table S1. Rate constants of the 4-nitrophenolate consumption (k) and 4-aminophenol production (k') under dark and illuminated conditions. The rate constants were averaged from three independent measurements.

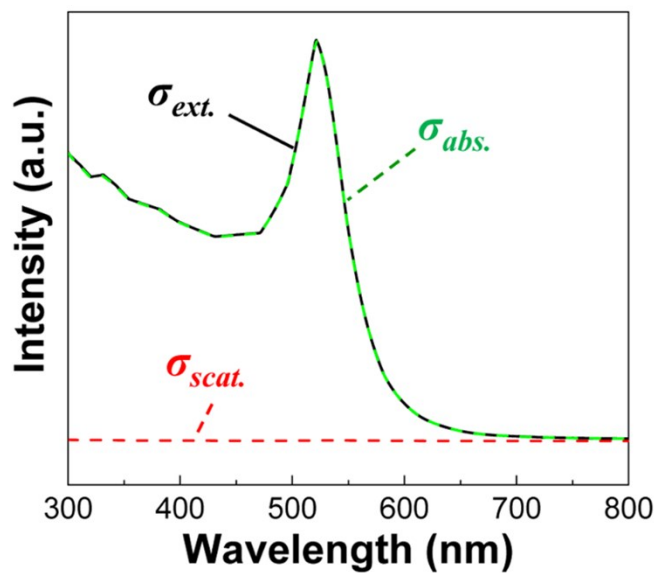| dark		illuminated	
k_{dark}	$3.43 \times 10^{-3} \, min^{-1}$	$k_{illum.}$	$6.16 \times 10^{-3} \, min^{-1}$
$k_{dark}^{'}$	$2.42 \times 10^{-3} \, min^{-1}$	$k_{illum.}^{'}$	$3.93 \times 10^{-3} \, min^{-1}$

Fig. S4 Calculated extinction (black solid), absorption (green dotted), and scattering (red dotted) spectra of Au NP having 12 nm diameter in water. For the calculation, open-source MieCalc program has been utilized.[1]

It needs to be noted that 4-nitrophenol reduction has a noticeable pH dependence.[2] Since the pH value of the original reaction mixture increased by hydrolysis of $NaBH_4$ in water (pH = ~10.7), we adjusted the pH value of 4-nitrophenol solution at the same level by adding an aqueous solution of NaOH (0.1 M). Then, PES/Au membrane was immersed into the pH-adjusted 4-nitrophenol solution without the addition of $NaBH_4$. Subsequently, time-dependent UV-Vis spectra were collected upon solar illumination as shown in Fig. S5.
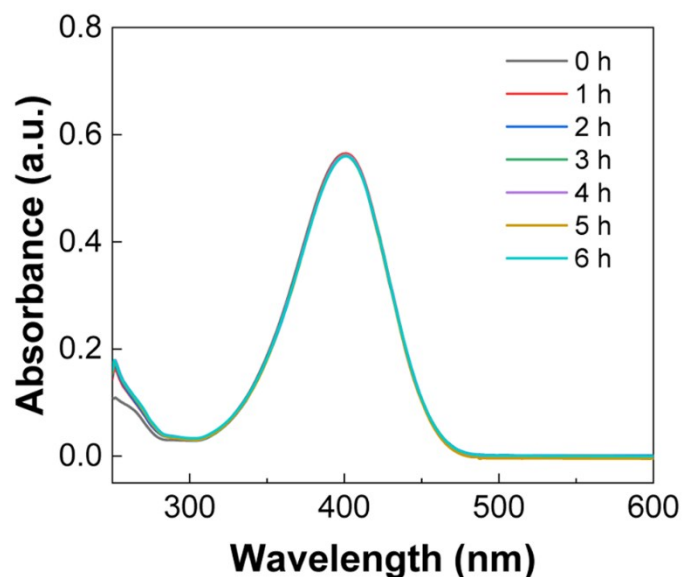

Fig. S5 Time-dependent UV–Vis spectra from the reaction mixture composed of 4-nitrophenol and PES/Au membrane in the absence of $NaBH_4$. The value of pH was adjusted as ~10.7 before the immersion of PES/Au membrane.
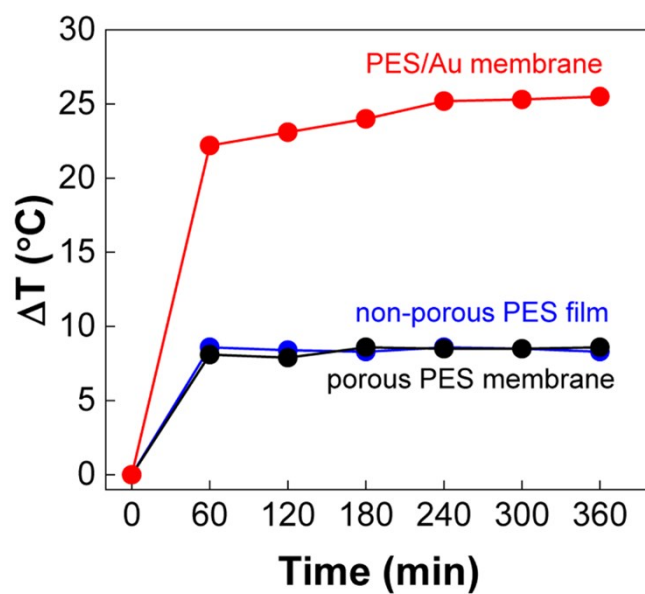
Fig. S6 Temperature profiles of porous PES membrane (black), non-porous PES film (blue), and PES/Au membrane (red) under illumination. The temperature profiles were obtained by IR camera under air environment with dried samples.
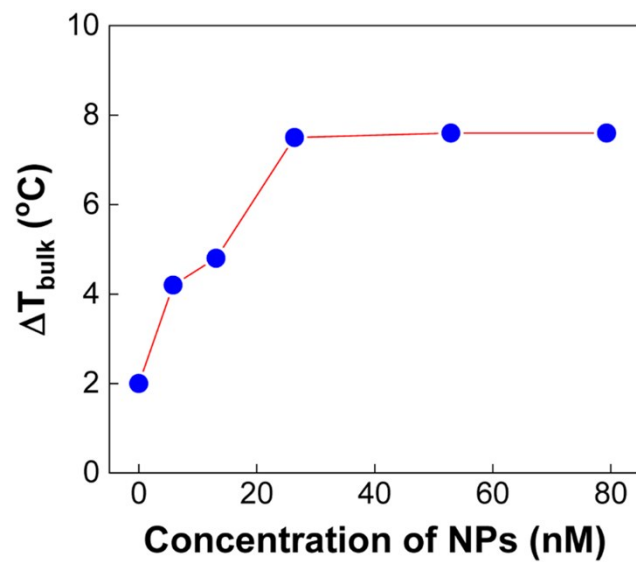
Fig. S7 The maximum temperature changes of bulk solutions with the molar concentration of NP solutions.

In this set of experiment, we performed the 4-nitrophenol reduction under different light intensities. As shown in Fig. S8, the rate of reduction increased with the light intensity, from which the corresponding rate constants were evaluated (Table S2). From the rate constants, the local temperatures of PES/Au membrane were calculated as 30.3, 36.9, and 54.1 °C under light intensities of 49, 54, and 112 mW/cm^2, respectively. Subsequently, we compared the calculated rate constants (k_{light}) with those obtained from oil bath heating under dark (k_{dark} from main text Fig. 2d). By comparing the reduction rates under illuminated and dark conditions at the similar temperatures, we found that the reduction rate under dark was always faster than that under illumination (Table S2). Since the oil bath heating uniformly increases the temperature of the reaction system, not only the reduction process but also the adsorption and diffusion of reactants/products thorough the porous membranes could be accelerated by the global heating. However, photothermal-mediated heating would mostly affect the temperature around Au NPs, which locally increases the temperature of reduction sites.
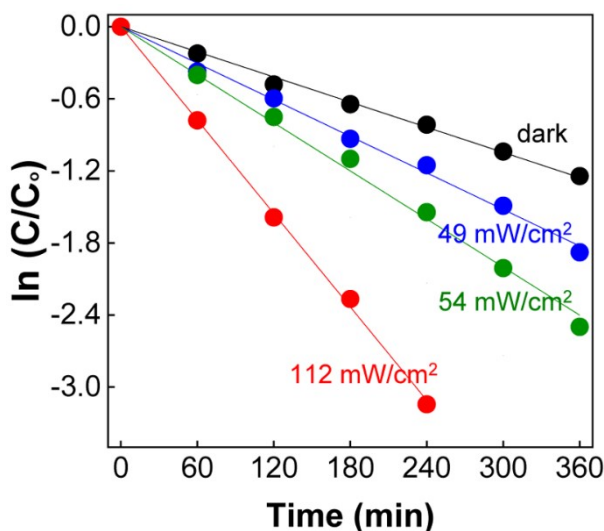

Fig. S8 Time-dependent absorbance value at 400 nm from the reaction mixture under different light intensities. The power of the incident light was adjusted as 0 (black), 49 (blue), 54 (green), 112 mW/cm^2 (red), respectively.

Table S2. Rate constants of 4-nitrophenol reduction from photothermal heating (k_{light}) and oil-bath heating (k_{dark}) conditions.

light intensity (mw/cm^2)	local temp. (°C)	rate constant (k_{light}, min^{-1})	oil bath temp. (°C)	rate constant (k_{dark}, min^{-1})	ratio (k_{dark}/k_{light})
49	30.3	5.07×10^{-3}	30.6	8.26×10^{-3}	1.63
54	36.9	6.67×10^{-3}	39.5	1.26×10^{-2}	1.89
112	54.1	1.30×10^{-2}	51.8	1.60×10^{-2}	1.23

References

1 P. Laven, MiePlot: A Computer Program for Scattering of Light from a Sphere using Mie Theory & the Debye Series, http://www.Philiplaven.com/mieplot.Htm. (accessed on 2 July 2020).

2 R. Grzeschik, D. Schäfer, T. Holtum, S. Küpper, A. Hoffmann and S. Schlücker, On the Overlooked Critical Role of the pH Value on the Kinetics of the 4-Nitrophenol $NaBH_4$-Reduction Catalyzed by Noble-Metal Nanoparticles (Pt, Pd, and Au), *J. Phys. Chem. C,* 2020, **124**, 2939-2944.