Accelerated Pyro-Catalytic Hydrogen Production Enabled by Plasmonic Local Heating of Au on Pyroelectric BaTiO$_3$ Nanoparticles

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Results and Discussion

The $d$-spacing ($d_{(hkl)}$) of material can be estimated by Bragg’s Laws,

$$2d_{(hkl)}\sin \theta_{(hkl)} = n\lambda$$  \hspace{1cm} (1)

where $n$, $(hkl)$, $\theta$ and $\lambda$ are diffraction order ($n=1$ is adopted), crystallographic orientation (miller indices), Bragg angle (in radius) and wavelength of X-ray, respectively. For tetragonal unit cell, the relation between $d$-spacing and lattice parameters is$^1$:

$$\frac{1}{d^2_{hkl}} = \frac{n^2+k^2}{a^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (2)

By using XRD data and Equations (1) and (2), the calculated lattice parameters are shown in Table S1.
Table S1 Calculated lattice parameters for BaTiO$_3$.

| Peak position (2θ) | d-spacing | Miller indices | Calculated lattice parameter |
|--------------------|-----------|----------------|-------------------------------|
| 45.01              | 2.012     | (002)          | \(c=4.025\)                  |
| 45.13              | 2.007     | (200)          | \(a=4.014\)                  |

Thus, the tetragonality (defined as the ratio of lattice parameters, \(c/a\)) of the material can be obtained by \(c/a=1.003\)

![Image](image.png)

**Fig. S1 | PFM characterizations of BaTiO$_3$.** **a.** Topographic image. **b.** Hysteresis loop measurement. Source data are provided as a Source Data file.

The ferroelectric property of BaTiO$_3$ was characterized by PFM, using dual alternating current resonance tracking modes. In PFM characterization, the coral-like shaped BaTiO$_3$ was shattered into separated particles by using ultrasonic vibration, as shown in Fig. S1a and the testing point was marked with a red dot. A butterfly-like hysteresis loop and phase switching can be observed in Fig. S1b. The phase angle
changes about $180^\circ$ under the reversal of 30 V DC bias field, revealing the ferroelectricity of the BaTiO$_3$.

The energy bandgap ($E_g$) of BaTiO$_3$ can be estimated by the Tauc relationship and Kubelka-Munk equations$^{2,3}$:

$$F(R)h\nu=A(h\nu-E_g)^n$$  \hspace{1cm} (3)

$$F(R)=\frac{(1-R)^2}{2R}$$ \hspace{1cm} (4)

where $F(R)$ is the so-called remission or Kubelka-Munk function, $R$ is reflectance, $h$ is the Planck’s constant, $\nu$ is the photon frequency, $A$ is a constant, $E_g$ is the energy bandgap, and $n$ is selected as 2 since BaTiO$_3$ is an indirect bandgap material$^{4,5,6}$.

Fig. S2 | Morphology characterizations of three-dimensional hierarchically structured coral-like BaTiO$_3$ NPs. a, TEM image. b, High-resolution HAADF-STEM image. c, HAADF-STEM image and corresponding elemental mapping of Ba, Ti, and O elements.

The TEM image of the BaTiO$_3$ NP is shown in Fig. S2a. The HAADF-STEM image (Fig. S2b) of the NP shows 3 characteristic lattice spacings, which agree well with the $d$-spacings of the (100), (0\(\bar{1}\)) and (\(\bar{1}1\bar{1}\)) planes of BaTiO$_3$. The HAADF-
STEM image and the associated elemental mappings of Ba, Ti and O (Fig. S2c) show uniform distributions of these elements.

**Fig. S3 | Surface area measurement.** Surface area characterization of BaTiO$_3$ NPs. Source data are provided as a Source Data file.
As shown in Fig. S4, the average particle size of the Au nanospheres is found to be around 18 nm.
Fig. S5 | Optical absorption. UV-visible absorption spectra of Au nanospheres and Au/BaTiO$_3$ NPs in aqueous solution (radius of Au is 9 nm). Source data are provided as a Source Data file.

Fig. S5 shows UV-visible absorption spectra of Au nanospheres and Au/BaTiO$_3$ NPs in water solution. Au nanospheres showed a narrower surface plasmon resonance band at 532 nm, which is characteristic of individual Au nanospheres, depending on the polydispersity and size of Au nanospheres$^7$. The characteristic peak around 532 nm was also observed in Au/BaTiO$_3$ sample, confirming the successful growth of Au nanospheres on BaTiO$_3$ NPs. Due to its large band gap (inset of Fig. 1c), BaTiO$_3$ does not present any noticeable absorption in the visible wavelength range. Comparing with UV-visible absorption spectra of Au nanospheres, the increasing absorption of Au/BaTiO$_3$ NPs below 400 nm may be related to the bandgap absorption of BaTiO$_3$ in the ultraviolet range.

Energy conversion efficiency calculation:

The light-to-chemical energy conversion efficiency is calculated as follows.

The value of the output chemical energy due to pyro-catalysis can be simply calculated as,

$$E_{\text{chem}} = 2n \cdot V_t \cdot N_A \cdot e$$

(5)
where \( n \) = mole number of hydrogen produced; \( V_t \) = threshold voltage (1.23 V) for water splitting; \( N_A \) = Avogadro’s number; \( e \) = elemental charge.

According to the above equation, the chemical energy output due to pyro-catalysis per second in the present case is:

\[
E_{\text{chem}} = 2n \cdot V_t \cdot N_A \cdot e = 2 \times 9.70 \times 10^{-11} \times 1.23 \times 6.02 \times 10^{23} \times 1.602 \times 10^{-19} \text{ (J} \cdot \text{s}^{-1})
\]

\[
= 2.30 \times 10^{-5} \text{ (J} \cdot \text{s}^{-1}) = 0.023 \text{ mW}
\]

The light-to-chemical energy conversion efficiency can be calculated as,

\[
\eta = \frac{E_{\text{chem}}}{E_{\text{input}}} = \frac{0.023 \text{ mW}}{500 \text{ mW}} = 0.0046\%
\]

This value is quite low since the catalyst used is dispersed in the liquid and the majority of illuminated part is actually water, not the catalyst.

**Fig. S6 | Hydrogen production.** Full water splitting by Au/BaTiO\(_3\) NPs after 90 min irradiation of 532-nm nanosecond pulsed laser. Source data are provided as a Source Data file.

Fig. S6 shows the full water splitting by Au/BaTiO\(_3\) NPs under the irradiation of a 532-nm nanosecond laser. The production ratio of H\(_2\) and O\(_2\) gas is less than 2:1, which may result from the air absorbed into the gas-tight syringe during manual injection and testing processes.
**Table S2** Hydrogen production via pyro-catalysis

| Pyroelectric catalysts | Cold-hot cycle condition | Catalyst dosage (sacrificial agent/concentration) | Catalytic applications | Catalytic efficiency/rate constant | Ref. |
|------------------------|--------------------------|---------------------------------------------------|-----------------------|-----------------------------------|------|
| BST nanoparticles       | 298K-323K, 10 min per thermal cycle | 10 mg catalyst/10 mL H₂O (20 vol% methanol) | H₂ production | 47 µmol·g⁻¹ (36 thermal cycles) | 8    |
| 2D few layers BP        | 288K-338K, 10 min per thermal cycle | 1 mg catalyst/10 mL H₂O (20 vol% methanol) | H₂ production | 540 µmol·g⁻¹ (24 thermal cycles) | 9    |
| BaTiO₃ single crystals   | 303-343K, 2 min per thermal cycle | 3.1 g catalyst (without sacrificial agent) | H₂ production | 300 vol.-ppb | 10 |
| PZT sheet               | 316K-319K                | 4.85 g, thickness of 170 µm, surface area of 49 cm² (without sacrificial agent) | H₂ production | 0.654 µmol·h⁻¹ | 11 |
| SiC                    | 300 K-333 K, 20 min per thermal cycle | 50 mg catalyst/20 mL H₂O (10 vol% methanol) | H₂ production | 32.84 µmol·g⁻¹ | 12 |
| Au/BaTiO₃ nanoparticles | 500 mW nanosecond laser/10 Hz | 2.62 mg catalyst/12 mL H₂O (without sacrificial agent) | H₂ production | 133.1±4.3716 µmol·g⁻¹·h⁻¹ | This work |
Fig. S7 | TEM image. Morphology of Au/BaTiO$_3$ NPs after pyro-catalysis.

Fig. S8 | Morphology characterizations of Au/BaTiO$_3$ NPs after pyro-catalysis. a, b and c, HRTEM image of Au/BaTiO$_3$ NPs after pyro-catalysis with different radii of decorated Au NPs. d, HAADF-STEM image and corresponding elemental mapping of Ba, Ti, O, and Au elements of b.

As shown in the Fig.S7 and S8, after pyro-catalysis, there is nearly no damage on Au/BaTiO$_3$ NPs.
**Fig. S9 | Optical simulation.** a, Structural model for optical simulation: a faceted Au nanosphere (h=0.5 nm) suspending over an BaTiO$_3$ nanowire (water gap=1nm). b, Absorption cross section of an Au nanosphere (in a radius of 6, 9 and 12 nm) suspended over BaTiO$_3$. c, Power density of one laser pulse. d, Electric field distribution of an Au nanosphere (R= 9 nm as an example) under optical excitation at $\lambda=532$ nm with the optical polarization along the radial direction of BaTiO$_3$. e, Electric field distribution of an Au nanosphere (R= 9 nm as an example) under optical excitation at $\lambda=532$ nm with optical polarization along the axial direction of BaTiO$_3$. Source data are provided as a Source Data file.
A simplified structural model is depicted in Fig. S9a, where \( R \) denotes the radius and \( h \) is the height of the sphere cap of Au nanosphere. The refractive index of water is set to be 1.33 and the optical properties of Au and BaTiO\(_3\) are taken from Johnson Christy's and Wemple's experimental results, respectively\(^{13,14}\). The sphere cap height \((h=0.5 \text{ nm})\) is chosen to reasonably comply with the morphology of the in situ grown Au nanosphere on BaTiO\(_3\) NPs. Due to the existence of ligand surrounding an Au nanosphere, the gap between BaTiO\(_3\) and the facet of Au nanosphere is chosen to be 1 nm. The absorption cross section peak of the Au nanosphere with different radii are located at 532 nm, as shown in Fig. S9b. The power density used to deduce the heating power of the Au NP during one laser pulse (around 68 ns in duration) is shown in Fig. S9c. The plasmonic modes at excitation wavelength of 532 nm with optical polarizations along radial and axial directions of BaTiO\(_3\) are shown in Fig. S9d and S9e, respectively, and are very akin to a dipolar electric mode. To investigate the plasmonic local heating effect during the laser irradiation, the thermal properties of Au nanosphere, BaTiO\(_3\) and water are set as follows: the heat capacities of gold and BaTiO\(_3\) are 129 and 527 J·kg\(^{-1}\)·K\(^{-1}\), respectively. The thermal conductivities of gold and BaTiO\(_3\) are 317 and 6 W·m\(^{-1}\)·K\(^{-1}\), respectively. The densities of gold and BaTiO\(_3\) are 19300 and 6060 kg·m\(^{-3}\), respectively\(^{15}\). All the temperature dependent thermal properties of water are taken from the built-in material library of COMSOL Multiphysics 5.5. Using the parameters above, the corresponding temperature distribution of Au/BaTiO\(_3\) NP can be obtained.
Fig. S10 | Simulated temperature evolution. Time evolution of the temperature of Au nanosphere, point (0, 0, 0), P-BaTiO₃, W-BaTiO₃ and surrounding water with different radii of decorated Au NPs: a, 6 nm and c, 12 nm. Zoom-in time evolution of the temperature of P-BaTiO₃, W-BaTiO₃, and surrounding water with different radii of decorated Au NPs: b, 6 nm and d, 12 nm. e, Time evolution of the temperature increase along axial direction of a BaTiO₃ NP decorated with a 9-nm Au nanosphere. Source data are provided as a Source Data file.
**Fig. S11 | Water temperature.** Temperature variation of water under prolonged irradiation of nanosecond laser during the plasmon induced pyro-catalysis. Source data are provided as a Source Data file.

As shown in Fig. S11, temperature change of water during plasmon induced pyro-catalysis is negligible. The overall temperature of water was monitored by a thermometer.
**Fig. S12 | Mechanism of pyro-catalysis.** a, equilibrium polarization state at temperature $T_1$. b, the temperature is raised from $T_1$ to $T_2$. c, equilibrium polarization state at temperature $T_2$. d, the temperature is decreased from $T_2$ to $T_1$.

The source of charges mainly comes from two origins: (1) free electrons in the conduction band, and (2) screen charges on the surface\textsuperscript{16}. The free electrons may come from defects (such as oxygen vacancies) to keep neutrality of the material’s internal charges. In the present case, the hot electrons injected from the Au nanoparticles to BaTiO$_3$ particles is another source of free electrons. Those free electrons will drift under the pyroelectrically induced internal field and migrate to the surface to participate in the catalytic reaction. The surface screen charges come from charged species in the liquid to compensate the polarization-induced surface bound changes. Under thermal fluctuation, the spontaneous polarization may vary and the redundant screen charges may participate in the catalytic reaction.

Fig.S12 schematically illustrates the pyro-catalysis mechanism. Initially, both free electrons and screen charges will accumulate at the surface of nanoparticles to compensate the polarization-induced surface bound changes (Fig.S12a). When the temperature is raised from $T_1$ to $T_2$, the spontaneous polarization is reduced. Hence the positively polarized surface will release electrons to have the hydrogen evolution reaction (HER) and the negatively polarized surface will accept electrons from water molecules to have the oxygen evolution reaction (OER) (Fig.S12b). Fig.S12c depicts the equilibrium state at the higher temperature of $T_2$. When the temperature is decreased from $T_2$ to $T_1$, the spontaneous polarization is increased. Hence the whole process is
reversed, that is, the positively polarized surface will accept electrons to have OER and the negatively polarized surface will release electrons to have HER (Fig. S12d).

**Fig. S13 | Optical Simulation.** Structural model for simulation: **a**, One faceted Au nanosphere (h = 0.5 nm) suspending over a cylindrical BaTiO$_3$ particle (water gap = 1 nm). Left panel: cut planes used to calculate the temperature difference in axial direction (their positions are represented by black lines and marked as $P_c$ and $P_e$). Right panel: side-view of $P_c$ and $P_e$ cut planes. **b**, The same schematic as that shown in **a**, but with two different cut planes, i.e., $P_t$ and $P_b$, used to calculate the temperature difference in z-direction. **c**, Surface-averaged temperature of $P_c$ (blue curve, marked as "center") and $P_e$ (red curve, marked as "extremity"). **d**, Surface-averaged temperature of $P_t$ (blue curve, marked as "top") and $P_b$ (red curve, marked as "bottom"). Source data are provided as a Source Data file.

To calculate the thermoelectrically induced charges, we set two circular cut planes,
marked as $P_c$ and $P_e$ in Fig. S13a. The temperature difference between the two planes ($P_c$ and $P_e$) will induce current flows due to thermoelectric effect in the axial direction of the cylindrical particle, as marked by red arrows. The length of red arrow schematically shows the magnitude of current density (not drawn to scale, Fig. S13a left panel). Similarly, we also consider the current flows in a direction perpendicular to the axial direction, as marked by blue arrows in Fig. S13b left panel. Two cut planes parallel to the $xyz$-plane are created within the cylindrical BaTiO$_3$ particle. By drawing tangent lines from the center of the Au nanosphere to the BaTiO$_3$ surface (Fig. S13b, right panel), the plane $P_t$ is formed by all the points of tangency. Simple calculation shows that $P_t$ is 7.98 nm from the top of the cylindrical BaTiO$_3$ particle. For symmetry consideration, the other cut plane $P_b$ is parallel to $P_t$ but at an equal distance of 7.98 nm above the bottom of BaTiO$_3$ particle, serving as a reference plane for calculating the temperature difference. These two planes are reasonably chosen to evaluate the thermoelectric effect in $z$-direction since the BaTiO$_3$ surface above $P_t$ (highlighted by red colored zone in Fig. S13b) is regarded as being directly heated by the Au nanosphere and thus be treated as the heat source in the thermal process. The surface-averaged temperature in the $P_c$ and $P_e$ cut planes are given in Fig. S13c. And the surface-averaged temperatures in the $P_t$ and $P_b$ cut planes are given in Fig. S13d. It can be seen that, the temperature difference in axial direction is much higher as $P_c$ and $P_e$ cut planes are far apart. On the contrary, the surface-averaged temperature difference in $P_t$ and $P_b$ cut planes is much smaller due to their smaller separation distance (84.04 nm).

The quantity of electrons induced by thermoelectric effect can be derived as follows:

$$ Q = \int I \, dt = \int \sigma(T) E \, dA \, dt = \int \sigma(T) \frac{V}{l} \, dA \, dt = \int S \frac{\sigma(T)\Delta T}{l} \, dA \, dt $$  \hspace{1cm} (7)

Where $I$, $\sigma$, $E$, $V$, $l$, $A$, $t$, $S$, and $\Delta T$ are the current, the electrical conductivity, electric field, thermoelectric voltage, the distance between two cut planes, surface area, time, Seebeck coefficient and the temperature difference between two end planes, respectively.
Fig. S14 | Simulation of thermoelectric effect. Quantity of electric charges induced by thermoelectric effect in a, axial direction; and b, z-direction. Source data are provided as a Source Data file.

It should be noted that although the surface-averaged temperature difference in P_Pb cut planes is much smaller than that in P_c-P_e cut planes (Fig.S13c and Fig.S13d), the larger surface area of P_Pb (542000 nm² vs. 7584 nm²) and their smaller separation distance (84.04 nm vs. 500 nm) finally result in a larger value in electrons induced by thermoelectricity (Fig.S14).
**Fig. S15 | Simulated temperature change.** Area integrated temperature change ($\int \Delta T (\hat{n} \cdot \hat{P}) dA$) over the upper half surface of the cylindrical BaTiO$_3$ particle after one laser pulse irradiation on a 9-nm Au NP. Inset shows the integrated area (shaded part) of the particle. Source data are provided as a Source Data file.

The total pyroelectric charges over the surface of BaTiO$_3$ NPs within the heating process during one pulse irradiation on a 9-nm Au NP can be calculated by:

\[
Q = p \cdot \int \Delta T (\hat{n} \cdot \hat{P}) dA
\]

where $p$ is the pyroelectric coefficient with a value between 20 and 30 nC·cm$^{-2}$·K$^{-1}$, $\Delta T$ is the temperature rise in heating (or drop during cooling), $\hat{n}$ is the unit vector along the surface normal direction, and $\hat{P}$ is the unit vector along spontaneous polarization direction.

Without losing generality, we compare the cases for polarizations along the axial direction and z-direction. The integral of $\Delta T (\hat{n} \cdot \hat{P}) dA$ over the upper surface (corresponding polarization along z-axis) of the cylindrical particle can be up to $1.71 \times 10^{-13}$ m$^2$K (Fig. S15), which is much larger than the integral over the $P_c$ cut plane (corresponding polarization along axial direction) (location of $P_c$ can be found from Fig. S13a). Moreover, the pyroelectric charges generated on the $P_c$ cut plane are difficult to
diffuse to the surface for catalytic reaction due to the low conductivity of BaTiO$_3$. Therefore, we consider only the polarization along $z$-axis for the estimation of the upper limit of H$_2$ production.

Taking the pyroelectric coefficient ($\rho$) of 30 nC-cm$^{-2}$-K$^{-1}$ as an example, we can easily calculate that the pyroelectric charges are $5.12 \times 10^{-17}$ C, which are much larger than those due to thermoelectric effect (Fig. S14). So the thermoelectric effect induced catalysis can be neglected in the present case.

The above results show that the maximum amount of pyroelectric charges produced over the surface of one BaTiO$_3$ NP by one single Au NP during the heating process by one-pulse illumination is about $5.12 \times 10^{-17}$ C, which is equivalent to 320 electrons. The pyroelectric charges produced over the lower half surface of the cylinder during the cooling process may also contribute to the catalytic H$_2$ production. They are estimated to be around 60% of that produced from the upper half surface during the heating process since the average temperature change of the lower half surface is around 60% of that of the upper half surface (Fig. S13d). So the total available pyroelectric charges for pyro-catalysis during one complete heating/cooling cycle is 512 electrons.

In the present case, the repetition rate of the laser is 10 Hz. Hence, the maximum number of electrons produced over the surface of one BaTiO$_3$ NP after one-hour nanosecond laser irradiation on one 9-nm Au NP for pyro-catalysis ($N_{\text{one particle}}$) can be calculated as,

$$N_{\text{one particle}} = 512 \times 10 \times 60 \times 60 = 1.84 \times 10^7$$  \hspace{1cm} (9)

The total number of BaTiO$_3$ NPs in 1 gram is,

$$N = \frac{m}{\rho V} = \frac{1 \text{ g}}{6060 \text{ kg m}^{-3} \times \pi \times 50 \text{ nm} \times 50 \text{ nm} \times 1000 \text{ nm}} = 2.09 \times 10^{13}$$  \hspace{1cm} (10)

where $\rho$ is density of BaTiO$_3$ ($= 6060$ kg·m$^{-3}$).

Thus, after one-hour nanosecond laser irradiation, for 1 g of BaTiO$_3$ NPs, the total number available electrons for pyro-catalysis is $n = N_{\text{one particle}} \times N = 3.85 \times 10^{20}$. Therefore, the pyro-catalytic hydrogen production rate (R) over the surface of BaTiO$_3$ NPs is
\[ R = \frac{n}{2N_A} = \frac{3.85 \times 10^{20}}{2 \times 6.02 \times 10^{23}} = 319.8 \, \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1} \]  

where \( N_A \) is the Avogadro’s number.

**Fig. S16 | Trapping of hydroxyl radical.** Fluorescence spectra for •OH trapping after experiencing 0, 10, and 30 min pyro-catalysis reaction time. Source data are provided as a Source Data file.

During the pyro-catalytic reaction, hydroxyl radicals (•OH) can also be generated, which was captured by a photoluminescent •OH trapping agent, terephthalic acid. Terephthalic acid can react with •OH to produce a highly fluorescent product, 2-hydroxyterephthalic acid, which emits a unique fluorescence signal with its peak wavelength at 425 nm\(^{19}\). The PL intensity of 2-hydroxyterephthalic acid relies on the amount of •OH generated in water\(^{19}\). This sensitive and specific method has been widely used for the •OH detection\(^{20,21,22}\). In the current work, around 0.5 mg Au/BaTiO\(_3\) NPs were dispersed in 4 mL terephthalic acid aqueous solution (0.5 mM) with a concentration of 2 mM NaOH in a quartz reactor. After experiencing various irradiation time by a 532 nm nanosecond laser, the PL spectra of the generated 2-hydroxyterephthalic acid was measured via a spectrofluorometer under an excitation wavelength of 321 nm. In Fig. 16, with increasing reaction time, the 425 nm fluorescence intensity gradually increases, which indicates the increasing amount of •OH radicals synthesized under pyro-catalysis.
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