Supporting Information

Remarkably Enhanced Photocatalytic Activity of Laser Ablated Au Nanoparticle Decorated $BiFeO_3$ Nanowires under Visible-light

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Experimental section:

Synthesis of $BiFeO_3$ NWs: 2.425 g $Bi(NO_3)_3 \cdot 5H_2O$ and 1.352 g $FeCl_3 \cdot 6H_2O$ were mixed in 50 mL of acetone (99.8 %) and sonicated for 30 min. Then 200 mL of D.I. H_2O and concentrated ammonia were added under vigorous stirring until the pH value of the solution reached 10-11. After filtering and rinsing with distilled water, the red co-precipitate was redispersed in 40 mL D.I. water. Under vigorous stirring, 8 g NaOH was added into the suspension. Next, the hydrothermal solution was placed inside a stainless steel autoclave with a Teflon liner and heated at 140 °C for 48 hours. The final product was dried at 80 °C for 2 h.

Synthesis of PLAL-AuNPs: Laser ablation was carried out with a KrF excimer laser (GSI Lumonics PM-846, wavelength: 248 nm, repetition rate 20 Hz). The beam was focused by an objective lens with a focal length of 7.5 cm onto a gold plate target with a diameter of 8 mm and 1.5 mm in thickness. The gold target was placed at the bottom of a glass vessel (6 mL) filled with D.I. H_2O ($pH \approx 6.0$). The depth of the water layer above the target was 10 mm. The laser fluence on the target was set at ~40.0 J/cm^2 during all ablation processes.

Synthesis[S1] and purification of Chem-AuNPs: First, 1 mL $HAuCl_4 \cdot 3H_2O$ aqueous solution (1 wt%) was added into 90 mL of distilled water, followed by injection of 2 mL of sodium citrate solution (38.8 mM). The reaction mixture was then stirred for 1 min. Subsequently, 1 mL of 0.075 wt% freshly prepared $NaBH_4$ solution (in 38.8 mM sodium citrate solution) was added and the reaction mixture was stirred for 12 h at room temperature. Subsequently the all as-synthesized Au colloidal solution was purified to remove un-attached or un-reacted chemical species, and 93 mL of 1.25 mM sodium citrate solution was loaded and sonicated to re-disperse the AuNPs. A delicate purification process was performed to the as-prepared Chem-AuNPs solution by using ultra-centrifuge filters. In a typical experiment, 12 mL of as-prepared Au colloidal solution was centrifuged at 4500 rpm with ultra-centrifuge filters into 4 mL concentrated solution (8 mL of the filtrate was discarded). And then 8 mL of distilled water was introduced to re-disperse the 4 mL highly concentrated AuNPs. After the pre-purification process, additional washing was repeated twice. Finally, AuNPs were re-dispersed in pure D.I. water and used immediately for hybridization and characterization.

Preparation of hybrid AuNPs/$BiFeO_3$ NWs nanocomposites: 50 mg of $BiFeO_3$ NWs powder was added to freshly prepared PLAL-AuNPs (or purified Chem-AuNPs) solution and mixed by shaking. The mixture solution was incubated at room temperature for 30 min. Then the precipitate was recovered by centrifugation, followed by washing with distilled water. Then the nanocomposites were heated at 200 °C for 10 h to enhance the bonding between the Au nanoparticles and $BiFeO_3$ nanowires.

Characterizations: The crystal structure of the as-prepared samples was characterized by X-ray spectroscopy (XRD, Bruker D8 Advanced Diffractometer, Cu K_α radiation). Field emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM-6300F scanning electron microscopy. Transmission electron microscopy (TEM) images were recorded on a JEOL 2100F high resolution transmission electron microscopy at an accelerating voltage of 200 kV. The UV-vis photoabsorption of the powder suspensions was analyzed by UV-visible spectrometer (Varian 5000). The chemical compositions of the products were studied using X-ray photoelectron spectroscopy (XPS, ESCALAB 220I-XL spectrometer) equipped with an Al K_α (1486.6 eV) monochromatic source. All binding energies of various peaks were calibrated using the binding energy of C1s (284.6 eV). Elemental analysis with neutron activation analysis (NAA) technique was performed using SLOWPOKE nuclear reactor (École Polytechnique de Montréal, Montréal, Canada) to quantify the Au component in the AuNPs/$BiFeO_3$ NWs nanocomposite and to determine the amount of catalysts used in the reactions. The Zeta-potential measurement was performed with a Brookhaven ZETAPALS Analyzer for colloidal samples (1.5 mL) at different pH values in standard 10 mm PMMA all-side transparent cuvettes. Steady state Photoluminescence (PL) of samples dispersed in ethanol (0.5 mg/mL) was measured using an excitation wavelength of 400 nm on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon). All experiments were carried out under ambient conditions.

Evaluation of photocatalytic water splitting activity: In the photocatalytic reactions, the photocatalyst powder (50 mg) was dispersed in $FeCl_3$ solution (4 mmol/L, 50 mL). The photocatalytic reactions were performed by adopting a 300 W xenon lamp (optical filter, $\lambda >$ 380 nm) as an outer irradiation source. The quartz cover allowed ample transmission from the xenon lamp into the chamber. The Pyrex chamber was cooled by partially submerging it in cold water during photocatalytic reactions. The gas in the chamber was sampled by vacuum-tight syringes and then immediately analyzed by a gas chromatograph (Shimadzu GC-8A) using a thermal conductivity detector (TCD). For wavelength dependence measurement, optical filters (530 ± 25 nm, and 630 ± 25 nm) from Edmund Optics were used.

Additional Figures:

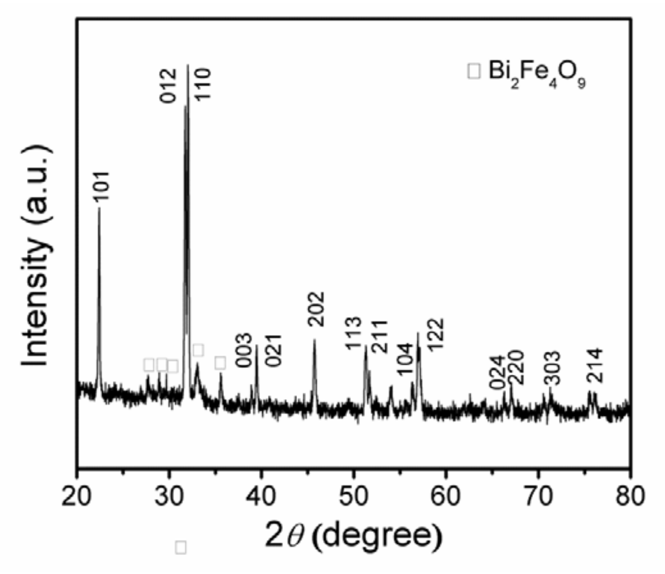

Fig. S1. XRD patterns of as-synthesized $BiFeO_3$ NWs.

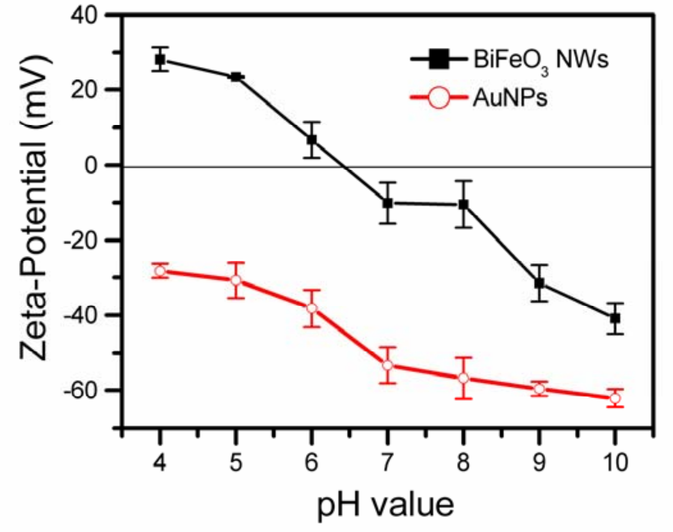

Fig. S2. Zeta-potential of $BiFeO_3$ NWs and PLAL-AuNPs aquoues solution at different pH values.

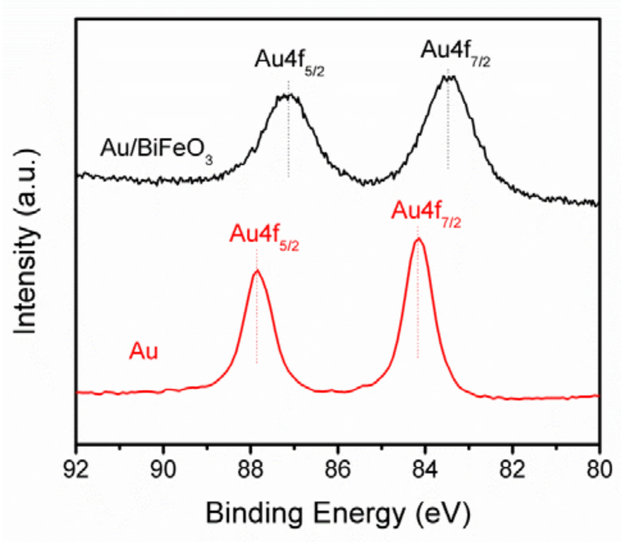

Fig. S3. XPS spectra of Au_{4f} in pristine PLAL-AuNPs and PLAL-AuNPs(1.0 wt%)/$BiFeO_3$ NWs nanocomposite.

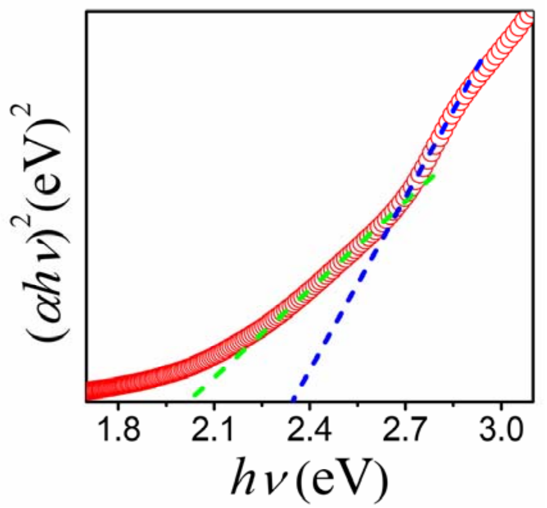

Fig. S4. Calculation diagram of the bandgap of $BiFeO_3$ NWs by using the equation of $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α, h, ν, E_g, and A are absorption coefficient, Planck constant, light frequency, band gap and a constant, respectively.[2]

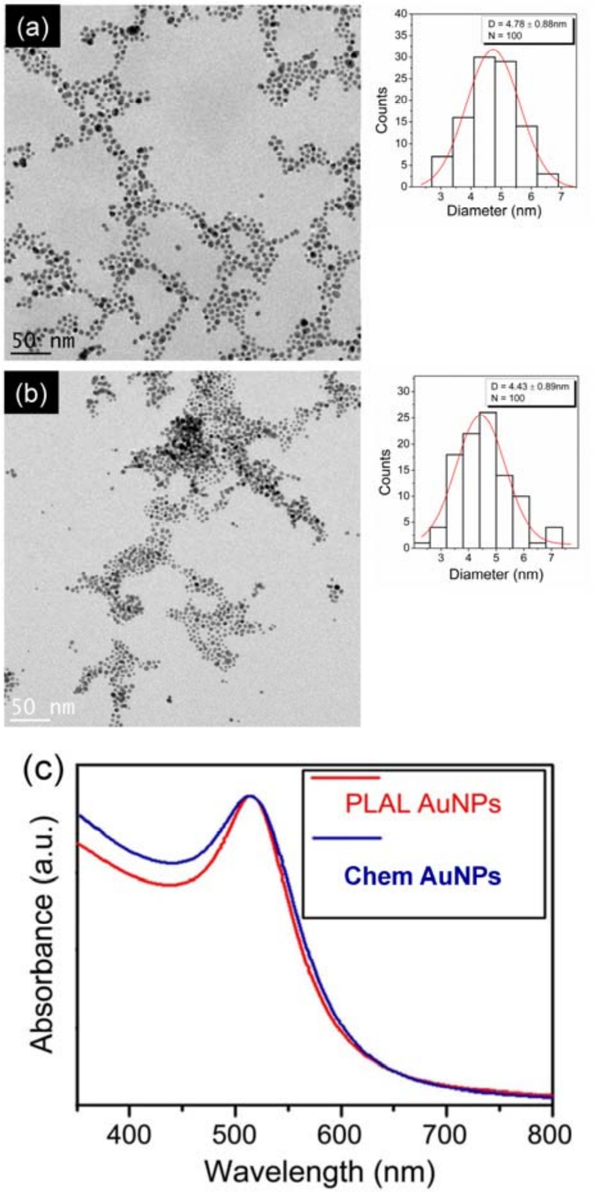

Fig. S5. TEM images of (a) PLAL-AuNPs and (b) Chem-AuNPs. On the right of each figure the histograms of size distribution are displayed, respectively. (c) UV-vis absorption spectra of PLAL- and Chem-AuNPs.

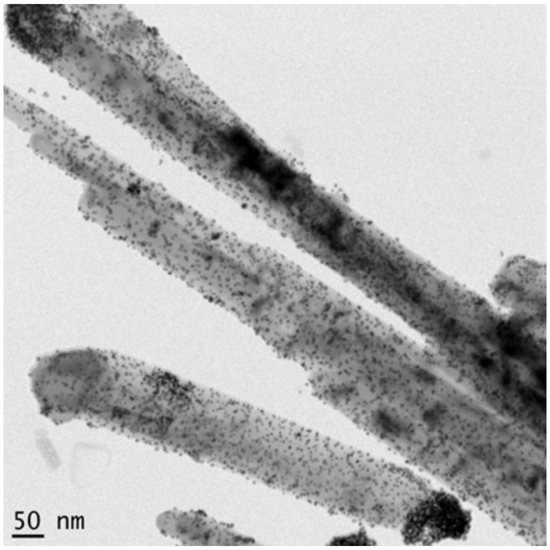

Fig. S6. TEM image of PLAL-AuNPs(5.0 wt%)/$BiFeO_3$ NWs nanocomposite.

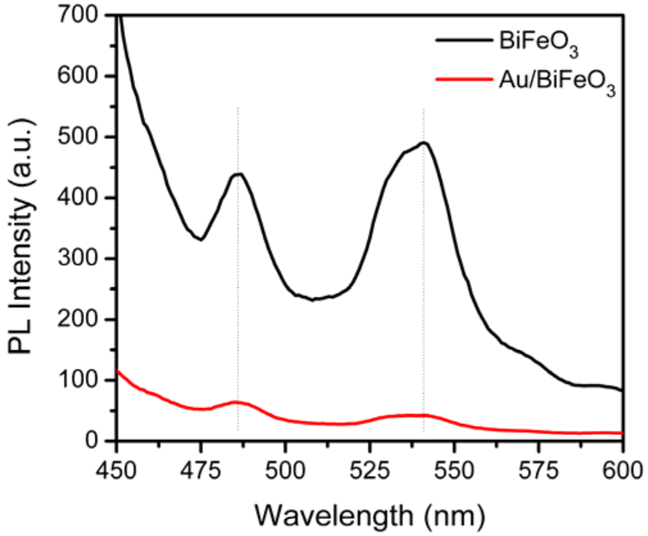

Fig. S7. Photoluminescence spectra of BiFeO$_3$ NWs and PLAL-AuNPs(1.0 wt%)/BiFeO$_3$ NWs nanocomposite.

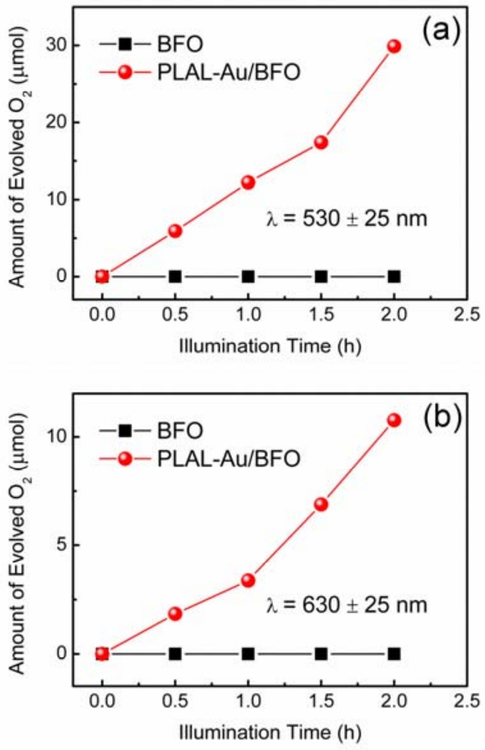

Fig. S8. Oxygen evolved upon visible light illumination at different wavelengths ((a) 530±25 nm, (b) 630 ± 25 nm) of $BiFeO_3$ NWs and PLAL-AuNPs(1.0 wt%)/$BiFeO_3$ NWs nanocomposite in $FeCl_3$ suspension (4 mmol/L, 30 mL) containing the photocatalysts (30 mg).

References:

[S1] W. Haiss, N. T. K. Thanh, J. Aveyard and D. G. Fernig, *Analytical Chemistry*, 2007, **79**, 4215-4221.

[S2] M. A. Butler, *Journal of Applied Physics*, 1977, **48**, 1914-1920.