

Supporting Information

Driving NiTiO₃ Photocatalyst for Oxygen Evolution Reaction with Near-infrared Light

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Experimental Section

Materials of the synthesis

Nickel (II) acetate tetrahydrate $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and titanium (IV) isopropoxide $[\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}]$ were purchased from Aladdin Bio-Chem Technology Co., Ltd, Shanghai, China. Anhydrous citric acid $[\text{C}_6\text{H}_8\text{O}_7]$, Cobaltous nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, and anhydrous ethyl alcohol $[\text{C}_2\text{H}_5\text{OH}]$ were purchased from Sinopharm Chemical Reagent Co., China. The chemicals were used as received without any purification. Deionized (DI) water was utilized in the experiment.

Synthesis of NiTiO_3 photocatalyst

NiTiO_3 (NTO) was synthesized via a modified Pechini method (including sol-gel and calcination). In detail, 2.488 g $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 11.53 g $\text{C}_6\text{H}_8\text{O}_7$ were dissolved in 100 mL $\text{C}_2\text{H}_5\text{OH}$ under constant stirring for 30 minutes to form a homogeneous solution. Afterward, 2.96 mL $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ was added to the solution dropwise while stirring in ambient conditions for an hour. The as-prepared solution was transferred into an oven and thermally heated at 343 K for 2 days at a 5 K/min ramping rate to form a gel-like precursor. The gel was calcined at 873 K for 4 hours with the ramping rate of 5 K/min and cooling down to ambient conditions to obtain NTO powder.

Synthesis of CoO_x loaded NiTiO_3 photocatalyst

CoO_x was deposited onto the surface of NTO by the “impregnation-sintering” method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the cobalt source and was firstly dissolved into DI water to form a 5 mg/mL solution. After that, a certain amount of Co solution was added to a beaker containing 200 mg of NTO powder. Through sonication and magnetic stirring, the mixed composite was dried by water-boiling. Finally, the powder was sintered in a muffle furnace at 623 K for 1 hour with a ramping rate of 5 K/min and cooling to ambient conditions. The composite photocatalyst was denoted as $x\text{CNTO}$, where x stands for the weight percentage of CoO_x , varying from 1%, 2%, 3%, and 4% to 5%, respectively.

Characterizations of materials

X-ray diffraction (XRD) patterns were measured in a Rigaku Miniflex 600 diffractometer with Cu-K α 1 radiation (1.54178 Å). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained in a Perkin Elmer Lambda 950 scan system. Raman spectra were collected on a LabRAM HR Evolution Raman spectrometer system under 325 nm excitation. The morphologies of the sample were obtained by a Hitachi New Generation SU8010 field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB250 instrument with a monochromatized AL K α line source (200W). Temperature-dependent photoluminescence (PL) was obtained using a steady state and time-resolved fluorescence spectrometers (FLSP920). Photoelectrochemical tests were conducted in an electrochemical workstation (CHI-750D, Shanghai Chenhua, China) with a three-electrode system, using Pt foil as the counter electrode and Ag/AgCl (3 M KCl) electrode as the reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO), where a mixed NTO and DMF were spread and dried. Nyquist plots and Mott-Schottky measurements were obtained using the electronic impedance spectroscopy (EIS) system in 0.2 M Na₂SO₄ solution (pH value ~ 6.8). The ultrafast fs-TA measurements were conducted under a pump wavelength of 360 nm on Helios (Ultrafast System) spectrometers using a regeneratively amplified femtosecond Ti:sapphire laser system (Spitfire Pro-F1KXP, Spectra-Physics).

Photocatalytic oxygen evolution reaction

The photocatalytic water oxidation reactions were performed in a Pyrex top-irradiation reaction vessel (200 mL). Typically, 50 mg catalyst was dispersed into a reactor containing 100 mL water, followed by adding 1 mM AgNO₃ and 0.2 g La₂O₃ as an electron sacrificial agent and a pH buffer agent, respectively. Before light illumination, the whole system was evacuated for 30 min to exhaust the air. A 300 W Xe lamp was used as the light source for photocatalytic half-water oxidation and reduction reactions. Various LED lights (50 W) with different wavelengths were also applied to the experiments. A water-circulating pump controlled the temperature of the reaction system at 12°C. The evolved O₂ was detected by online gas chromatography (SHIMADZU GC 8A) equipped with a thermal conductivity detector and Ar as carrier

gas.

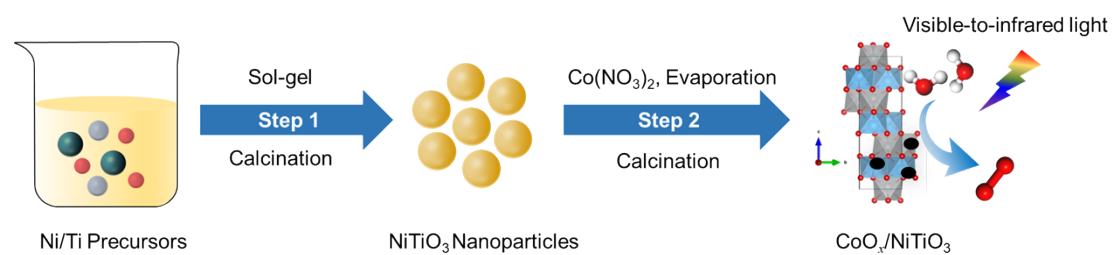
Apparent quantum yield (AQY) measurements

The AQY was calculated by the following formula:

$$AQY (\%) = \frac{N_e}{N_p} \times 100\% = \frac{4n_{O_2,t}N_Ahc}{PS\lambda_{inc}t} \times 100\%$$

Where N_e is the number of reaction electrons, N_p is the incident photons, $n_{O_2,t}$ (mol) is the amount of oxygen evolution, N_A is Avogadro's constant, h (m² kg/s) is the Planck constant, c (m/s) is the power density of the incident monochromatic light, S (m²) is the irradiation area, λ_{inc} (m) is the wavelength of the incident monochromatic light, and t (s) is the duration of incident light exposure.

Figure Legends



Scheme S1. Schematic illustration of the synthesis of CNTO photocatalyst.

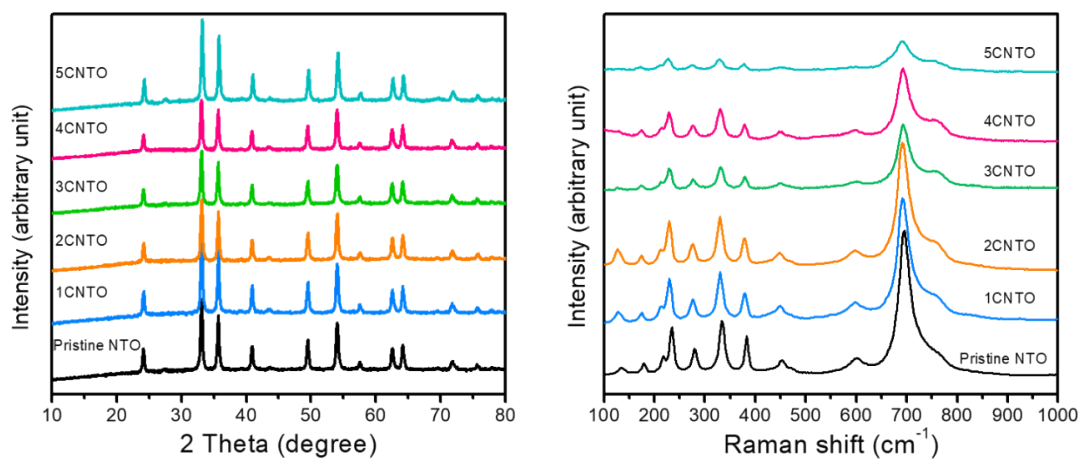


Figure S1. (a) XRD patterns and (b) Raman spectra of NTO and CNTO materials.

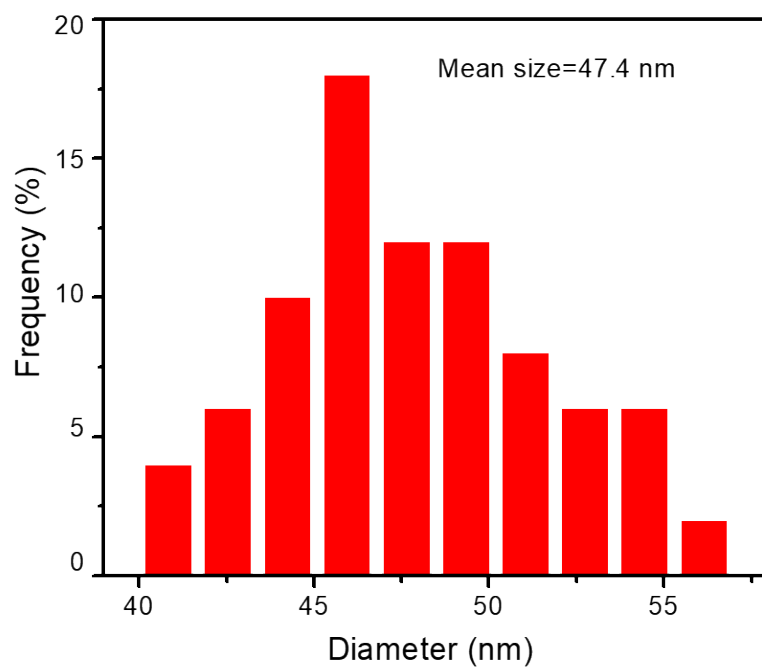


Figure S2. The size distribution of 4CNTO photocatalyst.

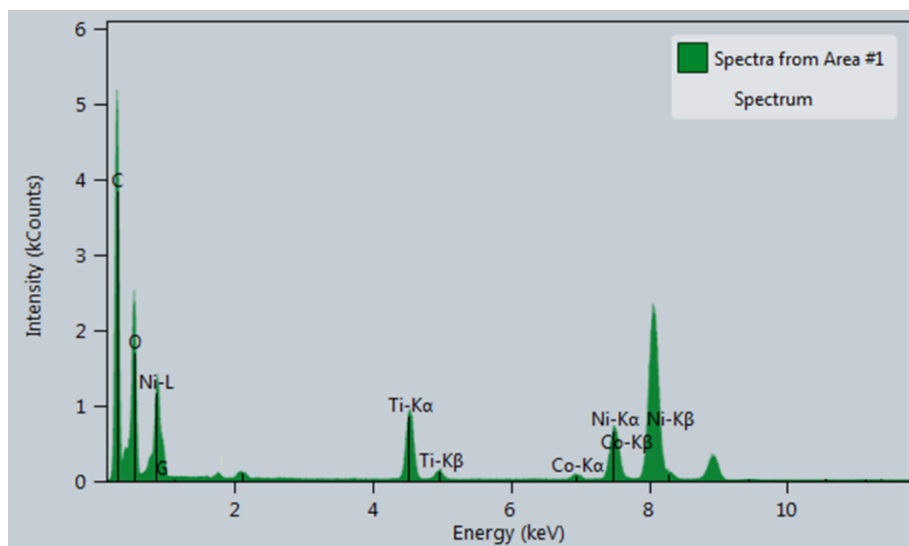


Figure S3. EDX elemental signals of 4CNTO.

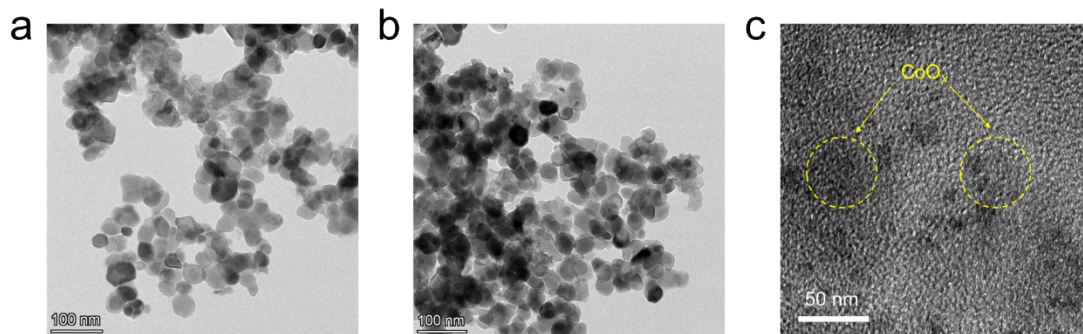


Figure S4. TEM images of (a) for NTO, (b) and (c) for 4CNTO.

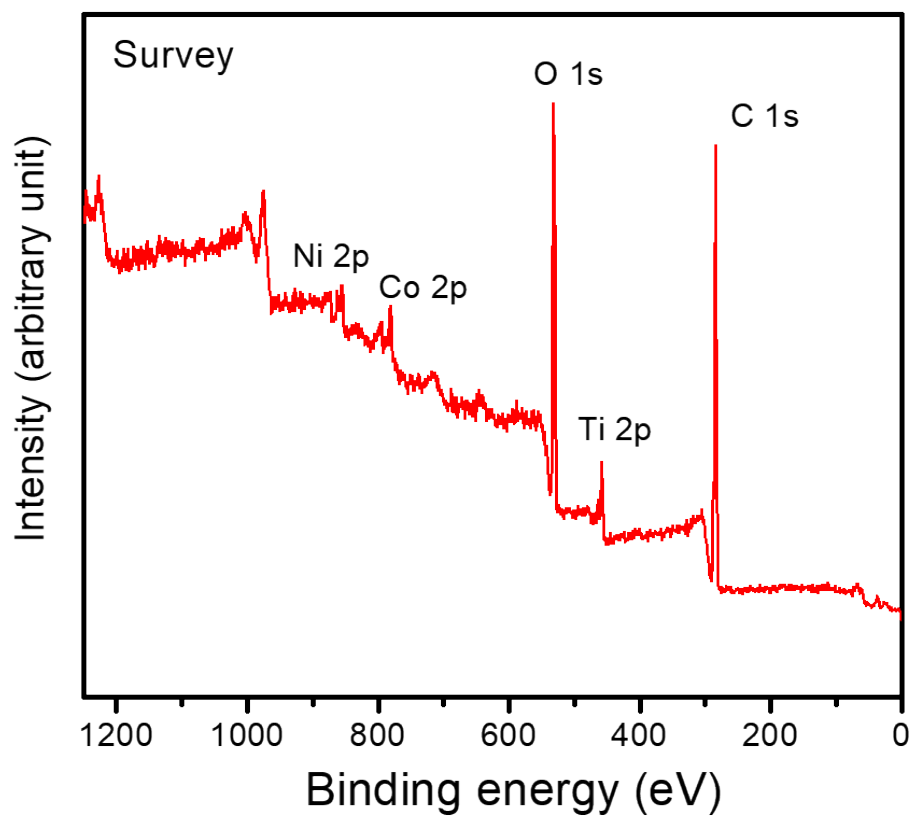


Figure S5. Survey XPS spectrum of 4CNTO.

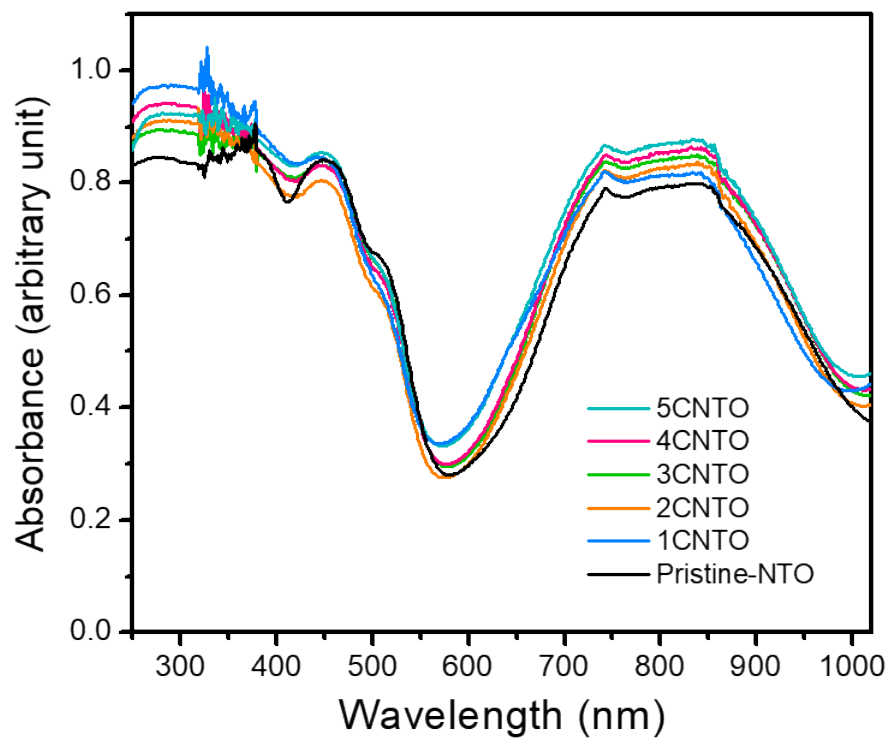


Figure S6. UV-Vis DRS spectra of NTO and CNTO series with the loading of different CoO_x weights.

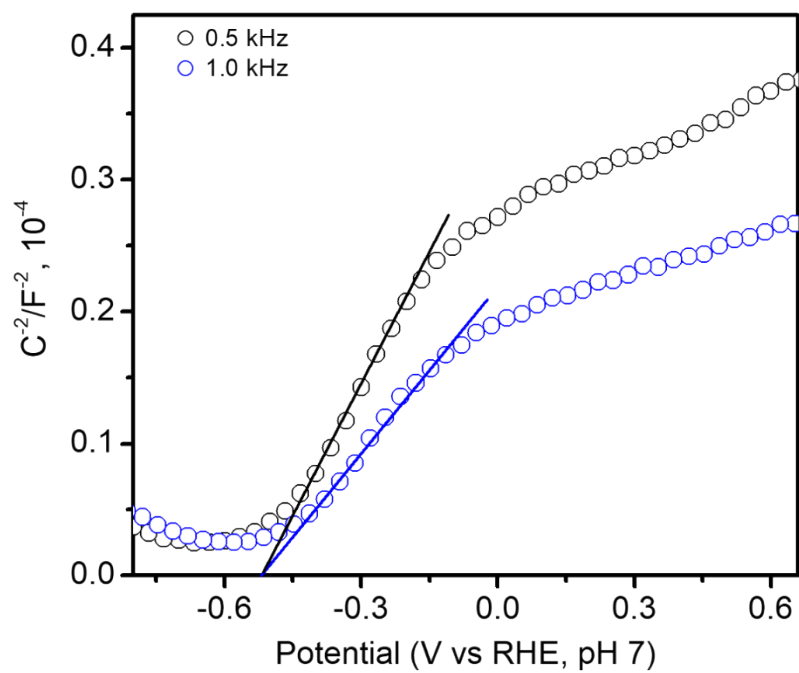


Figure S7. Mott-Schottky plots of NTO under different frequencies.

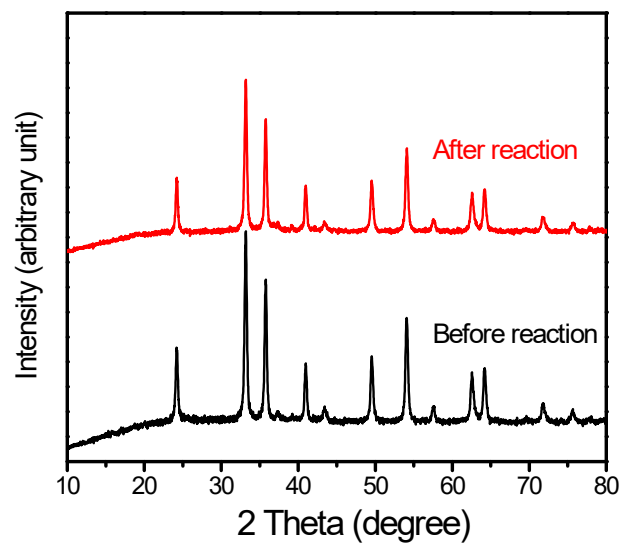


Figure S8. The before and after-reaction XRD patterns of the 4CNTO.

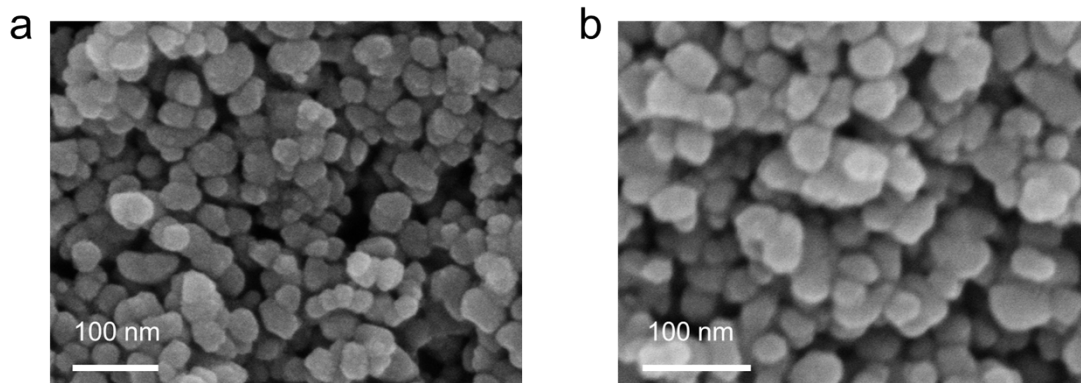


Figure S9. SEM images of 4CNTO for before (a) and after-reaction (b).

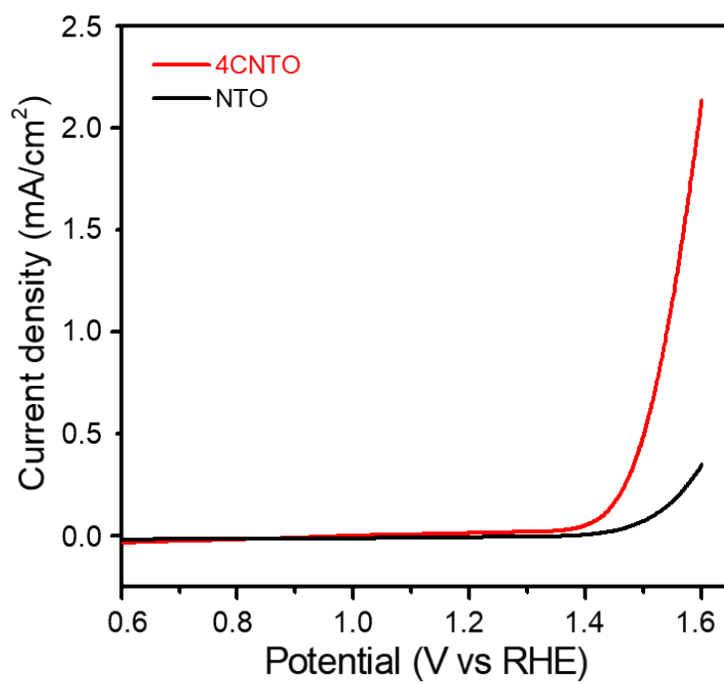


Figure S10. LSV curves of NTO and 4CNTO.

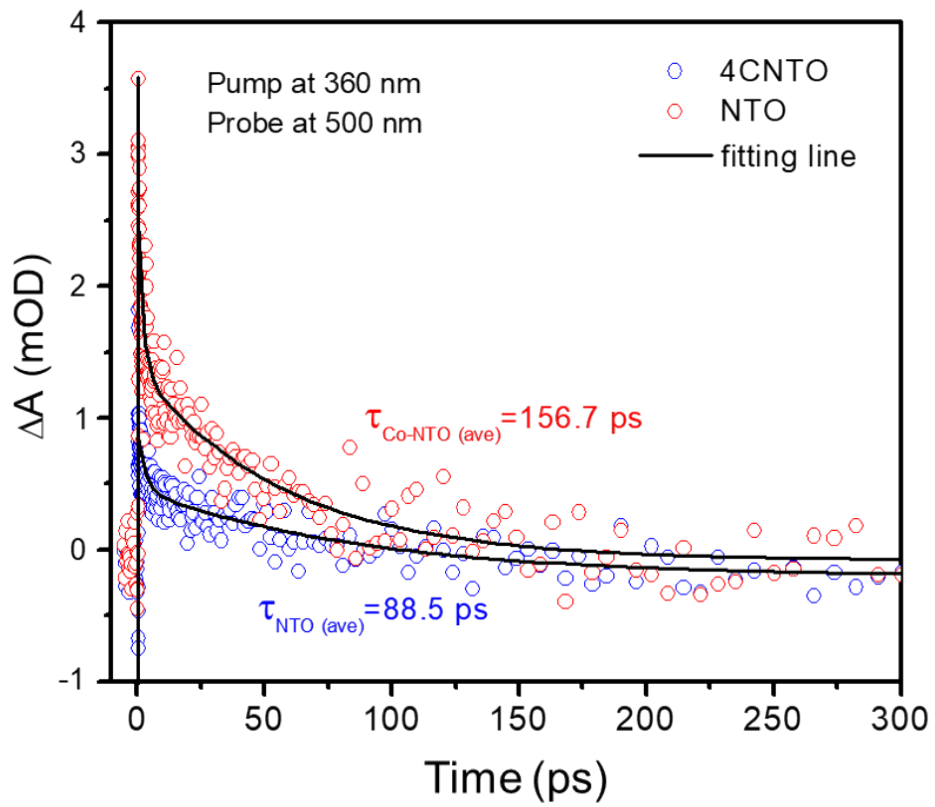


Figure S11. Time profiles of 4CNTO and NTO of kinetics decay.