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Electronic supplementary information

Facile synthesis of $PbTiO_3$ truncated octahedrons via solid state reaction and their application in low-temperature CO oxidation by loading Pt nanoparticles

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Experimental Section

Preparation: TiO_2 (Degussa P25) and $Pb(NO_3)_2$ were used as starting substance (Pb/Ti molar ratio is 1.25). Analytical grade Potassium hydroxide (KOH, 6 M) was used as mineralizer. A precursor was derived in an autoclave (80% filled) at 200 ^oC for 30 min and then filtered and washed with deionized water and ethanol, which was subsequently dried at 60 ^oC for 24 h in air. The dried precursor powder was annealed at 650 ^oC in air for different time to obtain PTO products, where the heating rate was set to be 50^oC/min and cooled to room temperature naturally. Finally, the as-obtained PTO product was dispersed in deionized water in an ultrasonic bath for 30 min. The Pt/PTO nanocrystals were obtained by adding 0.05 M chloroplatinic acid ($H_2PtCl_6 \bullet 6H_2O$, aq) into the above mentioned solutions containing PTO nanocrystals. After stirring for 15 min (RT), 0.2 M sodium borohydride ($NaBH_4$, reductant) solution was added dropwise into the mixture and then kept in the ultrasonic bath for 30 min. The final powder was derived after centrifuging, washing and then drying at 60 ^oC for 24 h.

Synthetic procedure for the PTO nanoplates: TiO_2 (Degussa P25) and $Pb(NO_3)_2$ were used as starting substance (Pb/Ti molar ratio is 1.25). Analytical grade Potassium hydroxide (KOH, 6M) was used as mineralizer. The hydrothermal treatment was carried out in an autoclave (80% filled) at 200 ^oC for 12 h. The resultant product was then filtered and washed with deionized water and ethanol, which was subsequently dried at 60 ^oC for 24 h in air.

Characterization: X-ray diffraction (XRD) patterns are obtained on RIGAKUD-MAX-C with CuKα radiation (λ=1.54056 Å). Scanning electron microscope (SEM) images were collected by the Hitachi field emission SEM MODEL S-4800. X-ray photoelectron spectra (XPS) were acquired using a Thermo ESCALAB 250 photoelectron spectrometer with Al Ka source. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis was carried out on a TGA-SDT (Q600 V8.2 Build 100) instrument. Nitrogen gas adsorption experiments are carried out on an Accelerated Surface Area and Porosimetry system (ASAP-2020, Micromeritics, Norcross, GA). High-resolution (S)TEM imaging was carried out on a FEI Titan ST microscope at 300 kV. A HAADF detector with inner detection angle of 76 mrad was used for the STEM imaging. HRTEM simulation was carried out using multi-slice method with the qSTEM code.

Electron tomography tilt series from -65° to 65° at 1° interval were acquired in STEM mode, which were aligned and then reconstructed to a 3D volume using the SIRT function in the FEI Inspect 3D software. The 3D volume rendering, density segmentation and isosurface construction were achieved by the Avizo software.

Catalysis: The ambient pressure CO oxidation was performed in a continuous flow fixed-bed quartz tubular reactor (6 mm i.d.). 50 mg (40-60 mesh) 1% Pt/PTO catalyst was packed in the reactor and pre-treated at 120 ^{o}C for 2 h under a 50 ml/min dry He flow. After cooling to room temperature, a dry 0.7 vol% CO/He and 33.3 vol%O_2/He mixture feed stock was introduced into the reactor, which corresponds to gas hourly space velocity (GHSV) of 36,000 mL (h gcat^{-1}) in order to achieve different CO/O_2 ratios and control the conversion of CO below 15%. All reactants and products were analyzed by on-line gas chromatography.

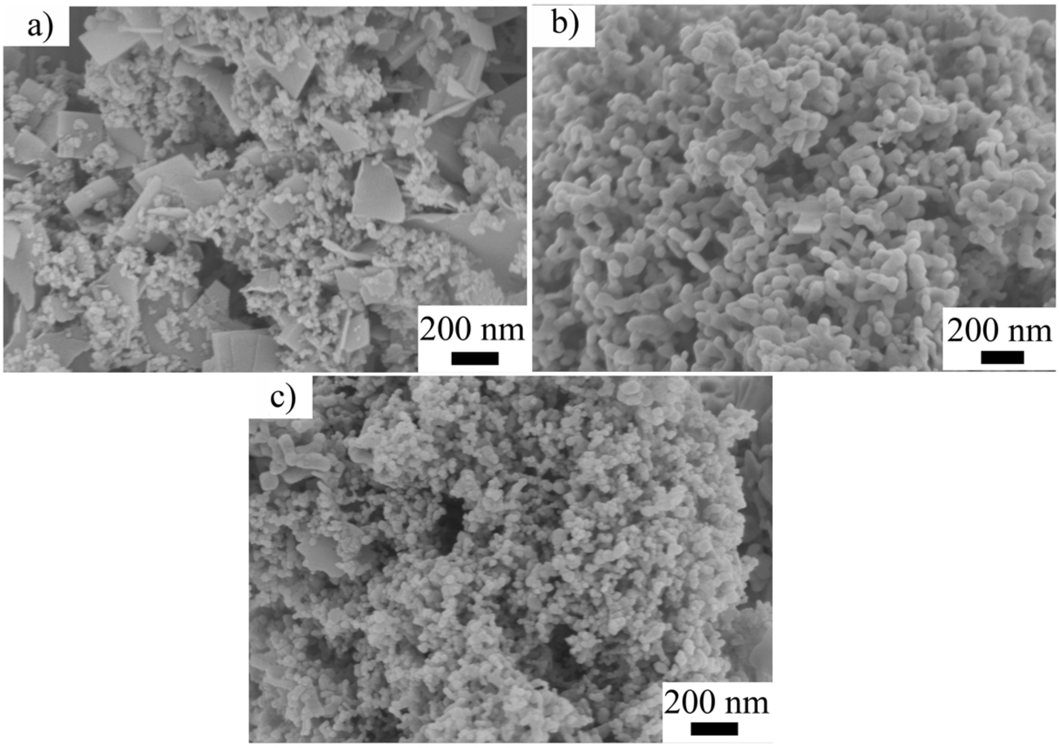

Figure S1 SEM images of a) hydrothermally obtained precursor powders and 650 ^{o}C heat treated samples of b) 650 ^{o}C for 10 min and c) 650 ^{o}C for 30 min.

Figure S1 shows the typical SEM images of the as-prepared samples for hydrothermal precursor powder and that annealed at 650 ^{o}C for 10 min and 30 min. The precursor powder consists of nanoparticles and thin nanoplates while the latter disappeared after subsequent heat treatment in 650 ^{o}C for different time. The particles size after the heat treatment was in range of 25~50 nm.

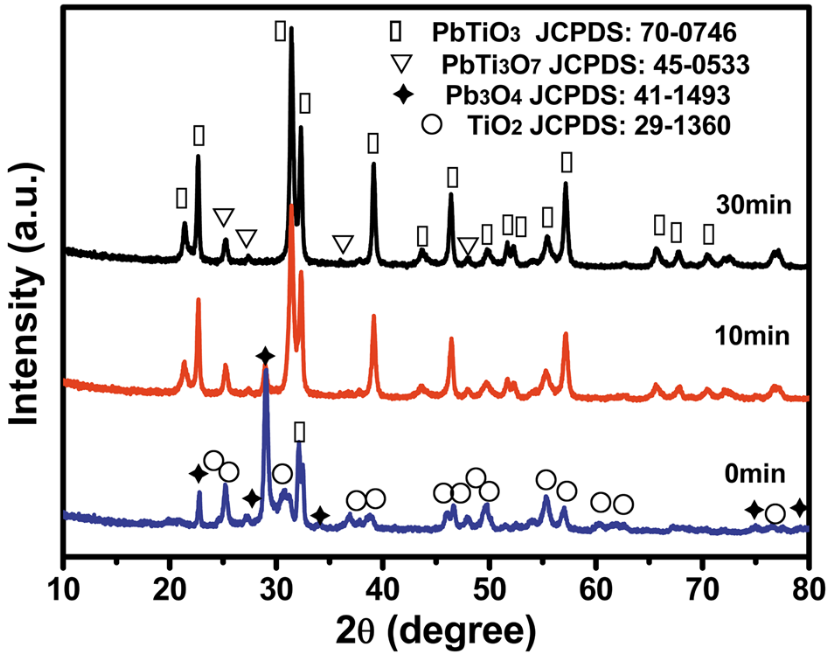

Figure S2 XRD patterns of hydrothermally obtained precursor powders and 650 ^{o}C heat treated samples.

Figure S2 shows the XRD patterns of the products treated at 650 ^{o}C for 0 min, 10 min and 30min. As identified, the precursor before treatment can be indexed to Pb_3O_4 (JCPDS no. 41-1493) and brookite TiO_2 (JCPDS no. 29-1360). When the treatment time was 10 min, tetragonal perovskite PTO began to emerge, and when the treatment time was further elongated to 30 min, the lead oxides and titanium oxides disappeared and PTO was obtained in large scale.

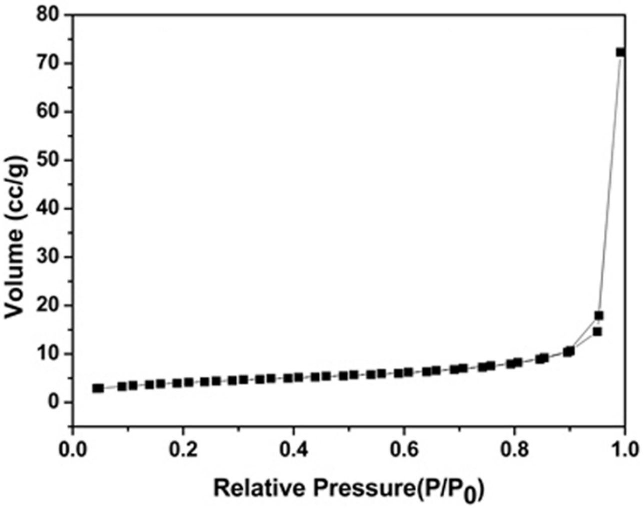

Figure S3 N_2 adsorption-desorption isotherms of PTO nanocrystals.

Figure S3 shows the N_2 adsorption-desorption isotherms of the as-prepared PTO nanocrystals. BET surface area of PTO nanocrystals was derived from the linear part of the BET (Brunauer curve in 0.05-0.35 partial pressure range). The N_2 adsorption-desorption isotherms were determined from the BJH model. The calculation result demonstrates a value of 14.50 m^2/g for external surface area of the PTO nanocrystals.

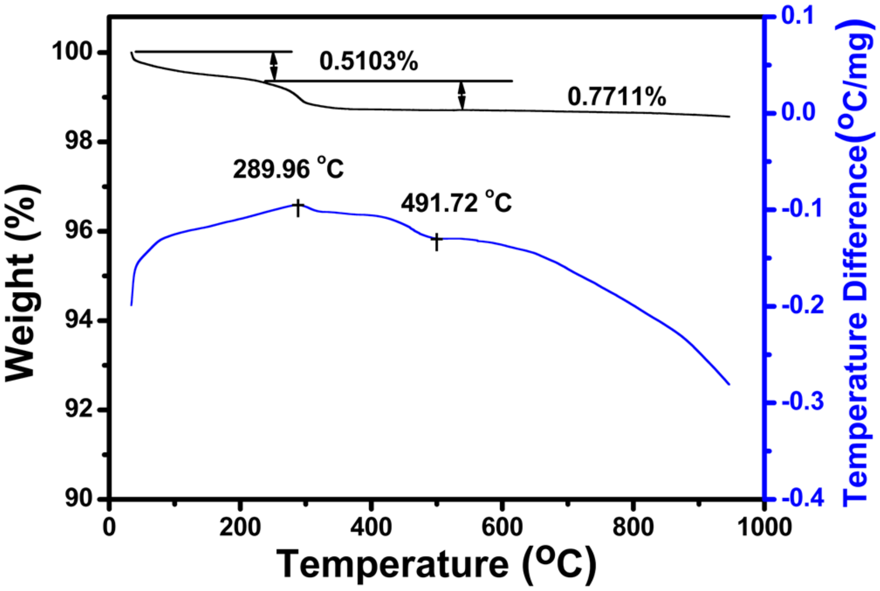

Figure S4 Differential thermogravity and scanning calorimetry (TG-DSC) spectra of PTO nanocrystals (Black and blue curves refer to TG and DSC spectrum, respectively). The exothermal peak at ~289 °C might arise from -OH desorption from the surface of the nanocrystals.[S1]

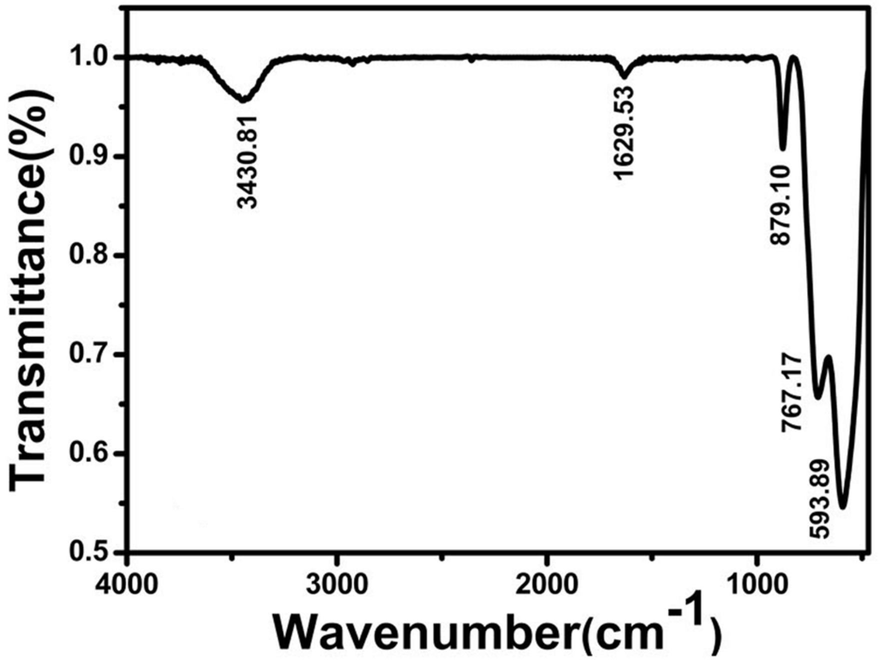

Figure S5 FT-IR spectrum of PTO nanocrystals

The Fourier transform-infrared spectrum (FT-IR) of the PTO nanocrystals was obtained by using a Nicolet Nexus 470 Fourier transformed spectrometer in the 400-4000 cm^{-1} region by KBr pellet. As presented in Figure S5, a broad hydroxyl (-OH) stretching peak situated at ~3430 cm^{-1} [S2] can be observed, which confirmed the discussion on exothermic peak at 289.96 ^{o}C in Figure S4. A second typical absorption band at ~1630 cm^{-1} could be assigned to physically adsorbed water molecules (H-O-H bending), as can be observed in Figure S5. The broad bands below ~ 950 cm^{-1} could be attributed to the characteristic vibrations of the inorganic Ti-O-Ti network in the $PbTiO_3$.[S2,S3]

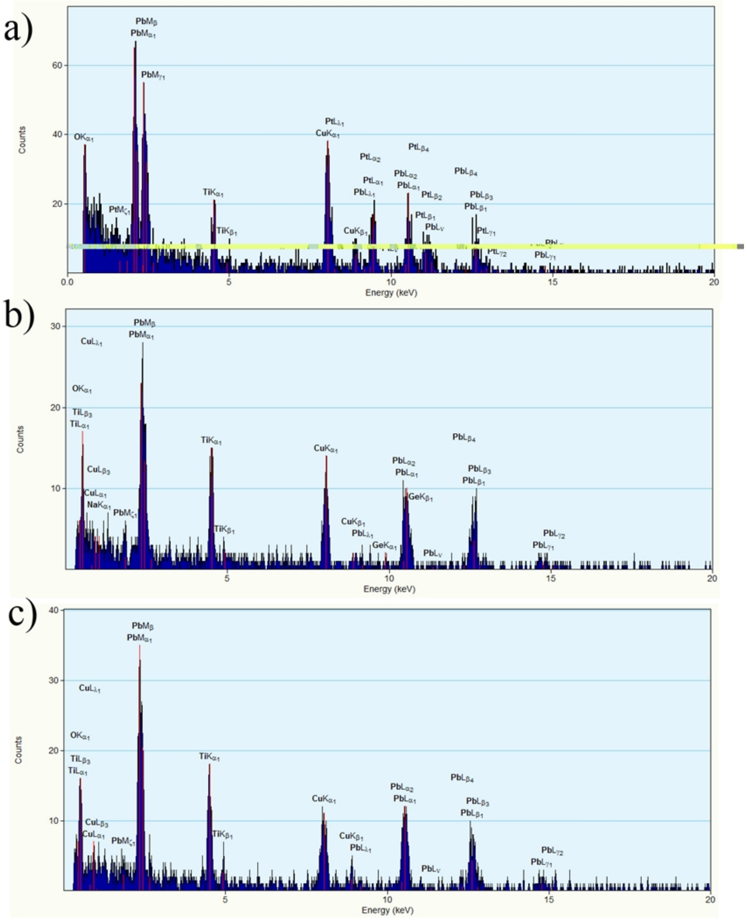

Figure S6 Energy-dispersive X-ray spectroscopy (EDX) patterns of regions a) A; b) B; c) C in Fig.2

Figure S6 displays the EDX analysis of the Pt/PTO nanocrystals from the same part indicated in Fig. 2(a), which have different diffraction contrast with segregated Pb as is confirmed by samples in regions A, B and C. Region A is characterized by Pt L edge signals, while region B and C are Pt-free.

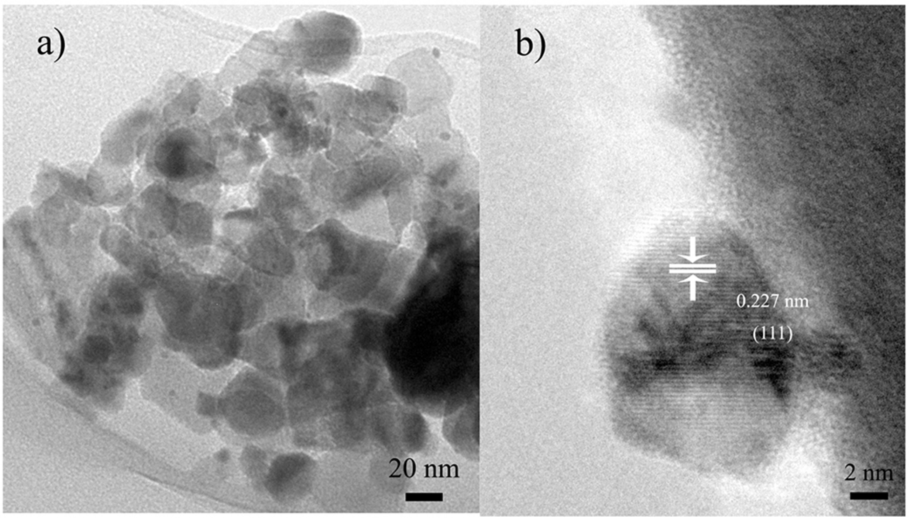

Figure S7 TEM (a) and HRTEM (b) images of the as-prepared Pt-loaded $PbTiO_3$ nanocrystals.

As shown in Figure S7 a), segregated Pt nanoparticles were dispersed evenly on the surface of PTO nanocrystals. And a single Pt nanocrystal in magnified TEM can be clearly identified in Figure S7 b). The crystal lattice of 0.227 nm can be well indexed to the Pt (111).

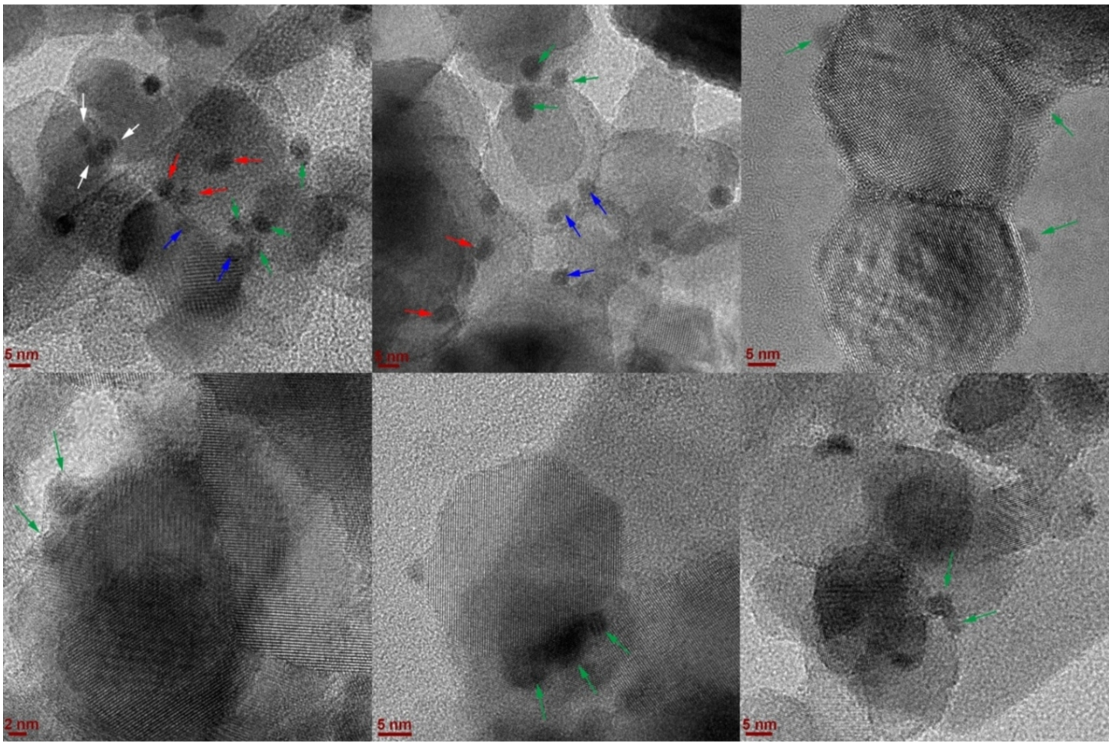

Figure S8 TEM images of Pt NPs on PTO nanocrystals. Arrows with the same colour refer to Pt NPs on the same side of the nanocrystals.

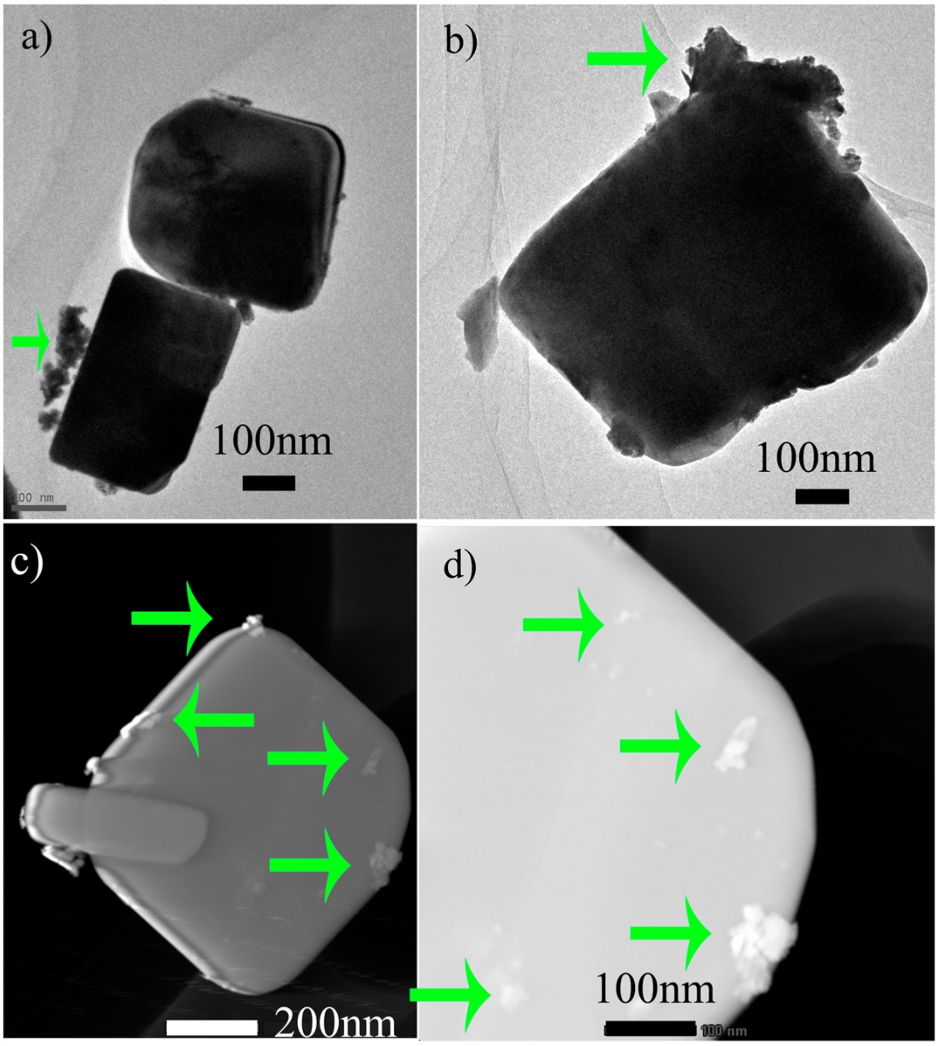

Figure S9 TEM and HAADF-STEM images of PTO nanoplates loaded with Pt NPs. Pt NPs tended to aggregate on the side or {001} facets of the nanoplates, leading to a size of several tens nanometers, as green arrows pointed.

Figure S9 shows the low magnification TEM images and HAADF-STEM images of the Pt loaded PTO nanoplates. Pt NPs tend to exist in aggregation on the {001} facets of the nanoplates, as green arrows refer to. It can scarcely be observed a single crystal on the surface of the nanoplate.

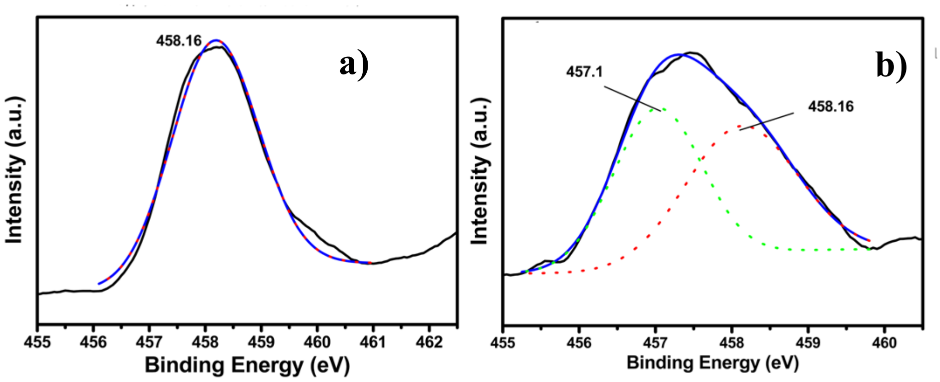

Figure S10 Ti2p XPS spectra measured for (a) Pt-PTO nanocrystal and (b) Pt-PTO nanoplate

References

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