

Electronic Supplementary Information

Sub-10-nm Au-Pt-Pd Alloy Trimetallic Nanoparticles with High Oxidation-Resistant Property as Efficient and Durable VOC Oxidation Catalyst

Experimental Section

Material Synthesis

EP-TiO₂. Mesoporous titania, EP-TiO₂, is synthesized following the reported procedure.¹ In a typical synthesis of EP-TiO₂ (1:9), 1 mmol of Ti(OC₄H₉)₄, 2.3 mL HOAc, 1 mL HCl and 9 mmol of mesoporous silica EP-FDU-12 were dissolved in 30 mL of ethanol. The mixture was stirred vigorously for 1 h and transferred into a Petri dish. The ethanol was evaporated at 40 °C. The Petri dish was then transferred into a 65 °C oven and aged for an additional 24 h. The as-synthesized products were annealed at 350 °C in air for 5 h (ramp rate 2 °C/min) to obtain mesoporous materials. The structural features of the as-prepared mesoporous materials are listed as follows: Cage diameter: 26.4 nm; Window size: 7.9 nm; Cell parameter: 44.4 nm; Pore volume: 0.70 cm³/g; BET surface area: 445 m²/g.

Photo-deposition method. Metal nanoparticles are supported onto EP-TiO₂ by a one-step photo-deposition method. Typically, for the AuPtPd sample (4 wt%) with molar ratio of Au:Pt:Pd=1:1:2 (denoted as Au₂₅Pt₂₅Pd₅₀/EP-TiO₂), 100 mg EP-TiO₂ and desired amount of HAuCl₄ (10 mM), H₂PtCl₄ (10 mM), PdCl₂ (20 mM) were dispersed in 10 mL methanol solution in a Pyrex glass reactor. The mixture was subjected to the UV light irradiation for 2 h using a high-pressure Xe lamp (300W) as the light source. Before the irradiation process,

gaseous Ar was bubbled through the mixture for 30 min to ensure that the solution has no dissolved O₂. During the photo-deposition process, the color of the mixture gradually changed, indicating the reduction of metal precursors. Then the powder was collected by centrifugation and washed twice by ethanol, and dried at room temperature (RT) in a vacuum oven. The products were annealed in air at different temperatures for 5 h (ramp rate 2 °C/min). The photo-deposition efficiency and chemical composition of the products were analyzed by inductively couple plasma atomic emission spectrometry (ICP-AES) and energy dispersive X-ray spectroscopy (EDS). In the preparation of AuPtPd TMNPs supported on commercial anatase nanocrystals (denoted as AuxPtyPd_z/anatase), commercial anatase (~ 50nm) and desired amount of metal precursors were co-added into the methanol solution, followed by the same photo-deposition and annealing procedure.

Im-AuPtPd/EP-TiO₂: Here “Im” represents using conventional wet impregnation method to prepare AuPtPd nanoparticles. In a typical synthesis of 1 wt% Im-Au₅₀Pt₂₅Pd₂₅/EP-TiO₂, 100 mg EP-TiO₂ and desired amount of metal precursors were co-added into the ethanol solution. After 2 h stirring, the adsorption equilibrium had been reached and excess ethanol was removed in a rotary evaporator until dryness. Then, the impregnates were dried at room temperature and annealed in air at 800 °C for 5 h (ramp rate 2 °C/min).

3nm AuNPs colloid: 3nm AuNPs are synthesized by reported method² with minor revision. In a typical synthesis, 100 mg AuPPh₃Cl was mixed with 400 μL of dodecanethiol in 20 mL of benzene to form a clear solution, to which 84 mg of NaBH₄ was then added in one portion. The mixture was heated with stirring at 55 °C for 7 h before the reaction system was cooled to room temperature. AuNPs were precipitated out from the reaction mixture as black solid

powders by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol. Finally, the precipitate was dried at room temperature and dissolved in chloroform as Au NPs colloid.

C-AuPtPd/EP-TiO₂: Here “C” represents using colloidal-photo deposition method to prepare AuPtPd nanoparticles. In a typical synthesis of 1 wt% C-Au₅₀Pt₂₅Pd₂₅/EP-TiO₂, 3 nm AuNPs colloid was first loaded into EP-TiO₂ as previously reported.³ Typically, desired amount of AuNPs colloid were dissolved in 25 mL of chloroform, and then 100 mg EP-TiO₂ was added. After 30 min stirring, the solid product was centrifuged and dried at room temperature. Then the product was annealed in air at 350 °C for 5 h to remove organics. Followed by the same photo-deposition process, Pt and Pd were simultaneously deposited on it. The products were annealed in air at 800 °C for 5 h (ramp rate 2 °C/min).

Characterization

Power X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultimate IV with CuK α radiation. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed on a Profile Spec ICP-AES spectrometer (Leeman, USA). XPS measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. HAADF-STEM and EDS measurements were proceeded on FEI TITAN Cs-corrected ChemiSTEM which equipped with an energy dispersive X-ray (EDX) spectroscope, operating at 200 kV. The sample was embedded in epoxy resin, and then microtomed into sub-100 nm ultra thinfilm at room temperature. These thin film samples floated on water or other solvents were collected by copper mesh with polymer microgrid for HAADF-STEM imaging and elemental mapping.

Catalytic combustion of *n*-hexane.

Catalyst activity for *n*-hexane combustion was determined using a fixed bed laboratory micro reactor. In order to avoid intra-reactor gradients, the catalyst powder (40 mg) was diluted in 160 mg of quartz sand. Mass flow controllers were used to prepare the reactant feed composed by 1000 ppm of *n*-hexane in air. A total flow rate of 200 mL/min was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 10,000 h⁻¹

for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the range 140 ~ 400 °C and temperatures were measured by a thermocouple placed within the catalyst bed. Once the reaction temperature was attained, the catalyst was allowed to stabilize for 20 min before data were collected. Three consistent measurements were taken at each reaction temperature and then the reaction temperature increased. Conversion data were calculated by the difference between inlet and outlet concentrations. The products are CO₂ and H₂O, and the selectivity towards CO₂ was 99.9%. Experimental errors on conversion were 100% ± 2% and all carbon balances were in the range 100% ± 5%.

References

1. S. Xu, Y. Hong, C. Chen, S. Li, L. Xiao and J. Fan, *Journal of Materials Chemistry A*, 2013, **1**, 6191-6198.
2. N. Zheng, J. Fan and G. D. Stucky, *Journal of the American Chemical Society*, 2006, **128**, 6550-6551.
3. N. Zheng and G. D. Stucky, *Journal of the American Chemical Society*, 2006, **128**, 14278-14280.

Table S1 The photo-deposition efficiency and actual chemical composition of different samples.

samples	nominal total metal loading (wt%) ^a	actual total metal loading (wt%) ^b	actual composition (molar ratio) ^b
Au/EP-TiO ₂	4.0	4.0	/
Pt/EP-TiO ₂	4.0	3.8	/
Pd/EP-TiO ₂	4.0	3.6	/
Au ₅₀ Pt ₅₀ /EP-TiO ₂	4.0	3.6	Au ₄₅ Pt ₅₅
Au ₃₃ Pd ₆₇ /EP-TiO ₂	4.0	3.7	Au ₃₈ Pd ₆₂
Pt ₃₃ Pd ₆₇ /EP-TiO ₂	4.0	3.5	Pt ₃₇ Pd ₆₃
Au ₂₅ Pt ₂₅ Pd ₅₀ /EP-TiO ₂	4.0	3.6	Au ₂₃ Pt ₂₉ Pd ₄₈
Au ₅₀ Pt ₂₅ Pd ₂₅ /EP-TiO ₂	1.0	1.0	Au ₄₈ Pt ₂₅ Pd ₂₇

^a Determined by loading amount of metal precursors. ^b Determined by ICP-AES analysis.

The ICP-AES results show high photo-deposition efficiency, and the actual composition of various samples is in agreement with nominal composition. The current synthetic system is flexible with the tunable metal loading and composition of multi-metallic nanoparticles. In this paper we use nominal composition to represent samples for convenience.

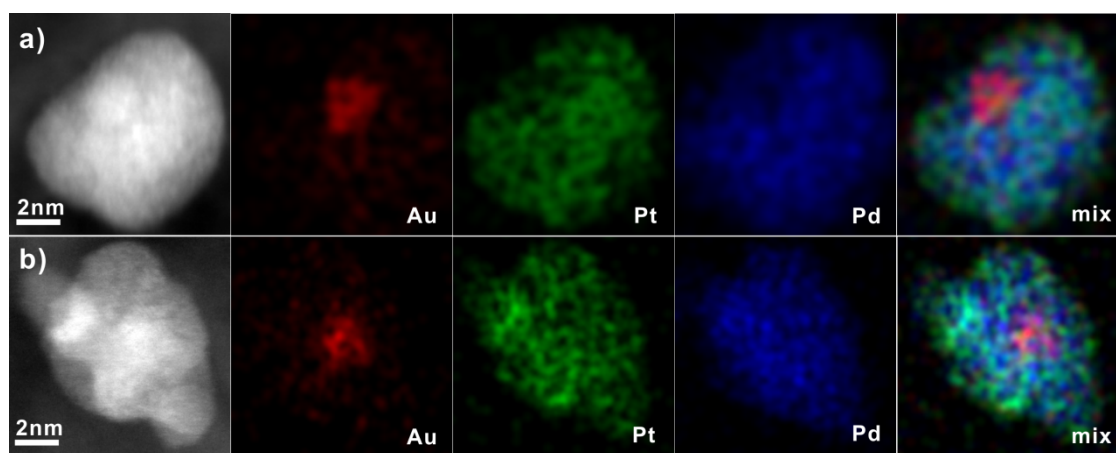


Figure S1. HAADF-STEM images and corresponding EDS mappings of several individual $\text{Au}_{25}\text{Pt}_{25}\text{Pd}_{50}/\text{EP-TiO}_2$ nanoparticles after the photo-deposition. The average chemical composition of several individual nanoparticles determined by EDS analysis is $\text{Au}_{22}\text{Pt}_{27}\text{Pd}_{51}$, agreeing with the nominal composition and ICP result (Table S1).

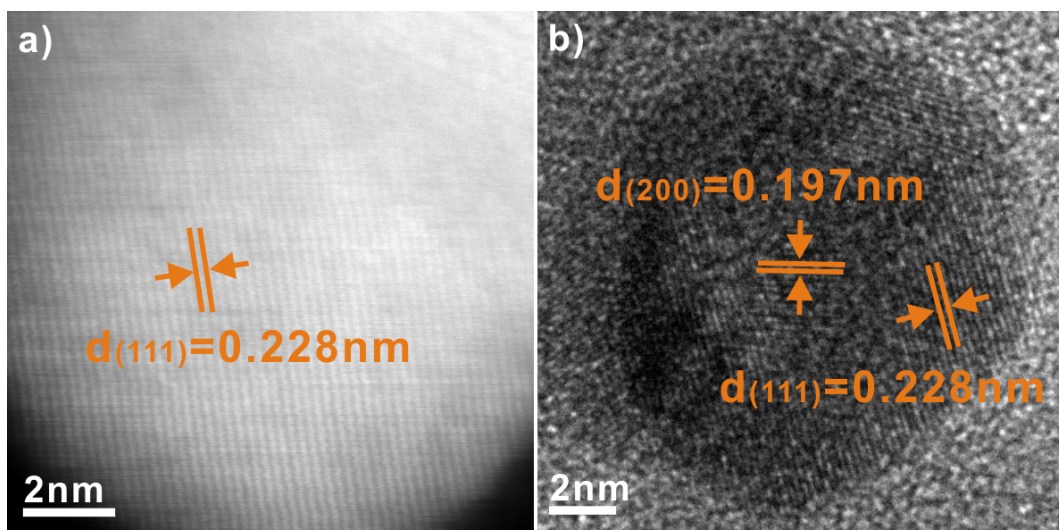


Figure S2. Typical HAADF-STEM and HR-TEM images of $\text{Au}_{25}\text{Pt}_{25}\text{Pd}_{50}/\text{EP-TiO}_2$ annealed at 800 °C.

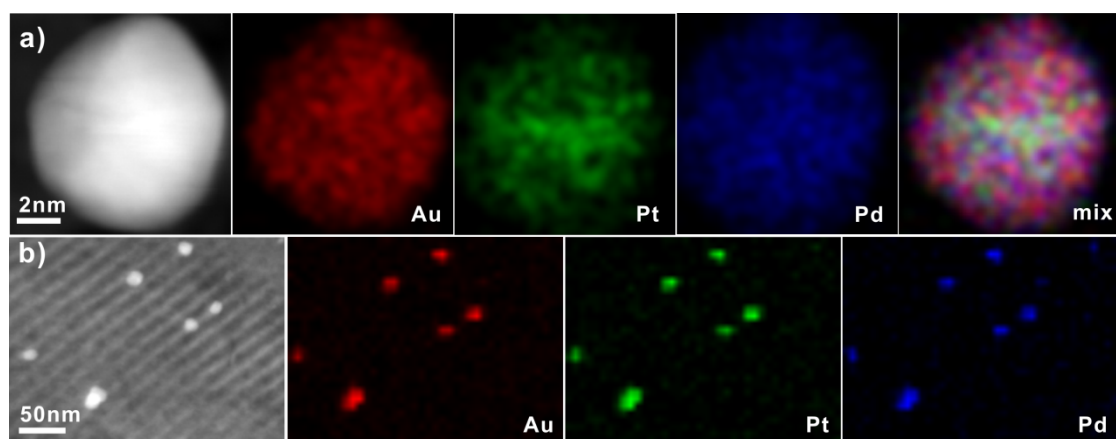


Figure S3. HAADF-STEM images and corresponding EDS mappings of a) an individual nanoparticle and b) a broad area for $\text{Au}_{25}\text{Pt}_{25}\text{Pd}_{50}/\text{EP-TiO}_2$ after annealing at 800 °C. The average chemical composition of several individual nanoparticles determined by EDS analysis is $\text{Au}_{28}\text{Pt}_{27}\text{Pd}_{45}$, close to the nominal composition and actual composition determined by ICP (Table S1).

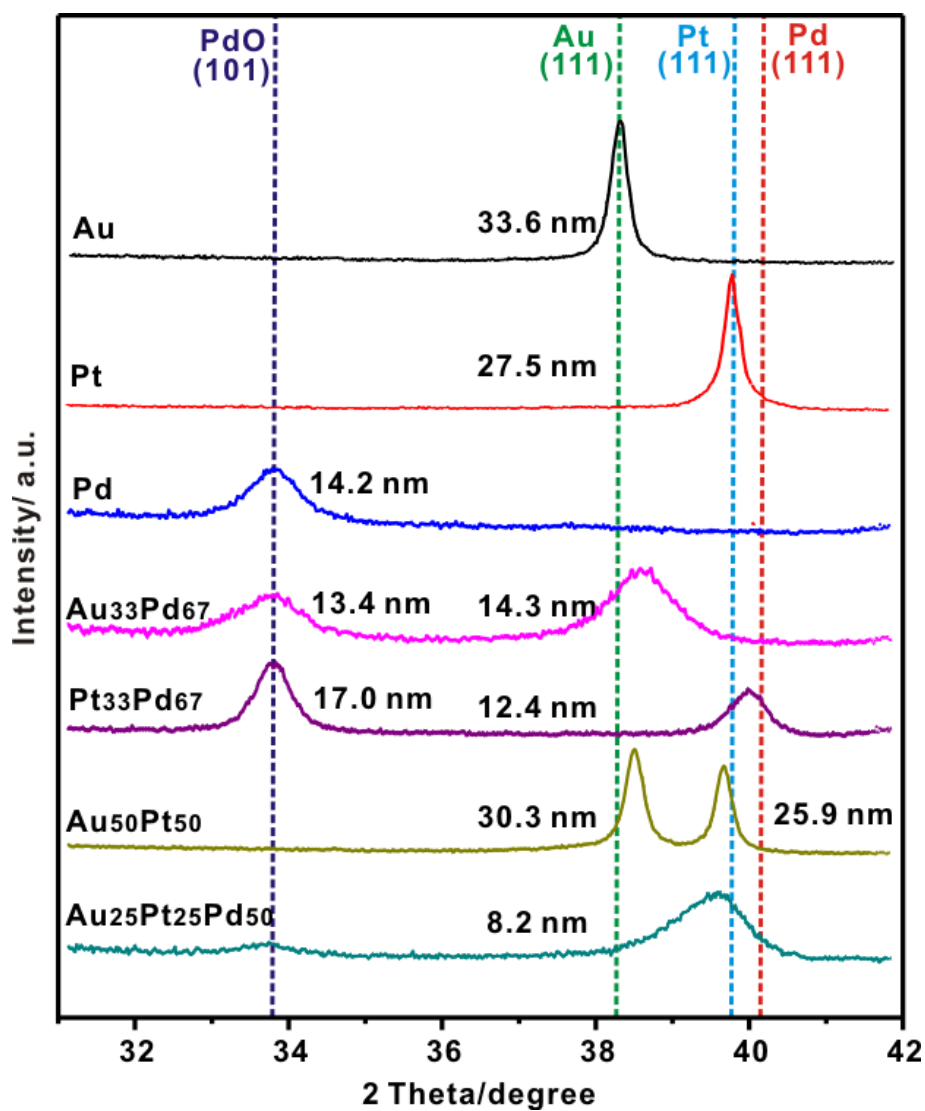


Figure S4. XRD patterns of monometallic and bimetallic nanoparticles supported EP-TiO₂ annealed at 800 °C. The metal loading concentration is fixed at 4 wt%. For comparison, XRD patterns of pure Au, Pt, Pd and PdO from the JCPDS are presented. The average particle size is calculated by the Debye-Scherrer equation based on the (111) or (101) plane reflection. The monometallic and bimetallic nanoparticles grew sharply after 800 °C annealing.

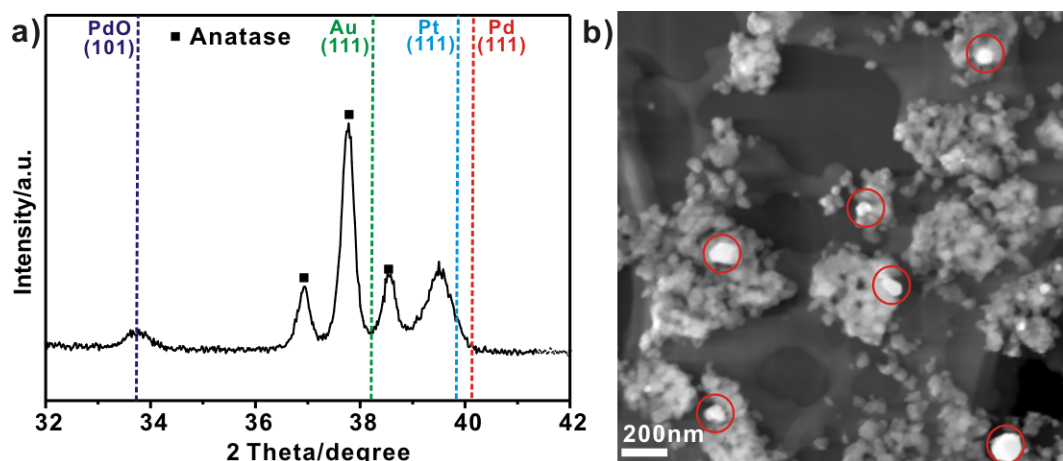


Figure S5. a) XRD pattern and b) HAADF-STEM image of $\text{Au}_{25}\text{Pt}_{25}\text{Pd}_{50}/\text{anatase}$ annealed at 800 °C. For comparison, XRD patterns of pure Au, Pt, Pd, PdO and anatase from the JCPDS are presented. By the Debye-Scherrer equation, the average particle size of AuPtPd TMNPs supported on commercial anatase is 20.6 nm, in line with HAADF-STEM analysis.

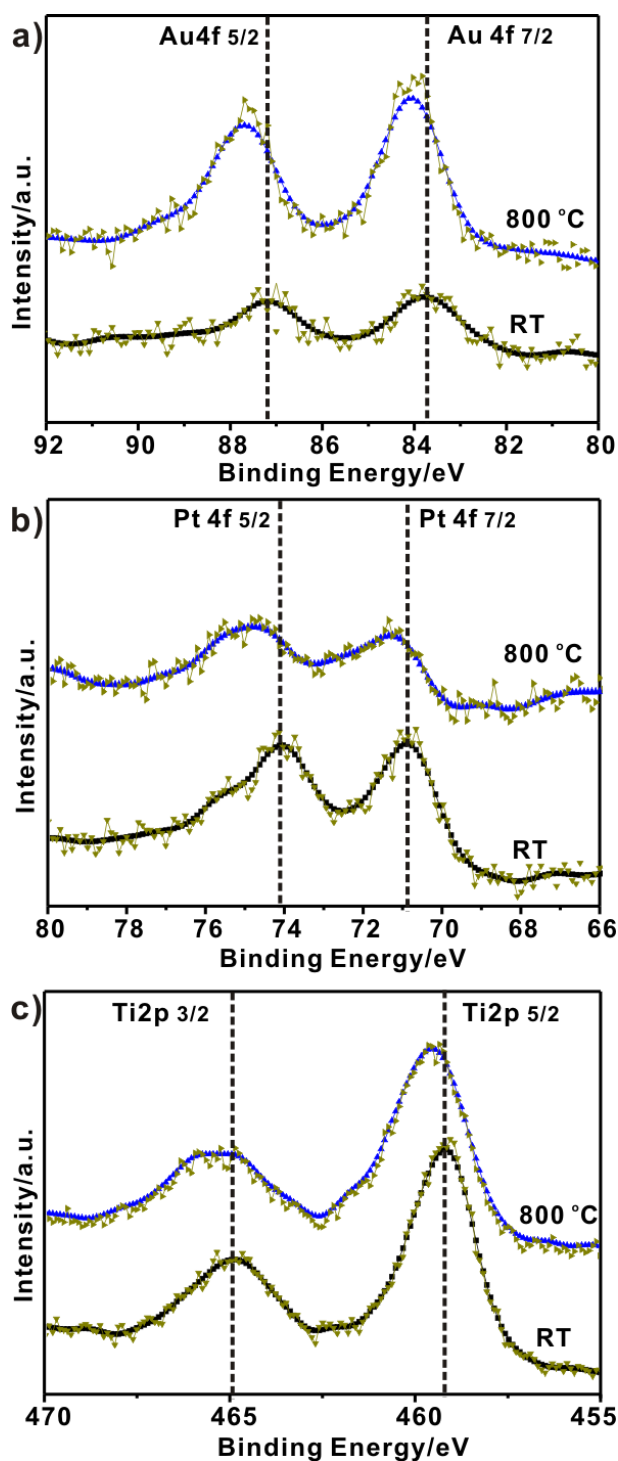


Figure S6. Normalized XPS spectra of a) Au 4f, b) Pt 4f and c) Ti 2p peaks for $\text{Au}_{25}\text{Pt}_{25}\text{Pd}_{50}/\text{EP-TiO}_2$ after the photo-deposition (RT) and after annealing at 800 °C. In Figure 2b, Pd 3d peaks exhibit two chemical states of Pd, both metallic (Pd^0) and oxidized (PdO). The overlapping of Au 4d_{5/2} peak with Pd 3d_{5/2} peak has been also normalized (the green line), taking into consideration the energy and intensity of Au 4d peaks of $\text{Au}/\text{EP-TiO}_2$. After annealing at 800 °C, the binding energy of Ti 2p, Au 4f and Pt 4f shift to the higher values, implying that there exist strong electronic interactions between Au, Pt, Ti and Pd.

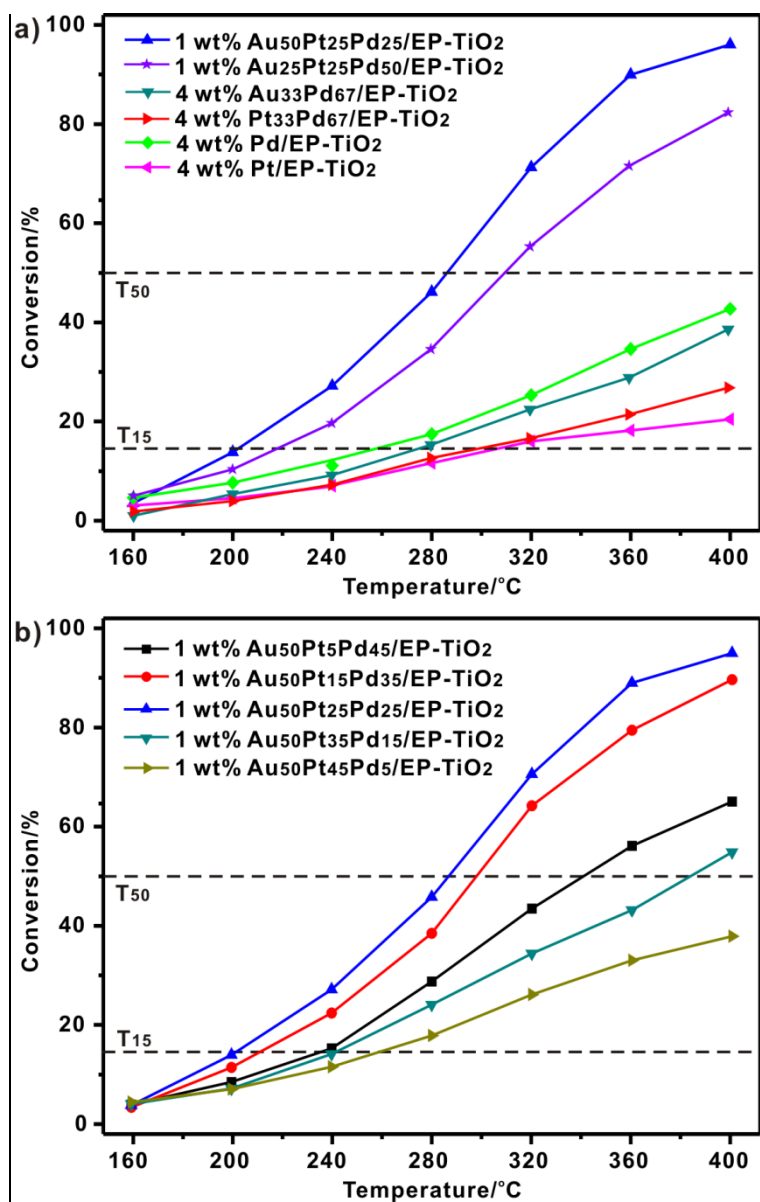


Figure S7. Catalytic activity of the supported metal nanoparticle catalysts annealed at 800 °C for the *n*-hexane combustion: conversion versus temperature for the oxidation of 1000 ppm *n*-hexane in air.

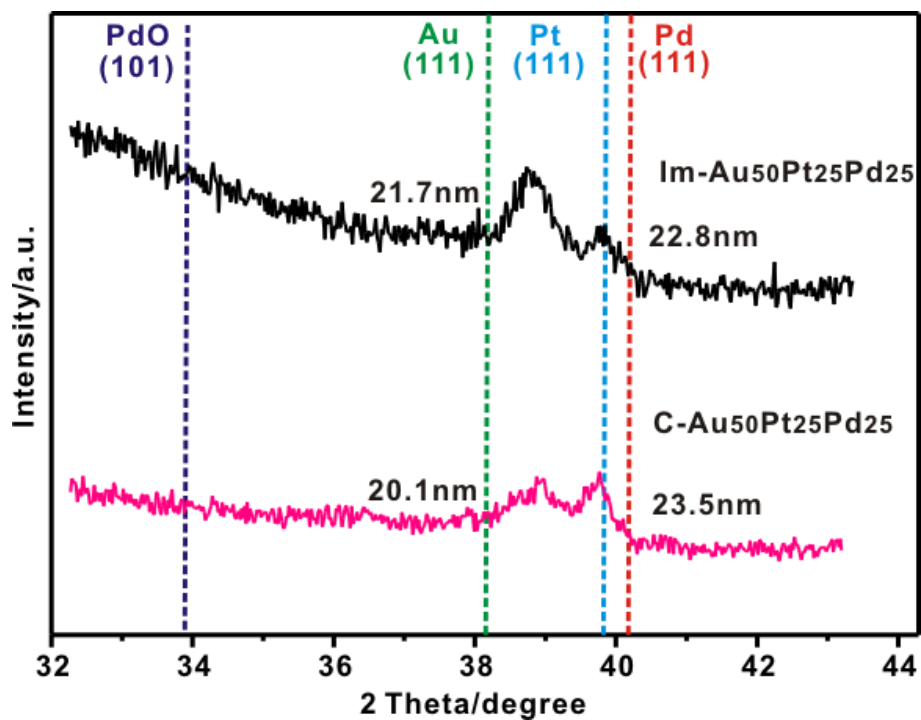


Figure S8. XRD patterns of 1 wt% Im-Au₅₀Pt₂₅Pd₂₅/EP-TiO₂ and C-Au₅₀Pt₂₅Pd₂₅/EP-TiO₂ annealed at 800 °C. For comparison, XRD patterns of pure Au, Pt, Pd and PdO from the JCPDS are presented. The average particle size is calculated by the Debye-Scherrer equation based on the (111) plane of samples. The results show that large nanoparticles (> 20 nm) are obtained after annealing.