Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information For

Superior Anti-CO Poisoning Capability: Au-decorated PtFe Nanocatalysts for High-performance Methanol Oxidation

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Experimental Section:

Chemicals and Instruments: $Pt(acac)_2$ (Pt≥48.0%), $Fe(acac)_2$ (≥98.5%) were obtained from Alfa Aesar, and other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC). All the reagents were of analytical grade and were used without further purification. The morphologies and sizes of as-synthesized samples were characterized by TEM (FEI G^2 20) and HRTEM (JEOL, JEM-2100, 200 kV). Scanning transmission electron microscopy measurements and energy dispersive X-ray spectroscopy mappings were performed with a 200 kV JEM 2010F microscope. XPS measurements were carried out with a PHI Quantera II XPS Scanning Microprobe. XRD patterns were collected on Shimadzu XRD-6000 with Cu Ka radiation (40 kV, 30 mA, λ=1.5418 Å), recorded with 2θ ranging from 30° to 90°. Elemental analysis was investigated by ICP-OES (Thermo Scientific iCAP 6300).

Synthesis of PtFe and PtFeAu Nanocrystals: In a typical synthesis, 10 mg of $Pt(acac)_2$ (acac=acetylacetonate), 6.4 mg of $Fe(acac)_2$, 26.8 mg of L-ascorbic acid, 170 mg KI and 80 mg PVP (K30) were added into the solution with 4 mL DMF and 1 mL deionized water. After vigorous stirring for 30 min, the mixture was transferred to a 10 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 4 h and then cooled to room temperature. The black precipitate was washed with ethanol and deionized water for several times and dispersed in ethanol for use. For PtFeAu nanocrystals, after treating with NaOH solution (1 M) to remove any remaining ascorbic acid molecules and by products, 2.5 mg of the as-prepared PtFe nanocrystals were dispersed in 10 mL deionized water under a nitrogen atmosphere, then an aqueous solution of $HAuCl_4$ (10 mL, 0.2 mM) was dropwisely added. The resulting solution was stirred and kept at 0 °C for 30 min. The black precipitate was collected by centrifugation and washed with a large amount of ethanol for several times. The obtained-products were redispersed in ethanol for further use. For PtAu nanocrystals, 13 mg of $H_2PtCl_6 \cdot 6H_2O$, 10 mg of $HAuCl_4 \cdot 4H_2O$, 38.6 mg of sodium borohydride and 80 mg PVP (K30) were added into 5 mL deionized water. After vigorous stirring for 10 min, the black precipitate was washed with ethanol and deionized water for several times and dispersed in ethanol for use.

Electrochemical Measurements: The electrochemical activities of the as-prepared PtFe, PtAu and PtFeAu nanocrystals and commercial Pt/C (40 wt.% Pt, Alfa) catalysts were characterized by cyclic voltammetry and chronoamperometry techniques. All experiments were performed in a standard three-electrode electrochemical cell with Pt foil (1 cm^2) and saturated calomel electrode (SCE) was used as counter electrode and reference electrode at room temperature (~20 °C) using a CHI 660D electrochemical workstation. For preparation of the electrochemical testing sample, PtFe, PtAu and PtFeAu catalysts were respectively mixed with carbon (Vulcan XC-72) with a mass ratio of 2 : 3 and then dissolved in ethanol with a concentration of about 0.5 mg Pt/mL. For Pt/C catalyst, the catalysts were dissolved in ethanol to make a solution with a concentration of about 0.5 mg Pt/mL. The two catalyst suspensions were pipetted onto the glassy carbon surface to make a Pt loading of about 7.8 ug. CV curves of Pt/C, PtFe, PtAu and PtFeAu catalysts were tested in 0.5 M H_2SO_4 with a scan rate of 20 $mV\cdot s^{-1}$. Methanol oxidation experiments were carried out in a solution containing 0.5 M H_2SO_4 and 1.0 M CH_3OH with a scan rate of 50 $mV\cdot s^{-1}$. The working electrode was subjected to CV treatment in 0.5 M H_2SO_4 to reach a stable state, and then fuel oxidation tests were performed. CA curves were recorded at 0.65 V (vs. SCE) in a solution containing 0.5 M H_2SO_4 and 1.0 M CH_3OH. The CO stripping experiments were conducted in 0.5 M H_2SO_4. The potential was first held at -0.16 V (vs. SCE) for 10 min in CO-saturated solutions in order to allow sufficient CO adsorption onto the surface of catalysts. Subsequently, the solution was deaerated with N_2 for 10 min to remove freely dissolved CO molecules. The accelerated durability test was carried out in 0.5 M H_2SO_4 by applying linear potential sweeps between -0.2 and 1.0 V (vs. SCE) for 1000 cycles at 50 $mV\cdot s^{-1}$.

Calculation Methods: For all calculations, the First-Principles DFT was chosen with the Vienna ab initio simulation package. The projector augmented wave pseudopotentials method for describing electron-ion interactions and Perdew-Burke-Ernzerh of exchange-correlation functional were employed. A full optimization of all atom positions in the bulk Pt was performed via the action of a conjugate gradient optimization procedure. The cutoff energy was set to 400 eV. The Brillouin zone integrations were performed using a 7×7×7 Monkhorst-Pack grids for the bulk. A spin-unrestricted approach was adopted. For solving the self-consistent field convergence of Kohn-Sham equations, the energy change convergence criterion was 1×10^{-5} eV between two successive iterations. The slab PtFe (111), PtFeAu(111) and Pt model included 6 Pt layers in a (2×2×1) supercell, and was separated by approximately 16 Å of vacuum. The k-point sampling consists of 5×5×1 Monkhorst-Pack points. During structure relaxation, both the adsorbents the top four Pt, PtFe or PtFeAu layers in the structure of the (111) surfaces were relaxed. The rest four below layers were kept frozen at their positions.

Figures:

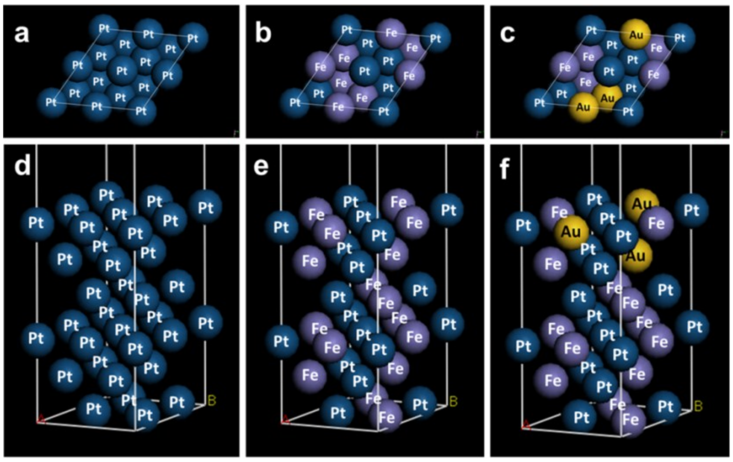

Figure S1. The top-view model of (a) Pt (111), (b) PtFe (111) and (c) PtFeAu (111); The model of the contour of (d) Pt (111), (e) PtFe (111) and (f) PtFeAu (111).

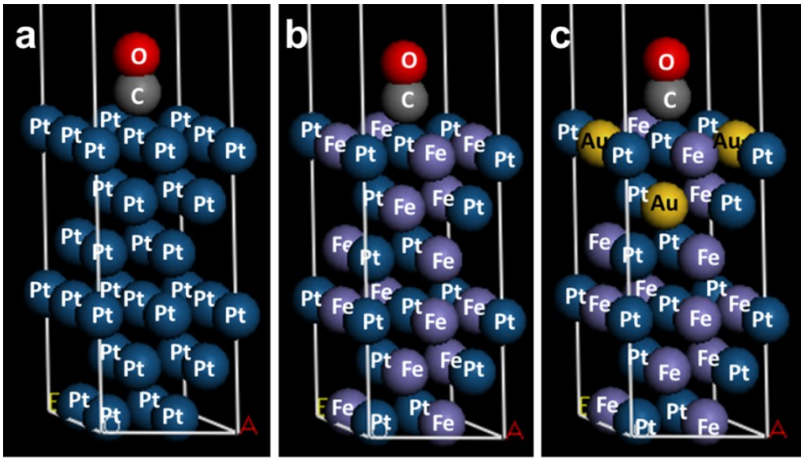

Figure S2. The model of adsorption of CO on top-site of (a) Pt (111), (b) PtFe (111) and (c) PtFeAu (111).

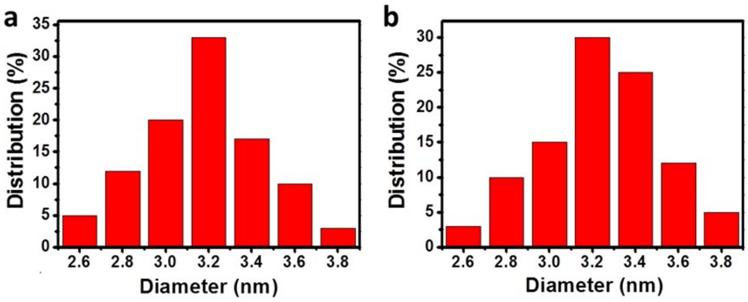

Figure S3. Size distributions of as-synthesized (a) PtFe and (b) PtFeAu nanocrystals, these statistical data were obtained by randomly measuring the size of at least 100 nanocrystals.

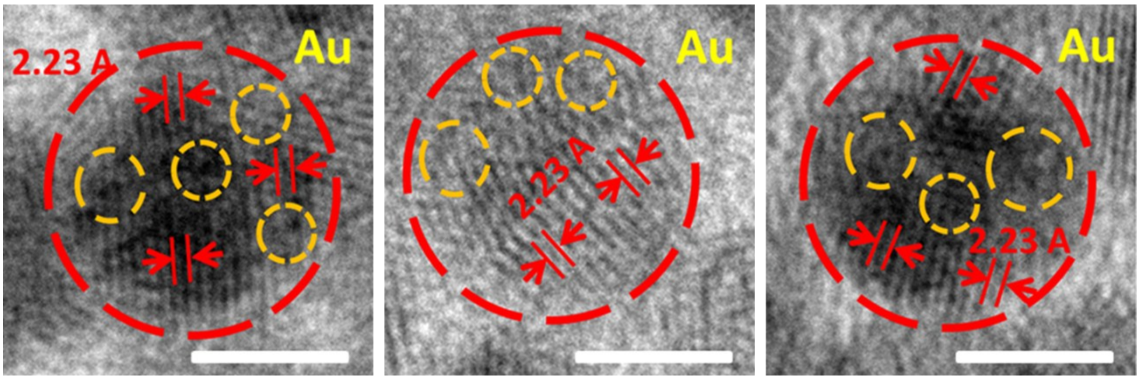

Figure S4. HRTEM images of surface Au-decorated PtFe nanocrystals, scale bar: 2 nm, the discontinuous lattice structures of PtFe strongly evidence the introduction of Au atoms.

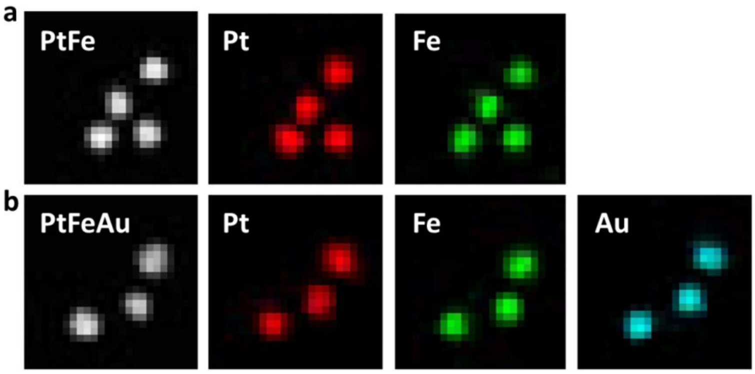

Figure S5. HAADF-STEM images and EDS elemental mapping images of (a) PtFe and (b) PtFeAu nanocrystals.

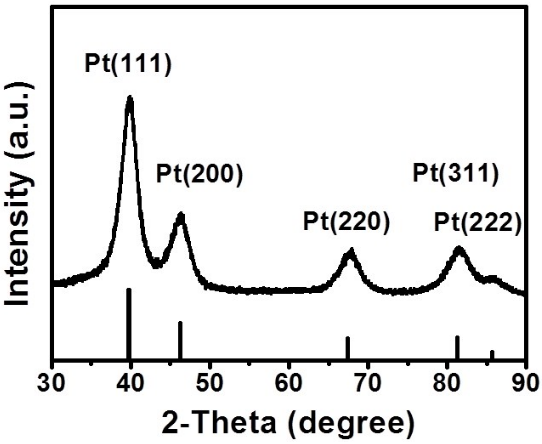

Figure S6. XRD pattern of the commercial Pt/C electrocatalysts.

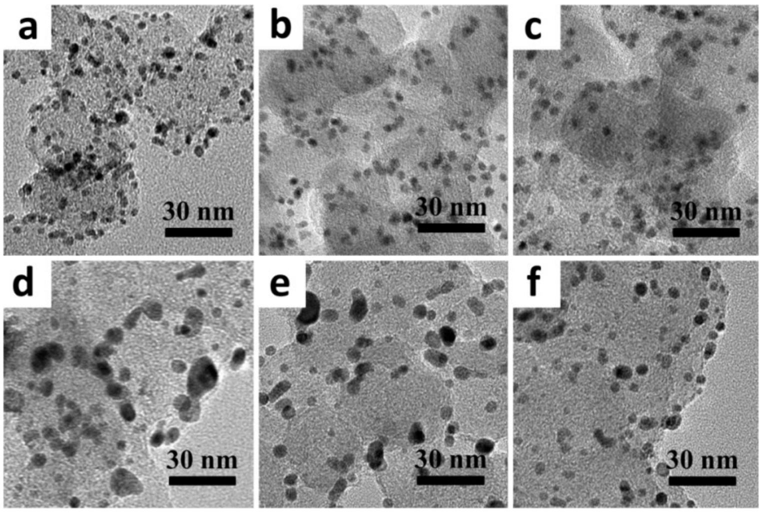

Figure S7. TEM images of (a) Pt/C, (b) PtFe/C, (c) PtFeAu/C before accelerated durability test and TEM images of (d) Pt/C, (e) PtFe/C, (f) PtFeAu/C after accelerated durability test.

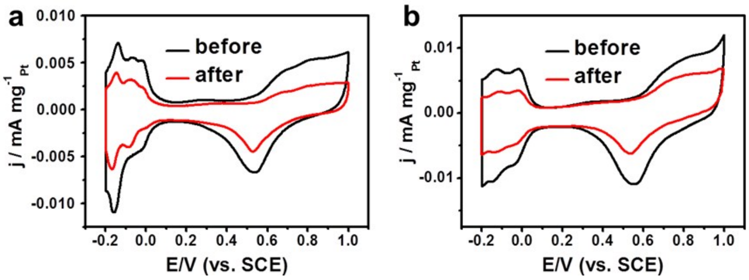

Figure S8. Cyclic voltammograms of (a) Pt/C and (b) PtFe nanocrystals before and after accelerated durability test.

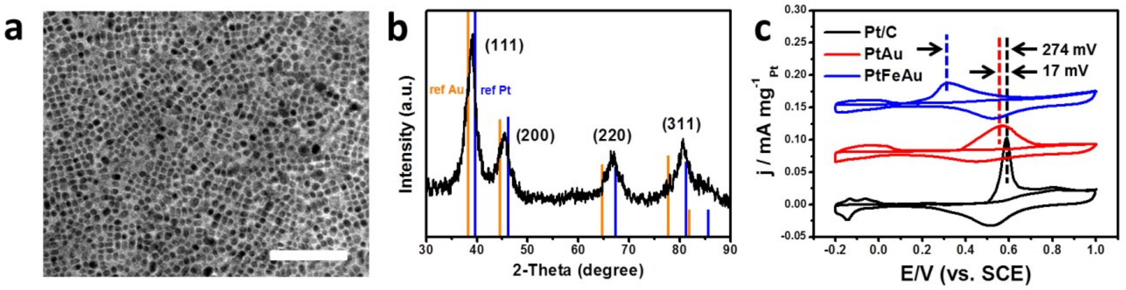

Figure S9. (a) and (b) TEM image and XRD pattern of as-prepared PtAu nanocrystals, scale bar: 40 nm; (c) CO stripping curves of Pt/C, PtAu and PtFeAu nanocatalysts.