Electronic Supplementary Information

One-Pot Synthesis of Heterostructured Pt-Ru Nanocrystals for Catalytic Formic Acid Oxidation

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Experimental Section

Chemicals. Ruthenium(Ⅲ) 2,4-pentanedionate (Alfa Aesar), platinum(Ⅱ)2,4-pentanedionate (Alfa Aesar, Pt content: 49.6 wt%), oleylamine (approximate C18-content 80-90%, ACROS), and oleic acid (A.R,Guangfu reagent in Tianjing), tungsten hexacarbonyl (99%, ACROS), toluene（A.R, Beijing chemical reagent）, Nafion solution (5 wt%, Alfa Aesar), perchloric acid ($HClO_4$, A.R. grade, Tianjin Chemical Reagent) and formic acid (HCOOH, A.R. grade, Beijing Chemical Reagent). All chemicals were used as received without further purification. Water was supplied by a Water Purifier Nanopure water system (18.3 MΩ cm).

Synthesis of Heterostructured Pt-Ru nanocrystals. The PtRu nanocrystals were synthesized according to the modified procedure described by Zhang et al.[13] Briefly, 0.020 g ruthenium(III) 2,4-pentanedionate, 0.020 g platinum(Ⅱ)2,4-pentanedionate, 12.0 ml oleyamine, 3.0 ml oleic acid were loaded into a three-neck flask equipped with a reflux condenser and attached to a Schlenk line. The mixture was heated to 130 °C with vigorous stirring under an argon stream in 12 min. After 2 min, 0.50 g tungsten hexacarbonyl was added into the solution. The temperature was then subsequently raised to 240 °C at a rate of approximately 7.5 $°C\ min^{-1}$ and kept for about 50 min with vigorous agitation. After the solution was cooled to the room temperature, the resultant products were obtained by centrifugation and washed with toluene for 3 times. Finally the products were redispersed in toluene for further use.

Characterization. The size and the aggregation status of the PtRu nanocrystals were examined by using Hitachi H-600 transmission electron microscopy (TEM) operated at 100 kV. UV-vis spectra were recorded on a VARIAN CARY 50 UV-vis spectrophotometer. High-resolution TEM (HRTEM) images and the corresponding Live Fast Fourier-transform (FFT), High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, element analysis mapping and EDX were carried out on a JEM-2010(HR) microscope operated at 200 kV. Powder x-ray diffraction (XRD) was performed on a PW1700 Powder Diffractometer using Cu-Kα radiation with a Ni filter (λ = 0.154059 nm at 30 kV and 15 mA).

Electrochemistry. Prior to the deposition of the PtRu nanocrystals onto an electrode surface for electrocatalytic assessment, a glassy carbon (GC) electrode (3.0 mm in diameter) was polished with alumina slurries (0.05 μm) and cleansed by sonication in 0.1 M HNO_3, H_2SO_4 and pure water for 10 min successively. 1 mg of the dried PtRu nanocrystals was dispersed ultrasonically in 0.7 ml pure toluene and 60 μl 5 wt% Nafion solution. After the ink formed homogeneously, 10 μl of the catalyst ink was then dropped on the clean GC electrode with a micropipette and then dried in vacuum at room temperature. The electrode was treated with Plasma cleaner (PDC-32G, Harrick Plasma, US) to remove the protecting ligands. The prepared electrode was denoted as PtRu/GC.

Voltammetric measurements were carried out with a CHI 750D electrochemical workstation. The PtRu/GC electrode prepared above was used as the working electrode. A Ag/AgCl (in 3 M NaCl, aq.) and a Pt coil were used as the reference and counter electrodes, respectively. All electrode potentials in the present study were referred to this Ag/AgCl reference. The impedance spectra were recorded between 100 kHz and 10 mHz with the amplitude (rms value) of the ac signal 10 mV. The solutions were deaerated by bubbling ultra-high-purity N_2 for 20 min and protected with a nitrogen atmosphere during the entire experimental procedure. All electrochemical experiments were carried out at room temperature.

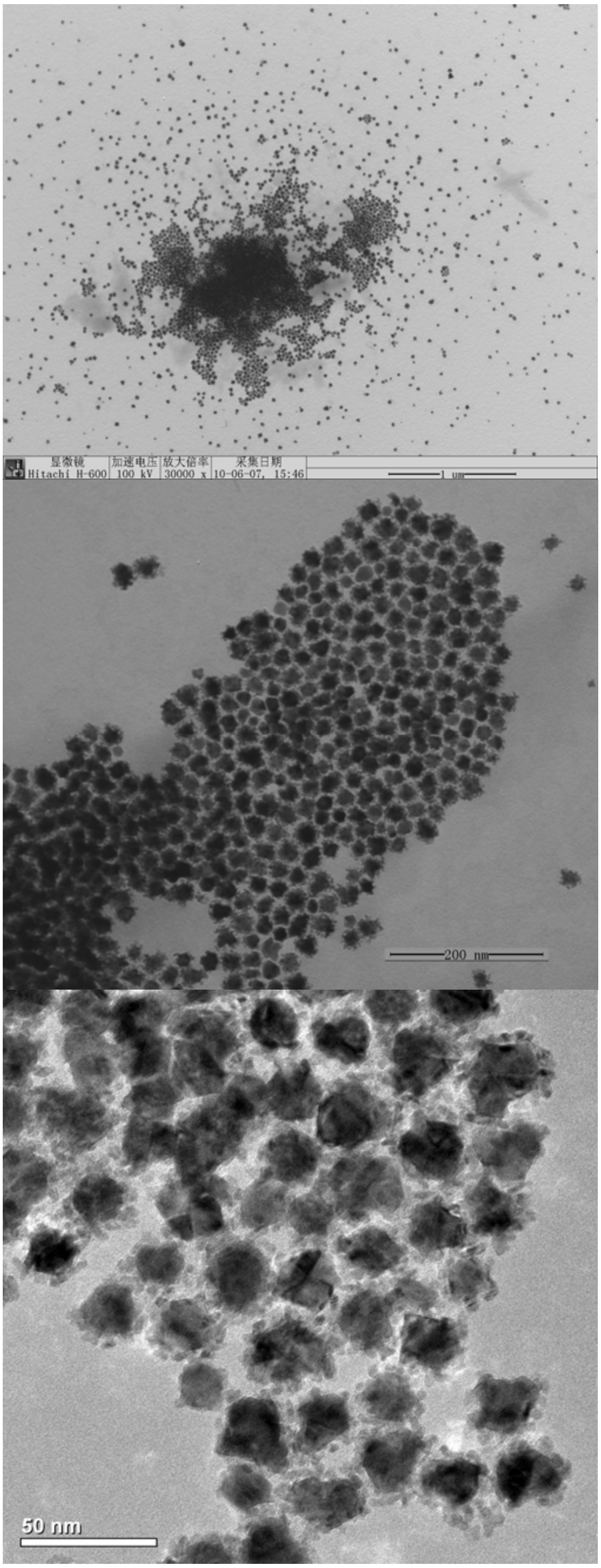

Fig. S1 Transmission electron micrograph (TEM) of the synthesized PtRu nanocrystals at different magnifications.

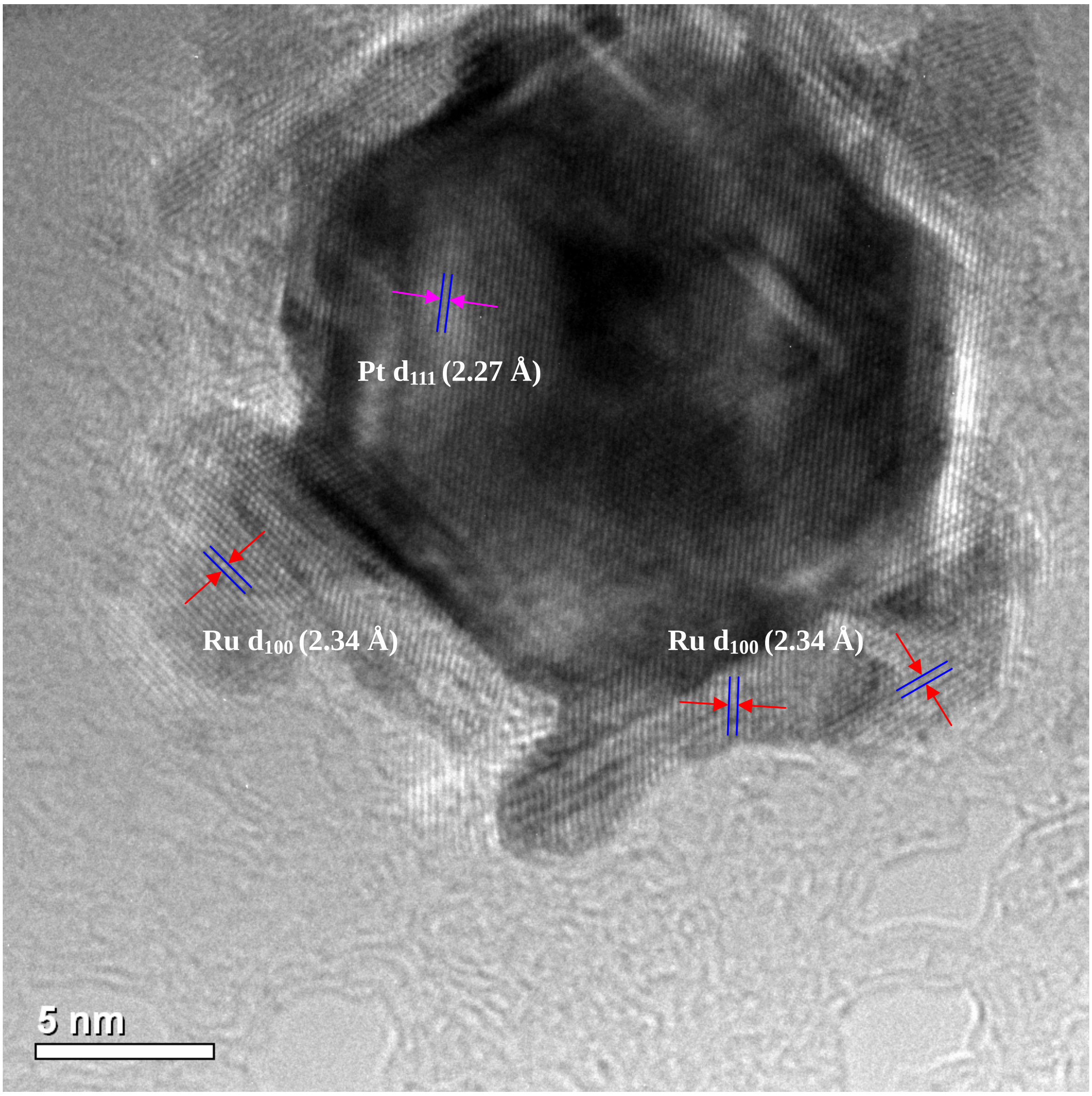

Fig. S2 High resolution transmission electron micrograph (HRTEM) of the synthesized PtRu nanocrystals.

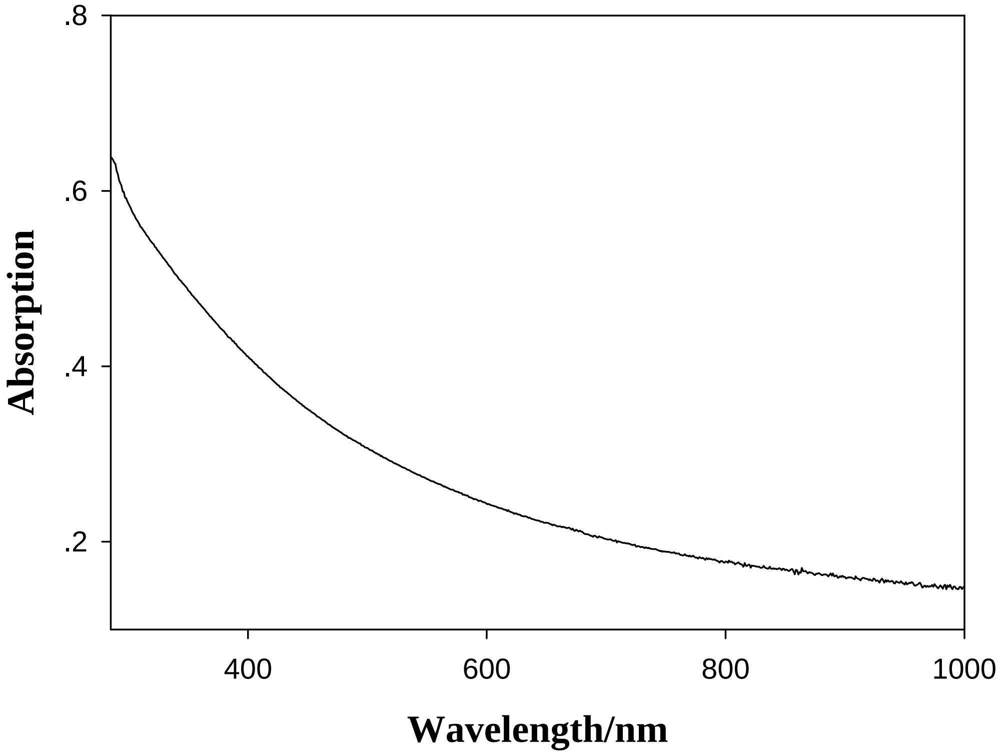

Fig. S3 UV-Visible absorption spectrum of the synthesized PtRu nanocrystals. Particle concentration is 0.1 mg/ml in toluene.

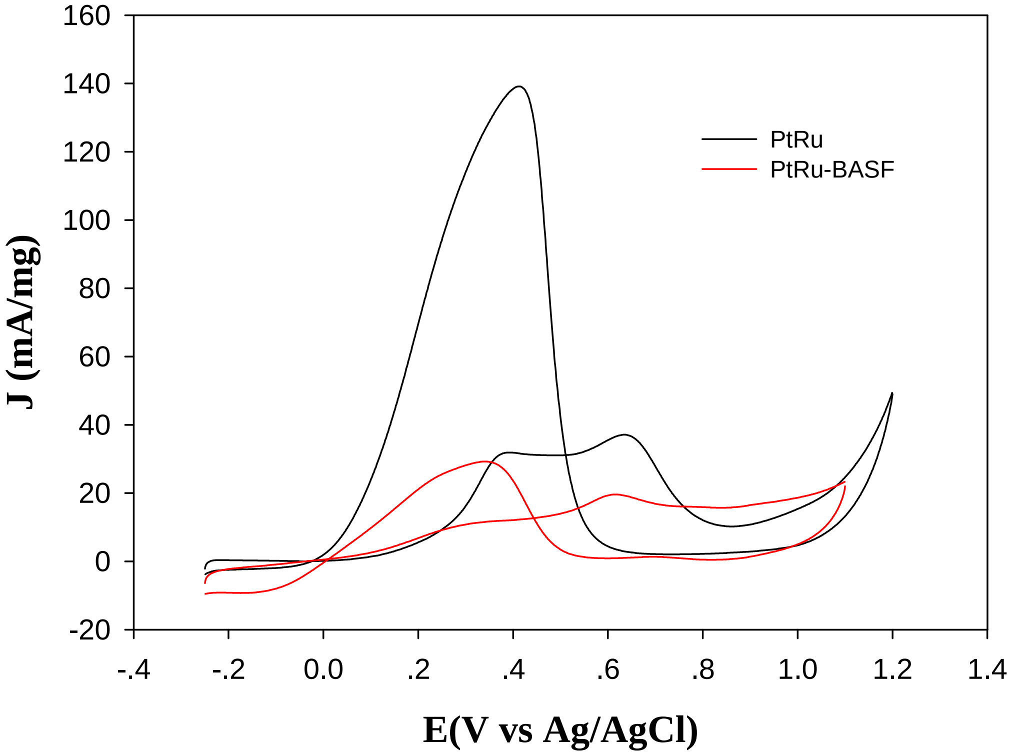

Fig. S4 Cyclic voltammograms (mass activity) of the PtRu/GC and PtRu(BASF)/GC electrodes in 0.1 M $HClO_4$ + 0.5 M HCOOH solution. Potential scan rate 0.1 V/s.

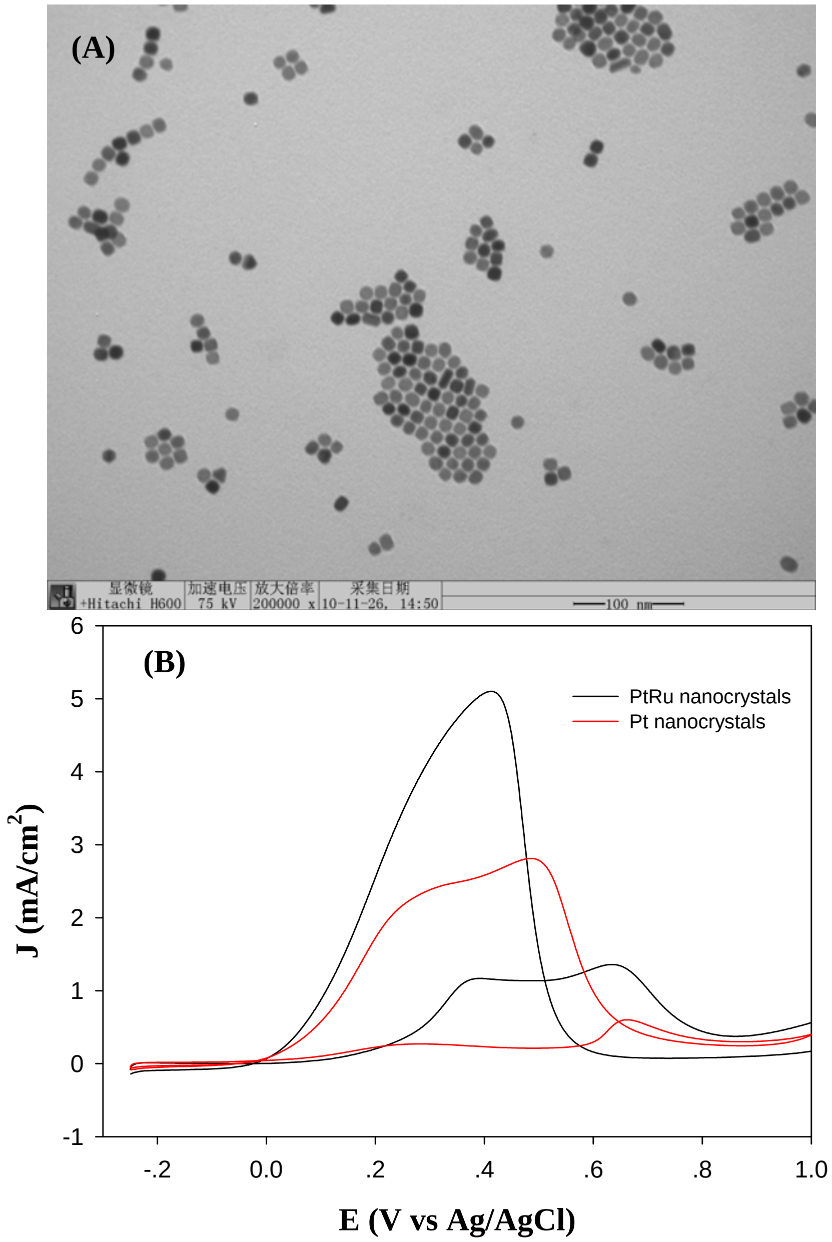

Fig.S5 (A) TEM image of Pt nanocrystals; (B) CVs of the PtRu/GC and Pt/GC electrodes in 0.1 M $HClO_4$ + 0.5 M HCOOH solution. Scan rate 0.1 V/s.

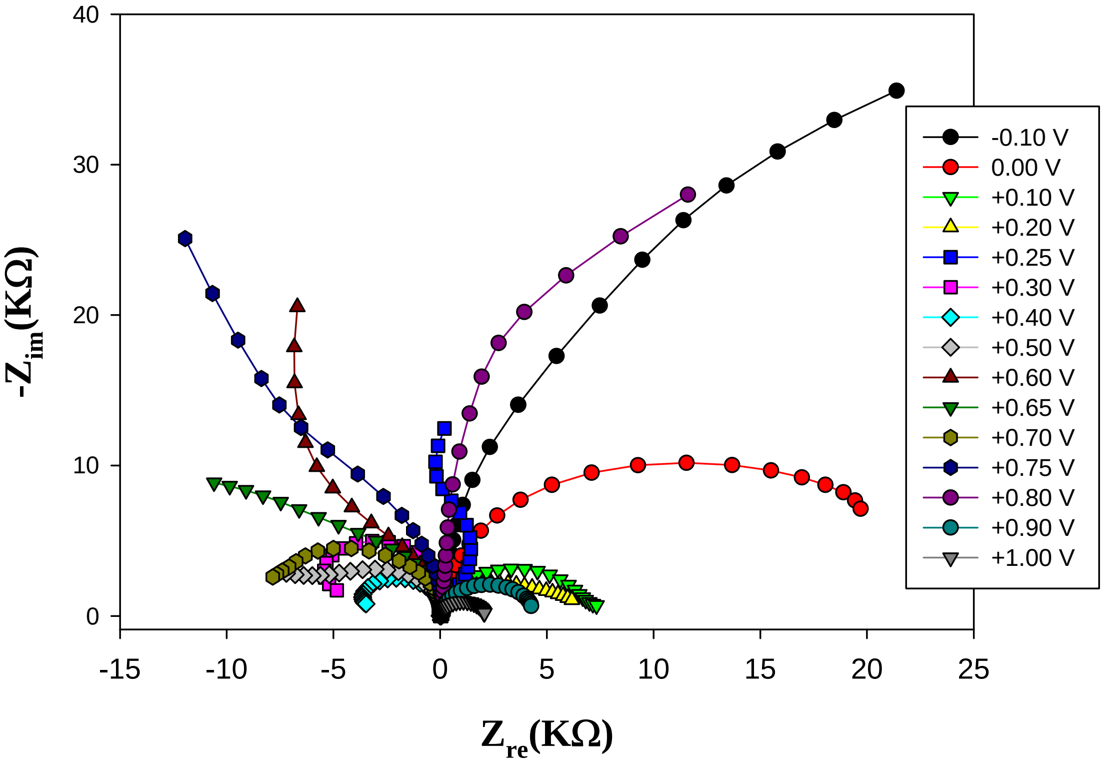

Fig. S6 Complex-plane (Nyquist) impedance plots of the formic acid oxidation on PtRu core-shell nanocrystals in 0.1 M $HClO_4$ + 0.5 M HCOOH at various electrode potentials, which are given in the figure legends.

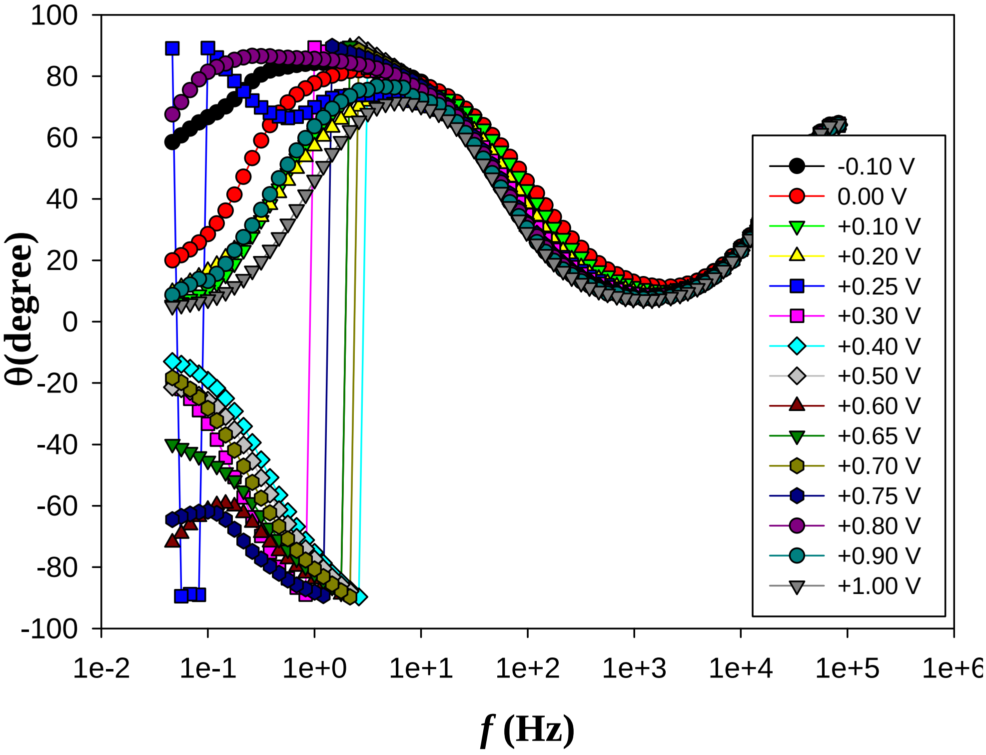

Fig. S7 Complex-plane (Bode) impedance plots of the formic acid oxidation on PtRu core-shell nanocrystals in 0.1 M $HClO_4$ + 0.5 M HCOOH at various electrode potentials, which are given in the figure legends.