Electronic Supplementary Material (ESI) for Chemical Communications

Posioning effect diminished on novel PdHoOx/C catalyst for the electrooxidation of formic acid

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Experimental Section

Preparation of HoOx/C hybrid support: A proper amount of Ho_2O_3 was initially dissolved in 10 mL of concentrated HNO_3 and diluted in 50 mL of distilled water and ethanol (1:1 in volume ratio). Next, a given amount of Vulcan XC-72 carbon was added into the above solution; the solution was sonicated for an hour and kept at room temperature (20 ºC) under vigorous agitation for 2 hours. After stirring, 0.5 M Na_2CO_3 and 2 M NaOH solution was added into the mixture to form precipitates. Subsequently, the suspension was stirred over night and finally filtered and the solid was transferred to a tubular oven at 550 ºC for 3 hours to obtain stable HoOx/C support under the protection of nitrogen.

Synthesis of PdHoOx/C catalysts: Firstly, a given amount of HoOx/C hybrid support and H_2PdCl_4 solution were ultrasonically dispersed in 50 ml of ethylene-glycol. And then the pH value of the suspension was adjusted by 2 M NaOH solution to ca. 11 under ultrasonication. After that, the suspension was kept at room condition for 2 hours. The suspension was then exposed in the middle of a microwave oven (LG MG-5021MW1, 2450 MHz) for 60 s at 700 W and cooled down to room temperature naturally. Finally, the suspension was filtered, washed and dried overnight at 80 ºC in a vacuum oven. The content of Ho and Pd were 15% and 20%,

respectively. As a comparison, Pd/C catalyst was also synthesized by the same method. All solutions were prepared using Millipore-MiliQ water and analytical-grade reagents.

Catalyst characterization

The X-ray diffraction (XRD) patterns were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with the Cu Kα (λ=1.5405Å) as a radiation source operating at 40 kV and 200 mA. The composition of catalysts was determined by energy dispersive X-ray analysis (EDX) on a JEOL JAX-840 scanning electron microscope operating at 20 kV. XPS was recorded on a Kratos XSAM-800 spectrometer with an Al Kα monochromatic source. The transmission electron microscope (TEM) images were obtained by using a JEOL 2010 microscope operating at 200 kV.

The electrochemical measurements were performed with an EG&G Par potentiostat/galvanostat (Model 273A Princeton Applied Research Co. USA) and a conventional three compartment electrochemical cell. A Pt plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All the potentials were quoted against the reference Ag/AgCl electrode. All electrochemical measurements were carried out in 0.5 M H_2SO_4 solution with or without 0.5 M HCOOH deaerated by pure nitrogen for 15 min before experiments. The working electrode was prepared as follows: First, 5 mg of the catalyst was dispersed ultrasonically in 1 mL of the alcohol solution containing 50 mL of Nafion solution (5 wt%, Aldrich Co. USA). Second, 10 μL of the above solution was pipetted and spread

on a mirrorfinished glassy carbon electrode with 3 mm diameter. At last, it was dried at room temperature for 30 min. The glassy carbon electrode was polished with alumina slurry of 0.5 and 0.03 μm successively before use. The apparent surface area of the glassy carbon electrode was 0.07 cm^2.

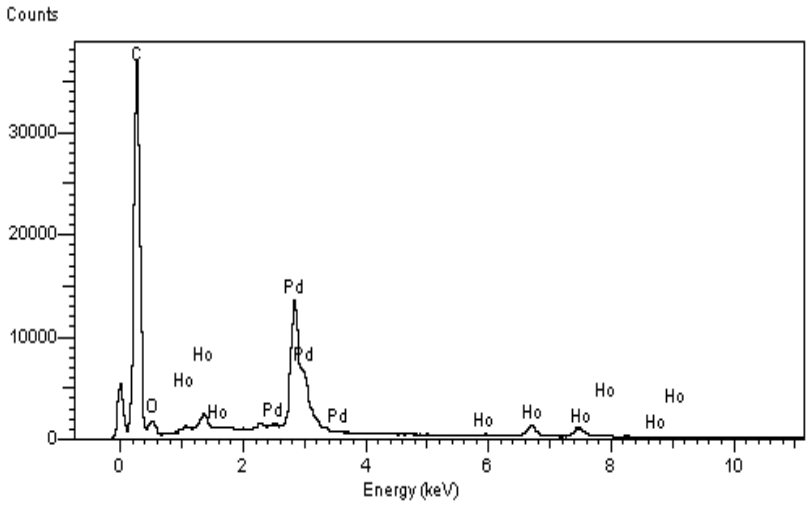

Fig.S1. EDX spectra of PdHoOx/C catalyst.

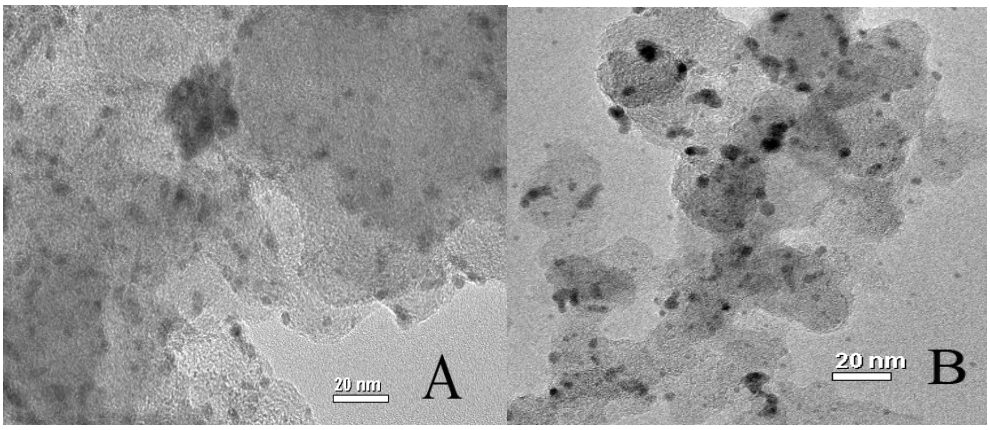

Fig.S2. TEM images of PdHoOx/C catalyst (A) and Pd/C-H catalyst (B).

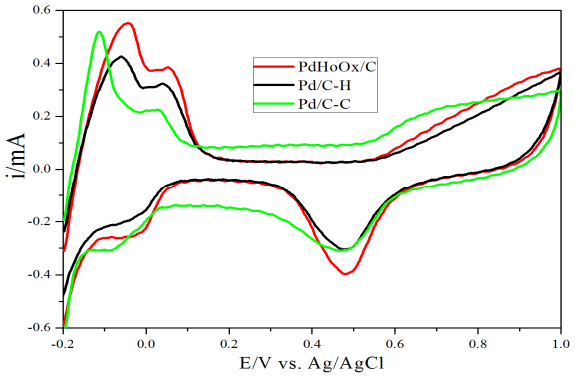

Fig.S3. Cyclic voltammograms of the PdHoOx/C, Pd/C-H and Pd/C-C catalysts with a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4.

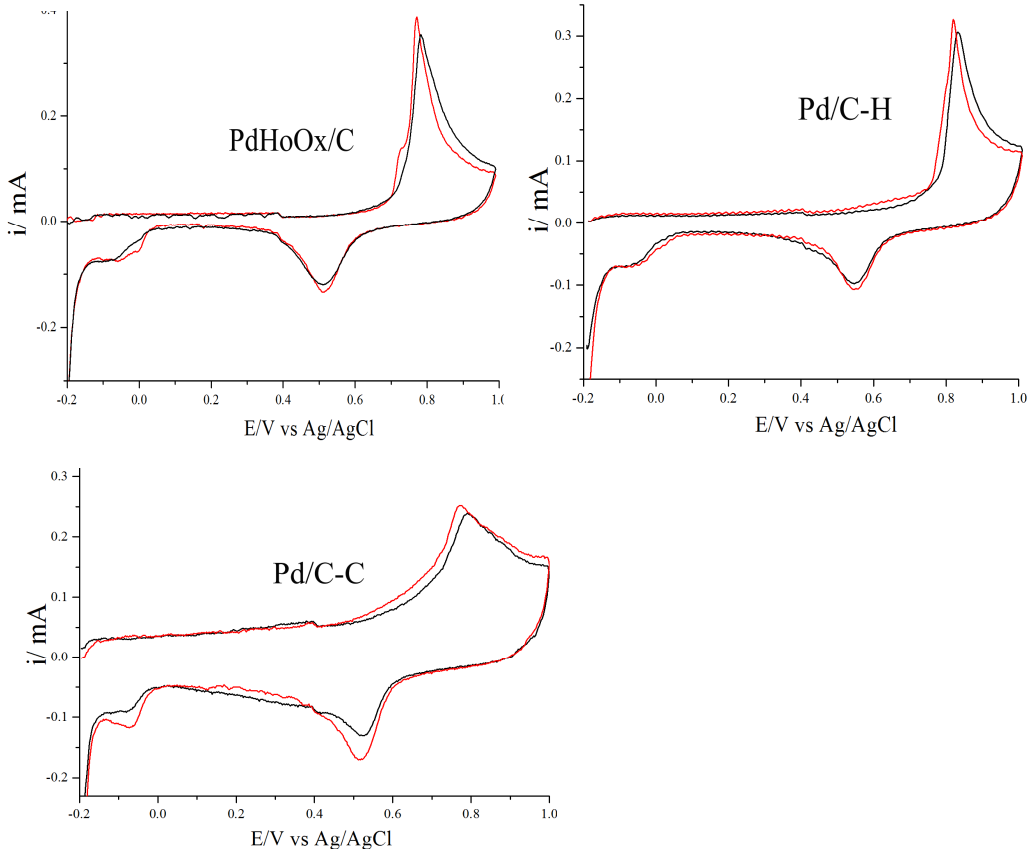

Fig.S4. The CO stripping voltammograms for the PdHoOx/C, Pd/C-H and Pd/C-C catalysts with a scan rate of 50 mV s^{-1}.