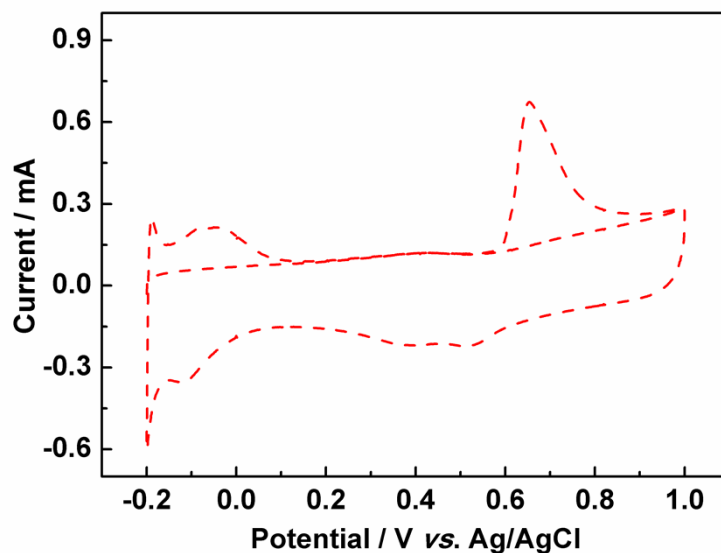


## Electronic Supplementary Information

### Synthesis of ultrafine amorphous PtP nanoparticles and the effect of PtP crystallinity on methanol oxidation

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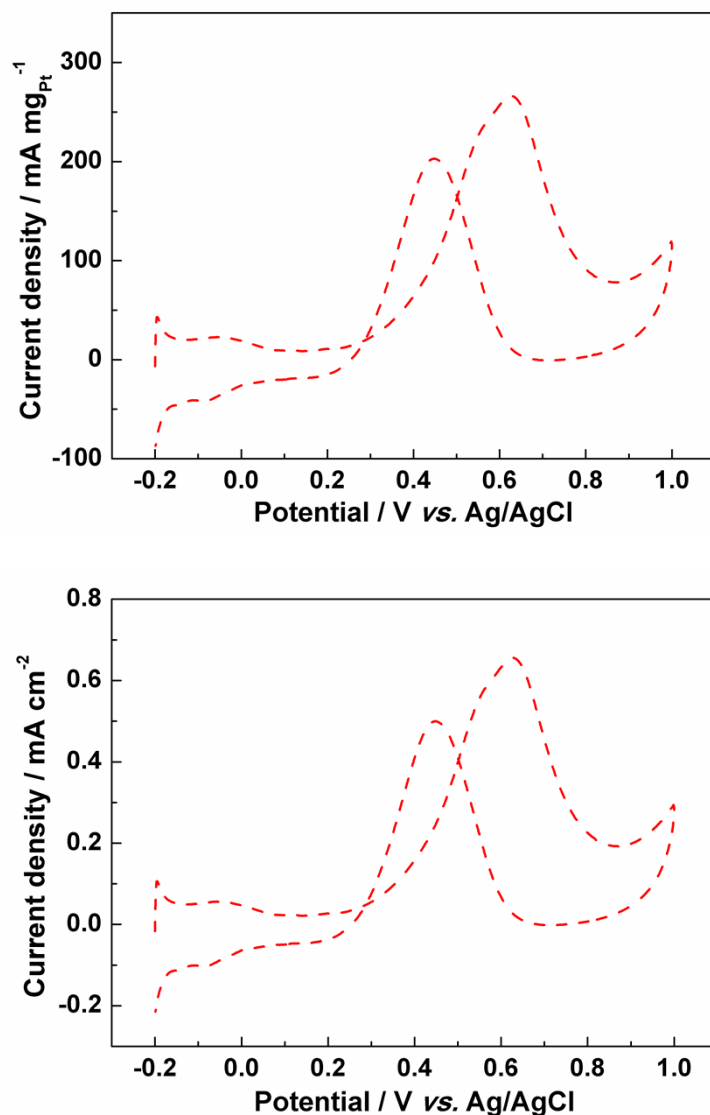


**Figure S1.** The CO stripping voltammetry of PtP-100/C in nitrogen-saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution.

Fig. S1 shows the CO stripping voltammeteries of PtP-100/C measured in nitrogen-saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. The onset potential of CO oxidation was ca. 0.567 V, higher than that of PtPa/C (0.560 V) and lower than that of PtP-200/C (0.588 V). The ECSACO was 40.6 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>, smaller than that of PtP<sub>a</sub>/C (41.5 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>) and larger than that of PtP-200/C (40.1 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>).

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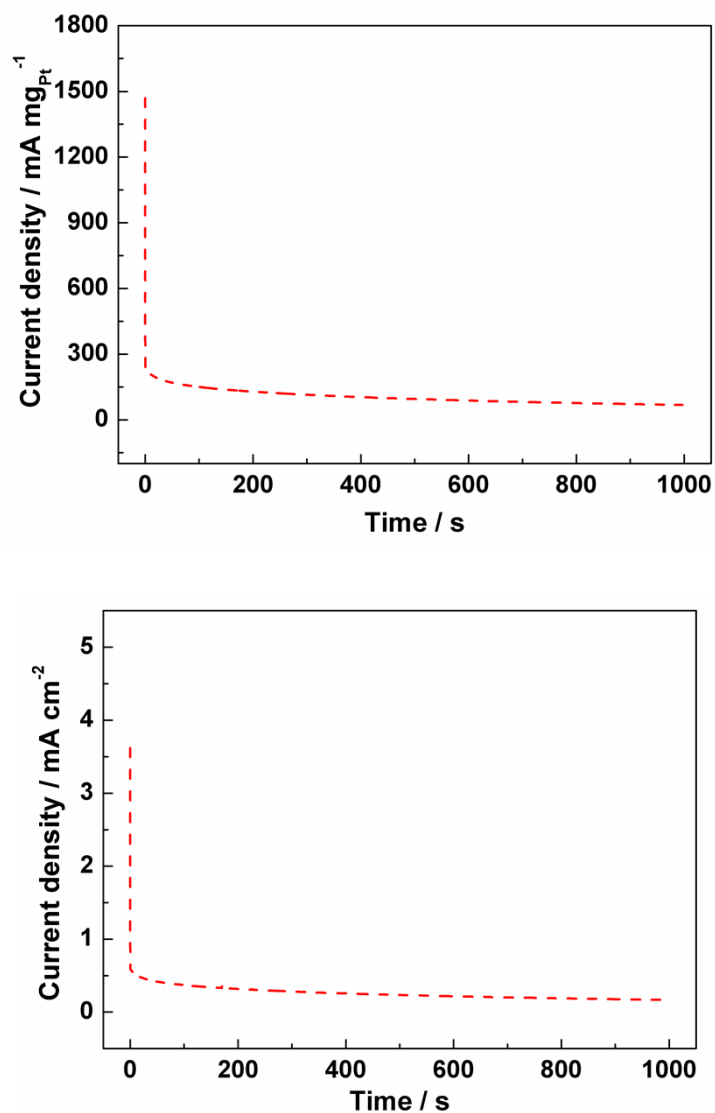
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**Figure S2.** (a and b) Cyclic voltammograms of PtP-100/C normalized by the Pt loading and  $ECSA_{CO}$  respectively, at  $50 \text{ mV s}^{-1}$  in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$  solution.

Fig. 9 shows the electrocatalytic methanol oxidation activity of PtP-100/C catalysts evaluated by CVs. The current was normalized to Pt loading and  $ECSA_{CO}$ , respectively. The current densities of oxidation peaks on PtP-100/C electrode reached  $265.8 \text{ mA g}_{Pt}^{-1}$  and  $0.658 \text{ mA cm}^{-2}$  respectively. Compared to

those of PtP<sub>a</sub>/C (301.8 mA g<sub>Pt</sub><sup>-1</sup> and 0.726 mA cm<sup>-2</sup>) and PtP-200/C (245.8 mA g<sub>Pt</sub><sup>-1</sup> and 0.612 mA cm<sup>-2</sup>), the catalytic activity of PtP-100/C was poorer than that of PtP<sub>a</sub>/C and better than that of PtP-200/C.



**Figure S3.** The chronoamperometry curves of PtP-100/C normalized to Pt loading (a) and  $ECSA_{CO}$  (a) in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.5 mol L<sup>-1</sup> CH<sub>3</sub>OH at a constant potential of 0.6 V.

Fig. S3 shows the chronoamperometry curves normalized to the Pt loading and  $ECSA_{CO}$  for the four catalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.5 mol L<sup>-1</sup> CH<sub>3</sub>OH

at a constant potential of 0.6 V. Fig. 10 shows the potentiostatic current was 67.5 mA g<sub>Pt</sub><sup>-1</sup> and 0.166 mA cm<sup>-2</sup> at 1000<sup>th</sup> s. respectively. As expected, these values are larger than that on PtP-200/C and lower than that on PtPa/C at 1000<sup>th</sup> s.