

Electronic Supplementary Information (ESI)

Effect of metal alloying on morphology and catalytic activity of platinum-based nanostructure thin films in methanol oxidation reaction

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X-ray photoelectron spectroscopy (XPS) analysis of the PtNi thin film was carried out in an Axis Ultra DLD system by Kratos Analytical using a monochromated Al-K α 1 X-ray beam as the excitation source. In order to obtain further insight into the chemical state, the interactions and the composition of the outer layers of the thin films, XPS (a more surface sensitive technique) was used for PtNi binary alloy thin film. Figure S1(a) presents the XPS spectra in the Pt 4f electron energy range for the PtNi thin film.

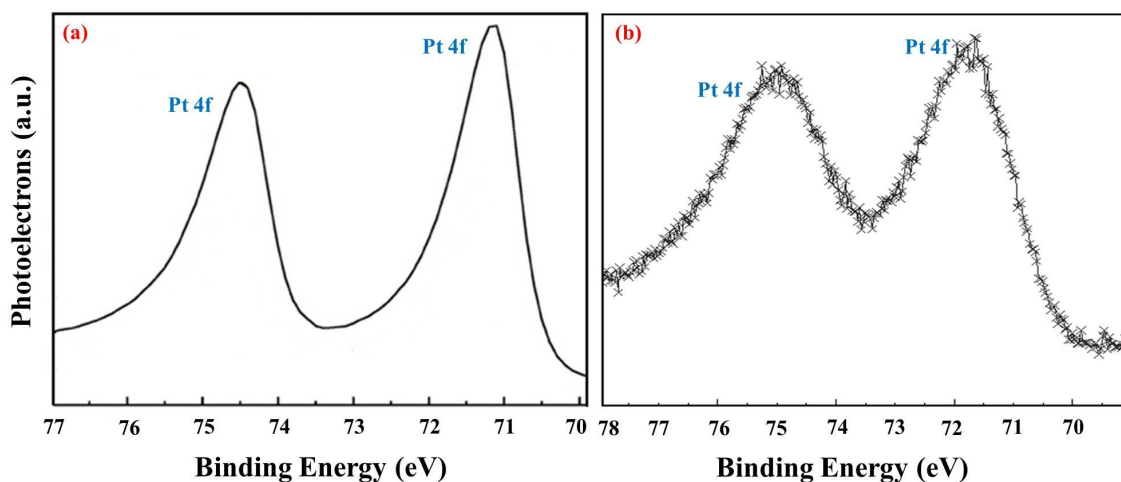


Figure S1. XPS spectra in the Pt 4f binding energy range for (a) PtNi nanoalloy thin film and (b) for Pt thin film.

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In conclusion after comparing the XPS spectra of PtNi thin film with Pt thin film (Figure S1 (a,b), respectively), we can see change in peak position (0.2 eV), indicating interactions of the Pt with Ni which reflected in a small shift of these peaks.

Typically, cyclic voltammograms recorded for the tetrametallic alloys of PtPdNiZn and PtPdNiSn thin films, trimetallic PtPdNi alloy thin film, bimetallic PtNi and PdNi thin films in 0.5 M H₂SO₄ and 0.5 M CH₃OH at different scan rates ranging from 20 to 100 mV s⁻¹ are shown in Figures (S2-S6)a. The increase in the current density with the scan rate is observed and the peak potentials almost show no change. Figures (S2-S6)b show that peak current densities are linearly proportional to the square root of the scan rates, suggesting that the electrocatalytic oxidation of methanol on these alloys thin films are diffusion-controlled process.^{1,2}

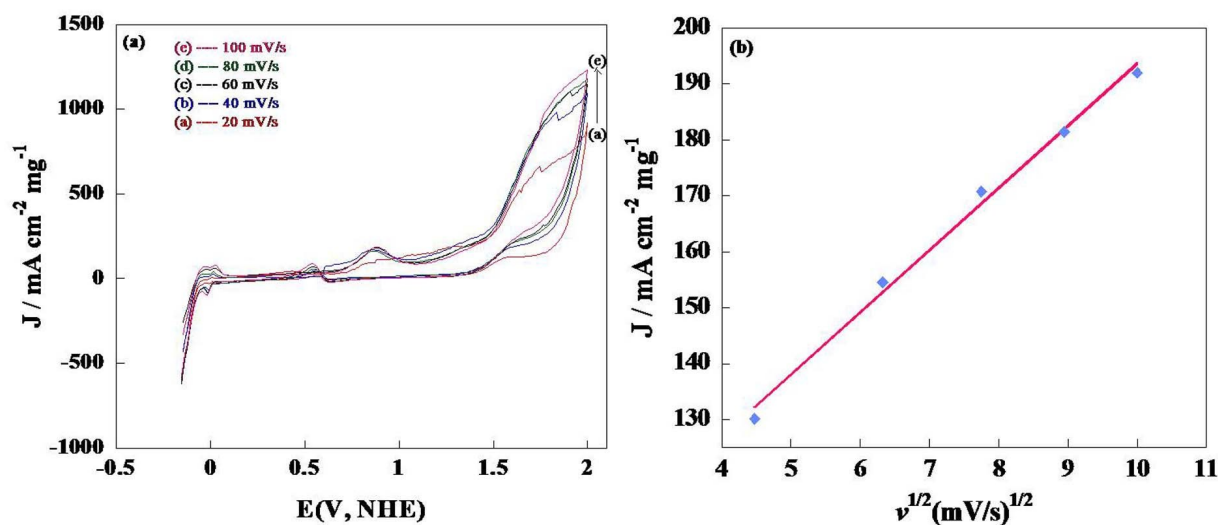


Figure S2. (a) Cyclic voltammograms of the PtPdNiZn ANS thin film at different scan rates in 0.5 M H₂SO₄ + 0.5 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates

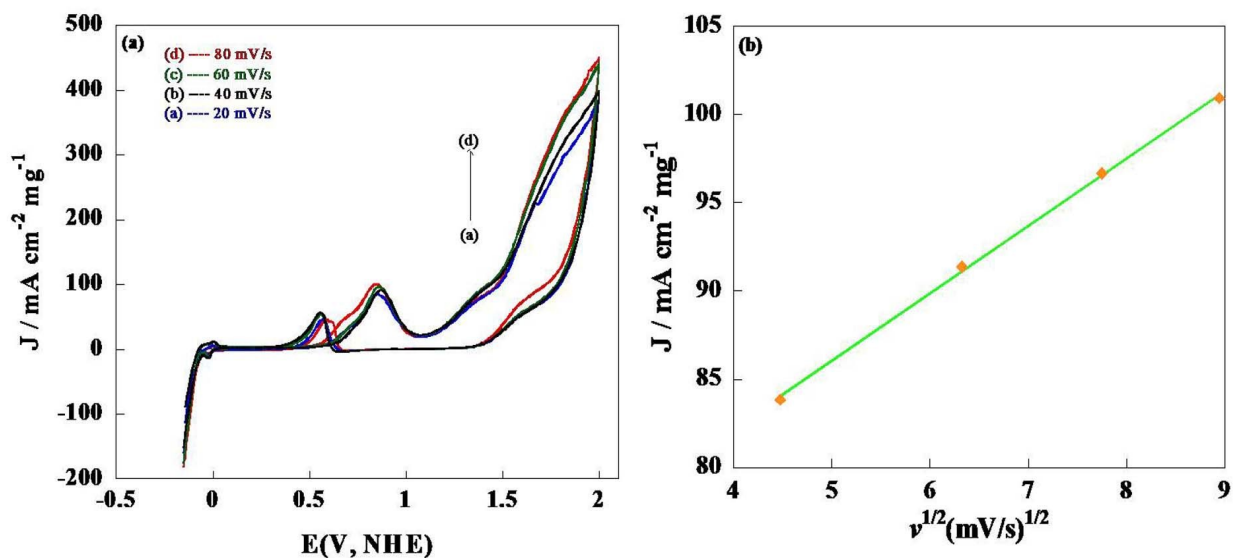


Figure S3. (a) Cyclic voltammograms of the PtPdNiSn NPs thin film at different scan rates in 0.5 M H₂SO₄ + 0.5 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates.

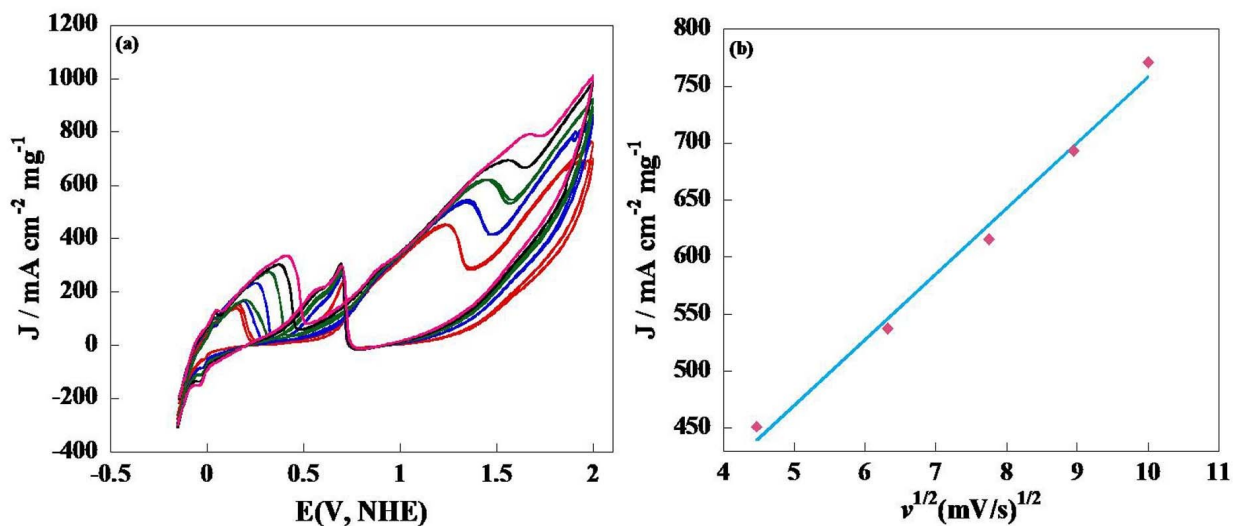


Figure S4. (a) Cyclic voltammograms of the PtPdNi ANSs thin film at different scan rates in 0.5 M H₂SO₄ + 0.5 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates

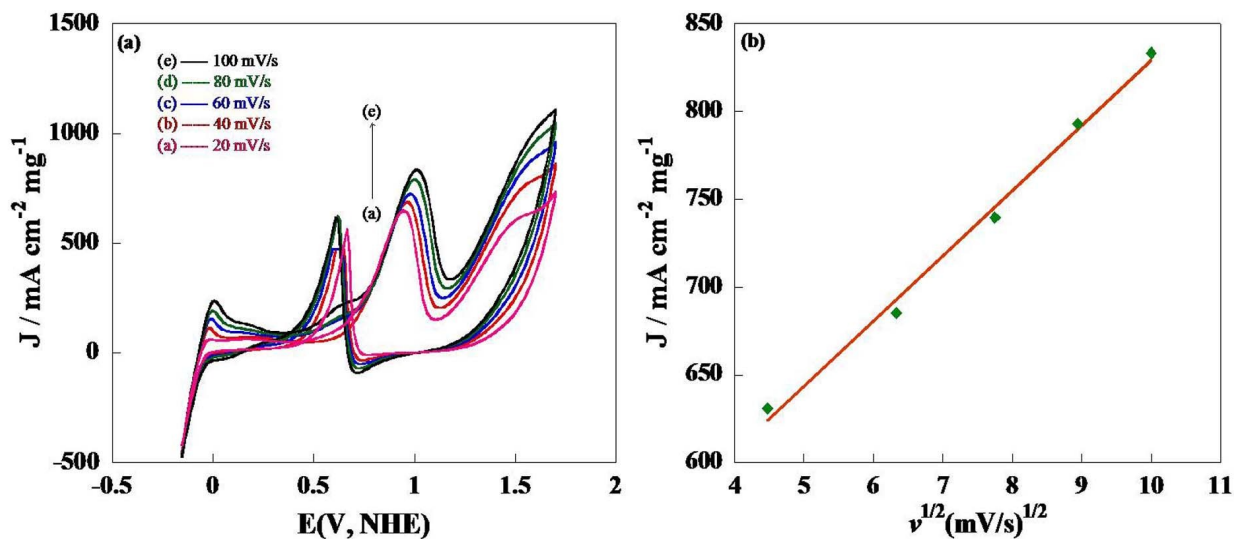


Figure S5. (a) Cyclic voltammograms of the PtNi NPs thin film at different scan rates in 0.5 M H₂SO₄ + 0.5 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates.

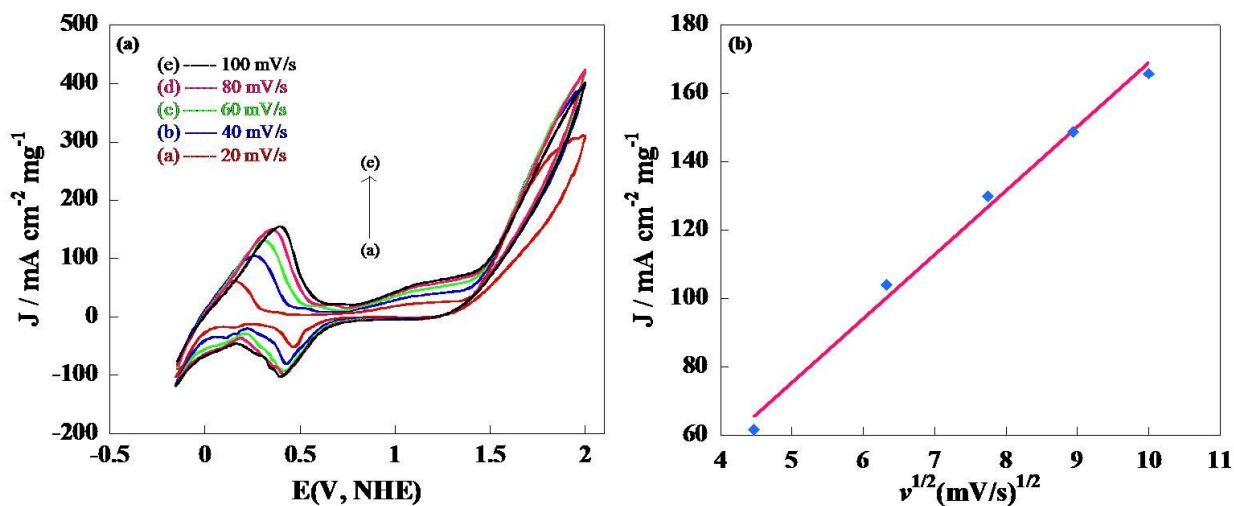


Figure S6. (a) Cyclic voltammograms of the PdNi NPs thin film at different scan rates in 0.5 M H₂SO₄ + 0.5 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates.

References:

- 1 H. J. Wang, H. Yu, F. Peng and P. Lv, *Electrochem. Commun.*, 2006, **8**, 499-504.
- 2 G. L. Che, B. B. Lakshmi, C. R. Martin and E. R. Fisher, *Langmuir*, 1999, **15**, 750-758.