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Supporting Information

A high performance Pt-based catalyst for methanol oxidation reaction; Effect of electrodeposition mode and cocatalyst on the electrocatalytic activity

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Reagents and instruments

The analytical grade of materials including methanol (CH_3OH, 99.6%), sodium hydroxide (NaOH, 97%), sulfuric acid (H_2SO_4, 95–97%), nickel(II) sulfate hexahydrate ($NiSO_4.6H_2O$, ≥99.99%), copper(II) sulfate pentahydrate ($CuSO_4.5H2O$, ≥ 99.0%), and potassium hexachloroplatinate(IV) ($K_2PtCl_6.6H2O$, 98%) were procured from Merck (Darmstadt, Germany). 4-methyl- 1,2-diaminobenzene (4-MDAB, 97%, coffee-brown pellet), multi-walled carbon nanotube (MWCNT), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. Fuel cell grade commercial Pt/C (Platinum on Vulcan xc 72) was acquired from Sainergy (USA). Aqueous solutions were fabricated with doubly distilled water all over the experiments.

Field Emission Scanning electron microscopy (FESEM, TESCAN/Vega3, Czech Republic) equipped with energy-dispersive X-ray spectroscopy (EDS, TESCAN/Vega3, Czech Republic) were used for consideration of the morphology and composition of the modified surface. Electrochemical measurements like cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) were performed on a ZIVE LAB workstation guided with Smart Manager 6.6.4.0 software. Electrochemical workstation was organized a conventional three electrodes configuration including modified glassy carbon electrode (GCE), Pt wire, and Ag/AgCl (saturated KCl) as working, counter, and reference electrode respectively. In the comparative table, the potentials were converted to the potentials versus the reversible hydrogen electrode (RHE) according to the equations S1.

$$E(RHE) = E\,(vs.ref.electrode) + (0.0591 \times pH) + \ E^{0}_{ref.\ electrode} \qquad \text{S1}$$

Electropolymerization of 4-MDAB

Fig. S1A shows electropolymerization of 4-MDAB on the surface of MWCNT/GCE. In the first cycle, three irreversible oxidative peaks are observed at about 0.32 to 0.82 V that are allocated to the oxidation of amine groups of monomer. As the potential sweeps continue, a characterized nucleation loop forms at the region of monomer oxidation that can be considered as a proof of the initiation of the nucleation process. The formation of this loop is the characteristic of CV curve during the electropolymerization of conducting polymers.[43,44] As potential sweeps continue, the current density of the oxidation peaks at about 0.32 to 0.82 V decrease and three pairs of the reversible peaks at about -0.42 to 0.32 V appear. The appearance of oxidative peaks at about 0.32 to 0.82 V results Red. species that theirs further oxidation produce the polymeric film.[30,45,46] The

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decrease in the intensity of peaks attributed to the monomer oxidation and increase in the intensity of the pairs of peaks related to the formation of polymeric film indicate gradual growth of polymer with high redox activity.[47,48] The 13th cycle (dashed red line in Fig. S1A) that is the most stable cycle clearly reveals the adsorption of the polymeric film on the surface of MWCNT/GCE.

The successful formation of p-MDAB with the desirable electrochemical stability were confirmed through applying 10 consecutive cycles at a scan rate of 60 mV s^{-1} on the surface of p-MDAB/MWCNT/GCE immersed in 0.1 M H_2SO_4 solution. Fig. S1B clearly exhibits gradual decrease in the peak intensity and achievement in the steady state peaks in about 8th cycle. These observations evident the formation of a stable polymeric film with the appropriate kinetics on the surface of MWCNT/GCE. The MWCNTs with intrinsic properties such as large surface area, high electrocatalytic activity, and fast electron transfer result in the successful formation of an electrochemically stable polymeric film.[44,47]

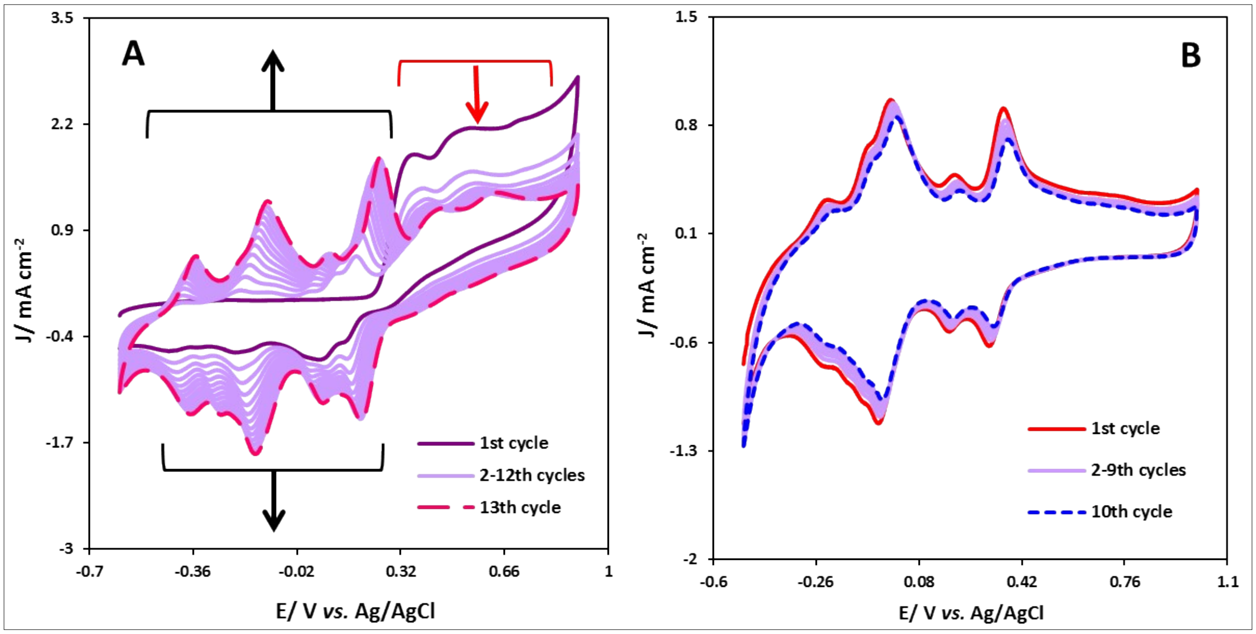


Fig. S1 (A) The multi sweep cyclic voltammograms of MWCNT/GCE during the electropolymerization of 4-MDAB at a scan rate of 60 mV s^{-1} (B) CV curves of p-MDAB/MWCNT/GCE during performing of 10 consecutive cycles in 0.1 M H_2SO_4 at a scan rate of 60 mV s^{-1}.

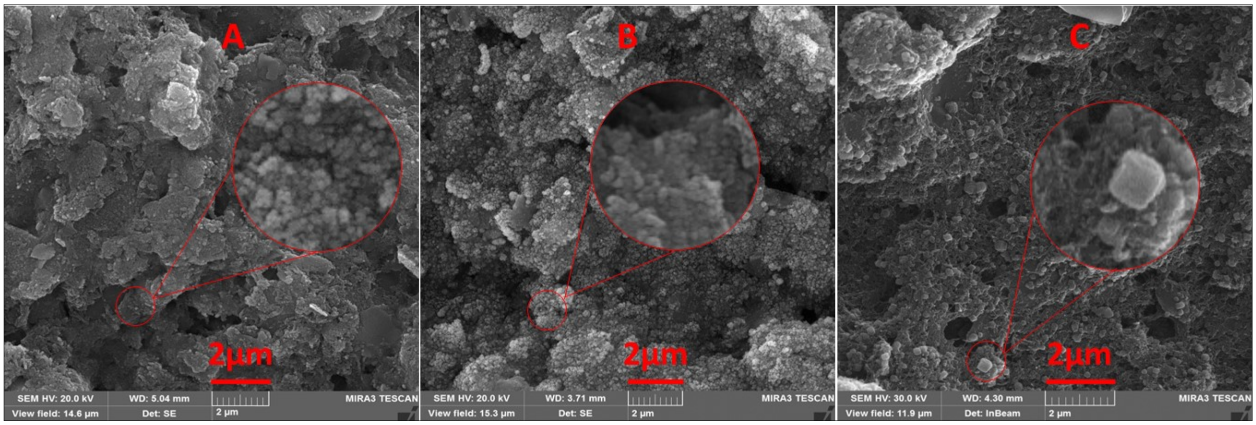
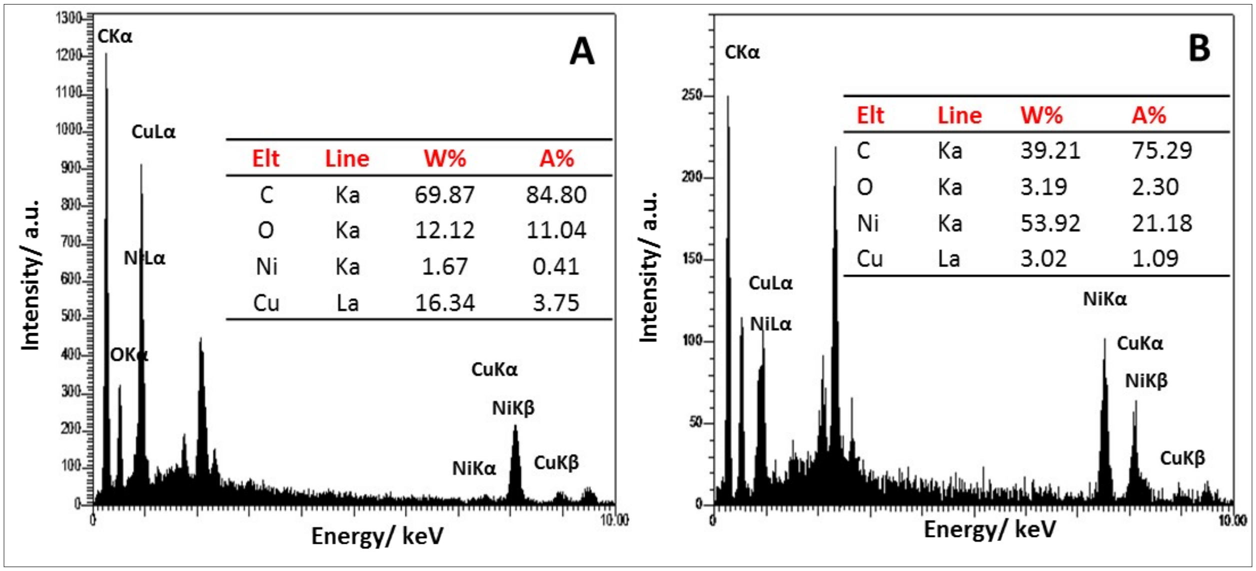


Fig. S2 FESEM images of (A) c-Pt/NiCu/p-MDAB/MWCNT, (B) c-NiCu/p-MDAB/MWCNT, and (C) p-NiCu/p-MDAB/MWCNT.



A

Elt	Line	W%	A%
C	Ka	69.87	84.80
O	Ka	12.12	11.04
Ni	Ka	1.67	0.41
Cu	La	16.34	3.75

B

Elt	Line	W%	A%
C	Ka	39.21	75.29
O	Ka	3.19	2.30
Ni	Ka	53.92	21.18
Cu	La	3.02	1.09

Fig. S3 EDS spectrum of (A) c-NiCu/p-MDAB/MWCNT and (B) p-NiCu/p-MDAB/MWCNT.

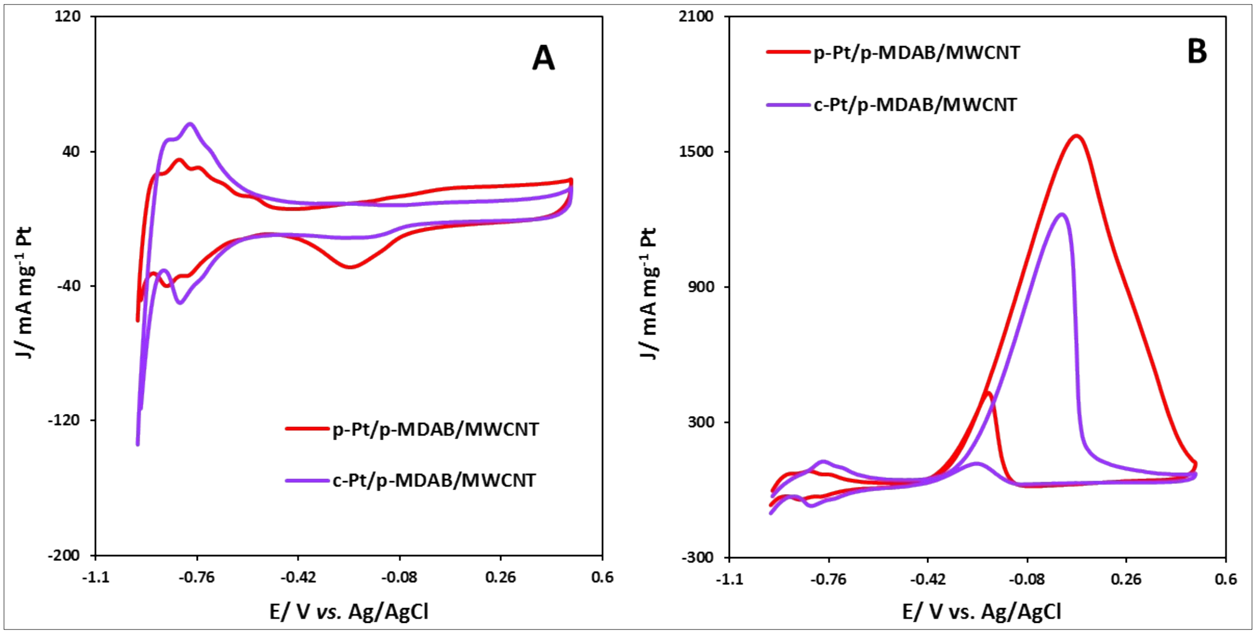


Fig. S4 The comparison between CV curves of c-Pt/NiCu/p-MDAB/MWCNT and p-Pt/NiCu/p-MDAB/MWCNT in a solution of (A) 0.1 M NaOH and (B) 0.1 M NaOH + 0.5 M CH_3OH at a scan rate of 0.05 V s^{-1}.

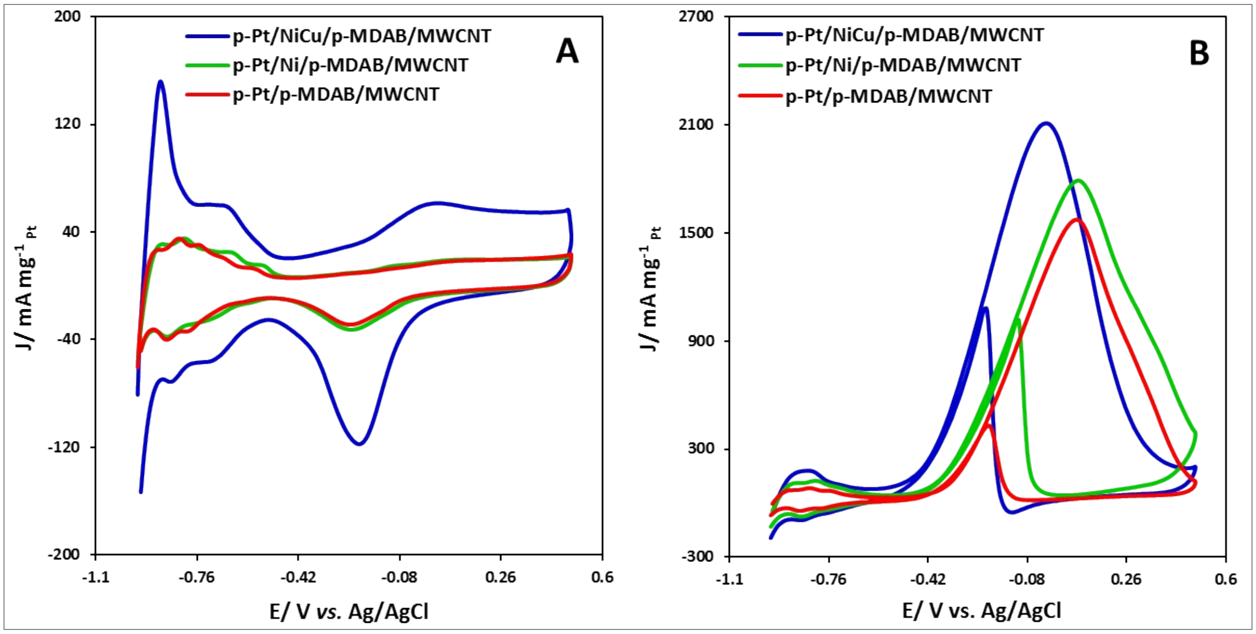


Fig. S5. The comparison between CV curves of p-Pt/NiCu/p-MDAB/MWCNT, p-Pt/Ni/p-MDAB/MWCNT and p-Pt/p-MDAB/MWCNT in a solution of (A) 0.1 M NaOH and (B) 0.1 M NaOH + 0.5 M CH_3OH at a scan rate of 0.05 V s^{-1}.

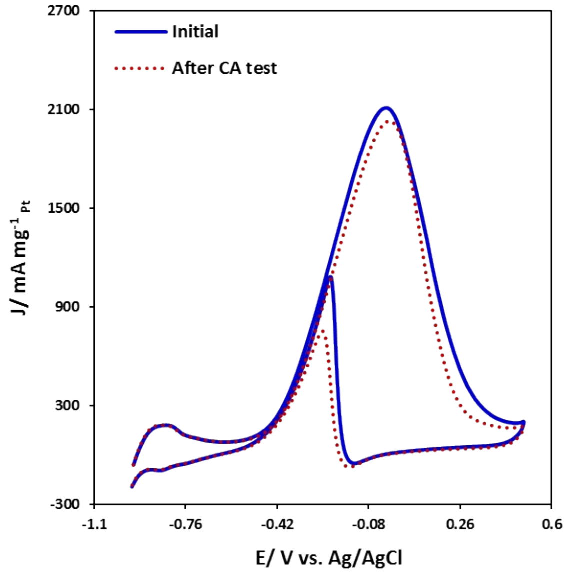


Fig. S6 CV curves of p-Pt/CuNi/p-MDAB/MWCNT catalyst measured in 0.1 M NaOH + 0.5 M CH_3OH initially and after CA test.

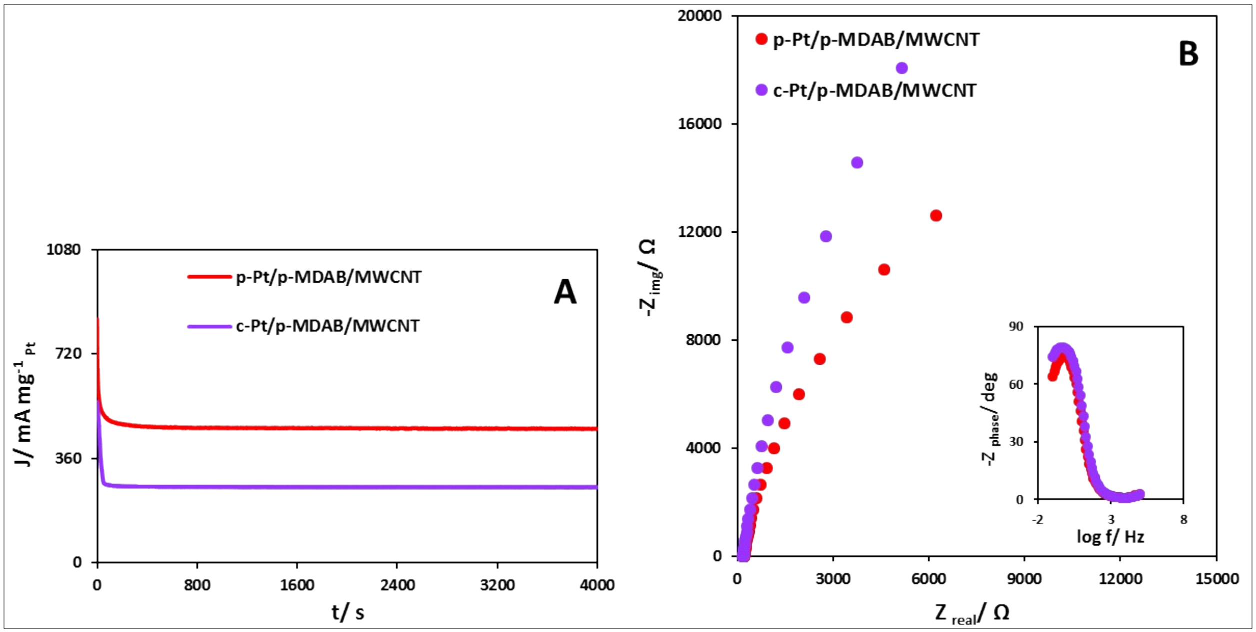


Fig. S7 Chronoamperometry curves at -0.15 V and (B) EIS Nyquist plots for c-Pt/NiCu/p-MDAB/MWCNT and p-Pt/NiCu/p-MDAB/MWCNT during electrooxidation of 0.5 M CH_3OH in 0.1 M NaOH.