Supporting Information

High Performance Platinized Titanium Nitride Catalyst for Methanol Oxidation

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(a) Preparation of TiN working electrode

TiN was coated on SS304 by cathodic arc deposition technique. A 20" Multi-Arc chamber was used for deposition. Before deposition, the coating plant was first evacuated to a base vaccum of 10^{-6} Torr. During deposition, reactive nitrogen gas pressure and substrate bias voltage were kept constant at 10 mTorr and –200 V. Deposition time was kept at 30 minutes. The electrodes were made by cutting the SS coated TiN into small pieces and attaching a Cu wire to one end by spot welding technique. The exposed Cu wire and stainless steel portions were insulted using epoxy adhesive. Prior to the electrochemical measurements, the TiN electrodes were degreased by wiping it with a tissue soaked in absolute ethanol and then thoroughly washed with doubly distilled water.

(b) Electrodeposition of Platinum onto TiN (Pt-TiN)

Pt was coated onto TiN by chronopotentiometry from a solution of 0.1 M H_2PtCl_6 using TiN as the working electrode, a larger area Pt foil as the counter electrode and SCE as the reference electrode. A current density of 5.2 mA/cm^2 was used for varying time scale (from 3 seconds to 40 seconds) for electrodeposition. The amount Pt deposited onto TiN was calculated using the charge passed (Reference 1).

(c)   Characterization

The TiN and Pt-TiN were characterized by SEM with EDX (FEI–Philips), XRD (JEOL JDX 8030), Cyclic Voltammetry (CH Instruments (USA) or Autolab Ecochmie Potentiostat or Eg&G 263A) and RAIR (Spectrum GX, Perkin Elmer) techniques. XRD of fresh TiN shows characteristic peaks corresponding to cubic NaCl type structure (Reference 2). The EDX pattern of bare TiN shows characteristic pattern for Ti and N. Pt-TiN shows clearly the presence of Pt. Cyclic voltammogram of Pt-TiN in H_2SO_4 shows well-defined hydrogen adsorption and desorption regions and Pt oxide formation and reduction, which is characteristic of polycrystalline Pt in acidic media.

(d)   Electrooxidation of methanol using Pt-TiN

Electrochemical measurements were carried out in a three electrode cell using Pt-TiN as the working electrode, a saturated calomel and Pt wire were used as reference and counter electrodes, respectively. All electrode potentials in this paper are with respect to SCE. A solution of 0.5 M Methanol + 0.5 M H_2SO_4 was used as the electrolyte. Cyclic voltammograms were recorded in the potential range 0 to 0.8 V vs SCE at a scan rate of 20 mV/s. The current versus time transient for the electrooxidation of methanol at 0.65 V vs. SCE is given later.
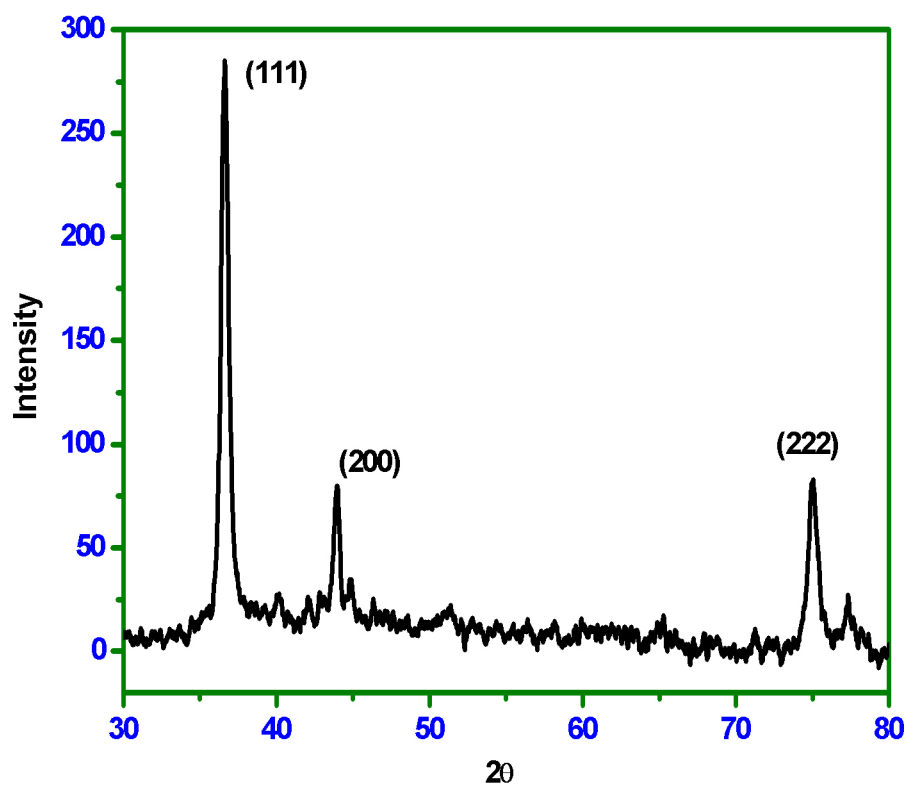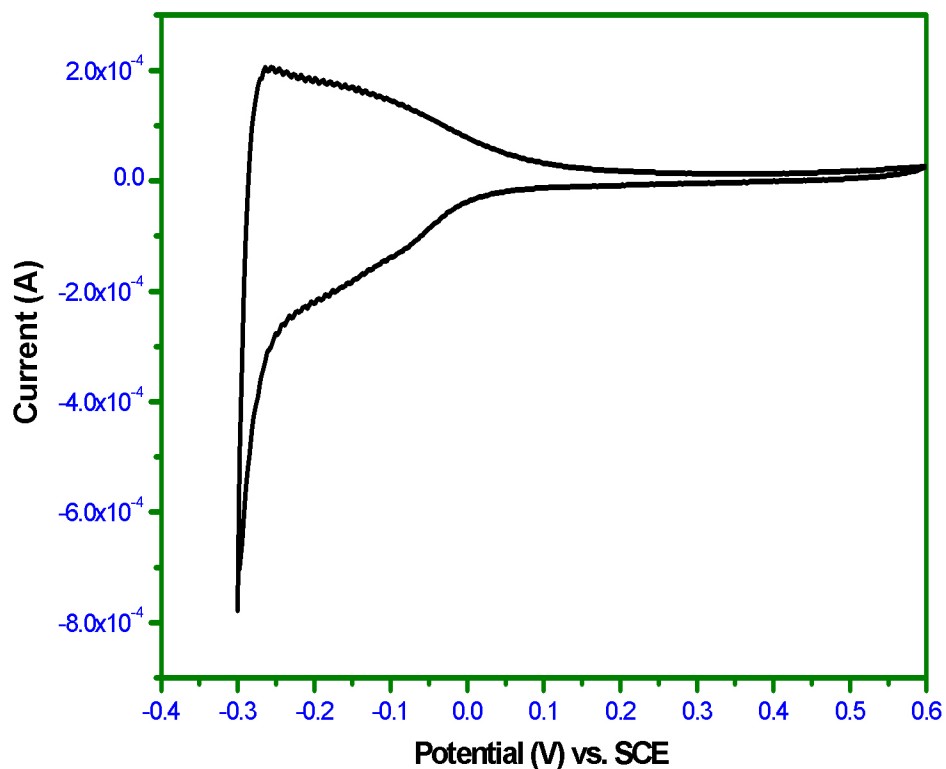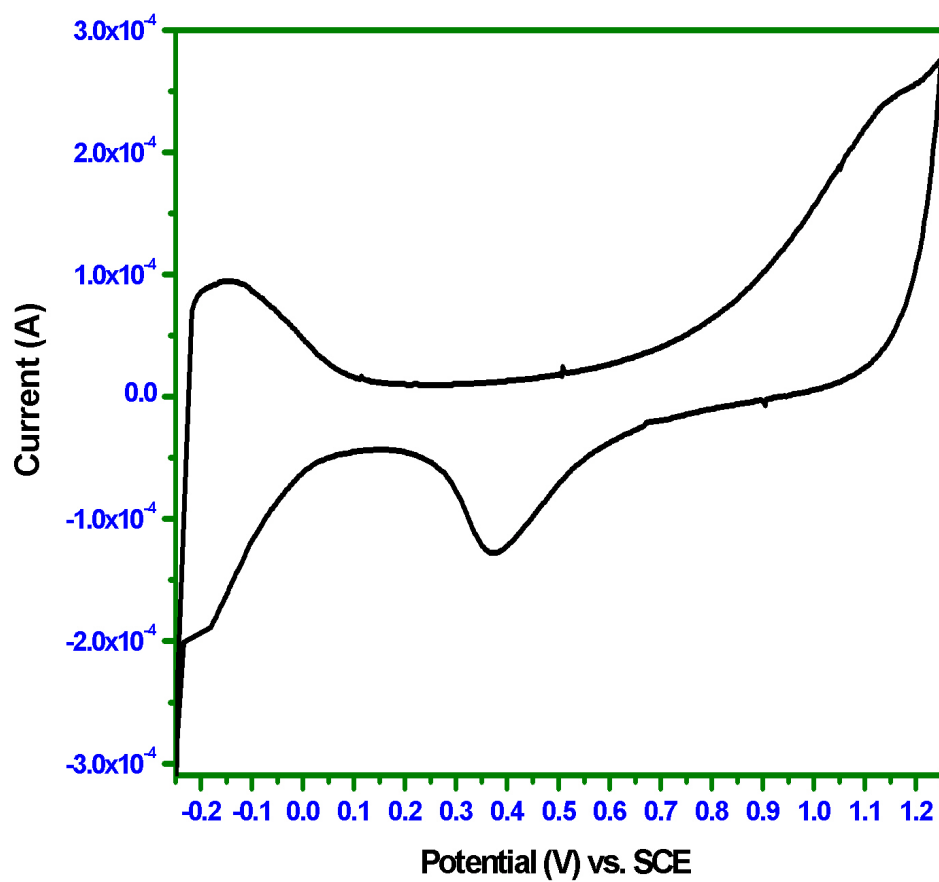
Figure S1: XRD pattern of TiN

Figure S2: Cyclic voltammogram of Pt-TiN in 0.5 M H_2SO_4 at a scan rate of 200 mV/s. Hydrogen adsorption and desorption region can be seen close to –0.2 V, indicating the presence of Pt on TiN. Geometrical are of the electrode, 0.25 cm^2. The loading of Pt is 22 µg/cm^2.

Figure S3: Cyclic voltammogram of Pt-TiN in 0.5 M H_2SO_4 at a scan rate of 50 mV/s. The loading of Pt is 80 $\mu g/cm^2$.
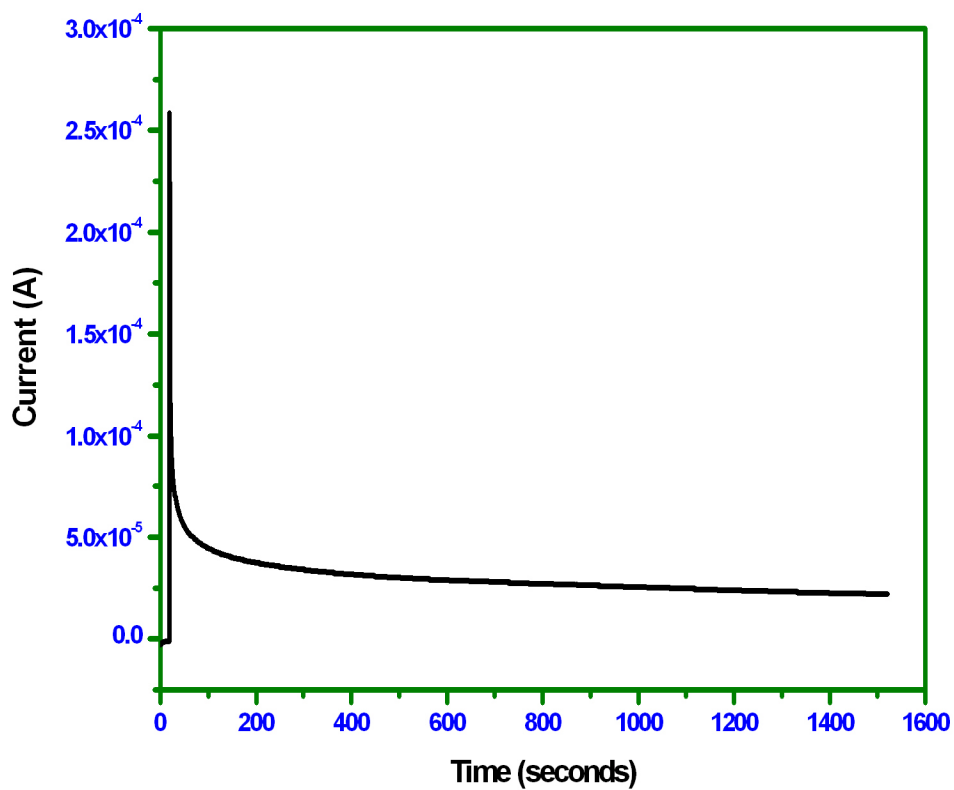
Figure S4: Chronoamperometric trace at 0.65 V for the electrooxidation of methanol on Pt-TiN. Electrolyte used is 0.5 M Methanol + 0.5 M H_2SO_4.
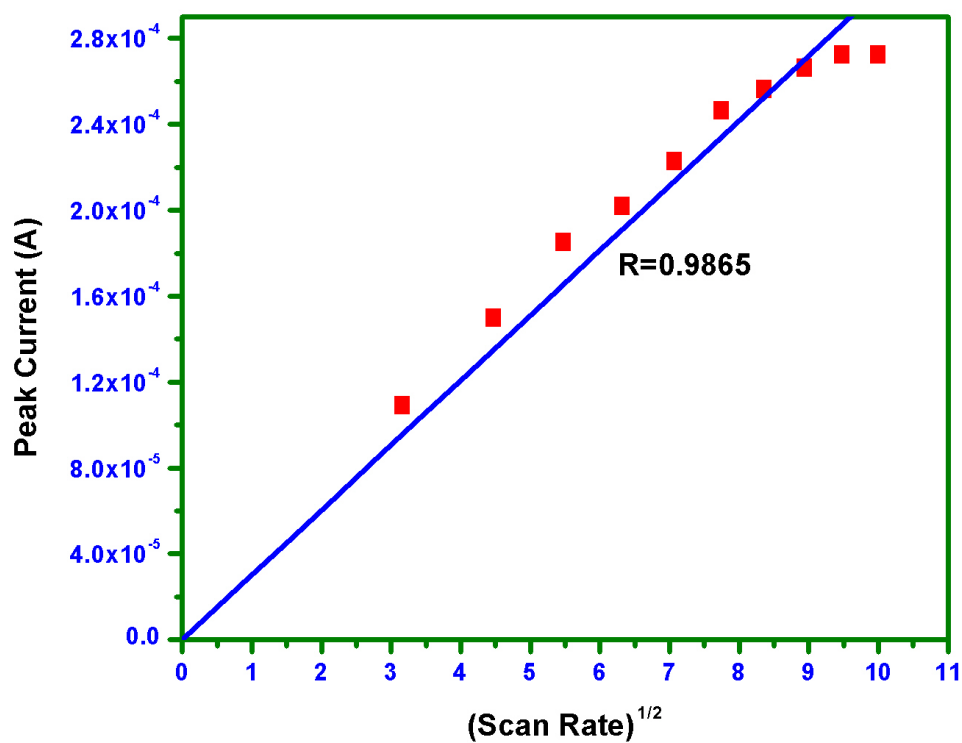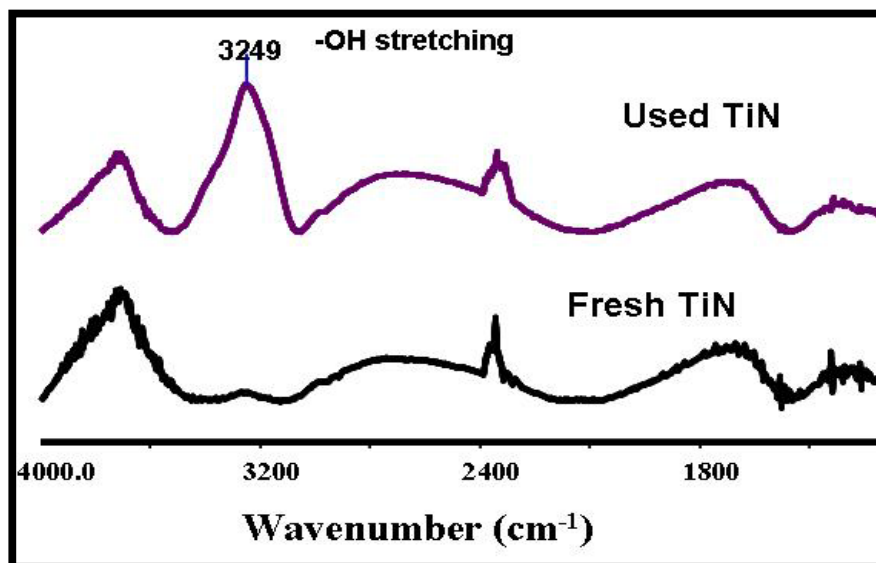
Figure S5: Plot of peak current (I_p) vs. (Scan rate)$^{1/2}$ for methanol oxidation on Pt-TiN (the scan rate dependence is carried out after several cycles to stabilize the voltammogram.
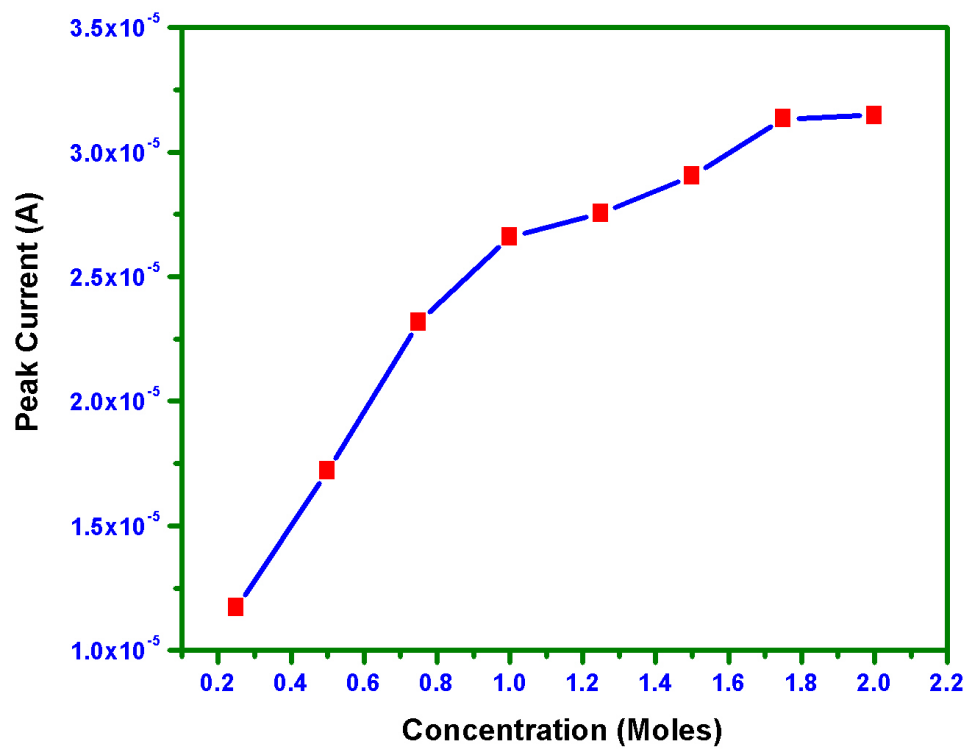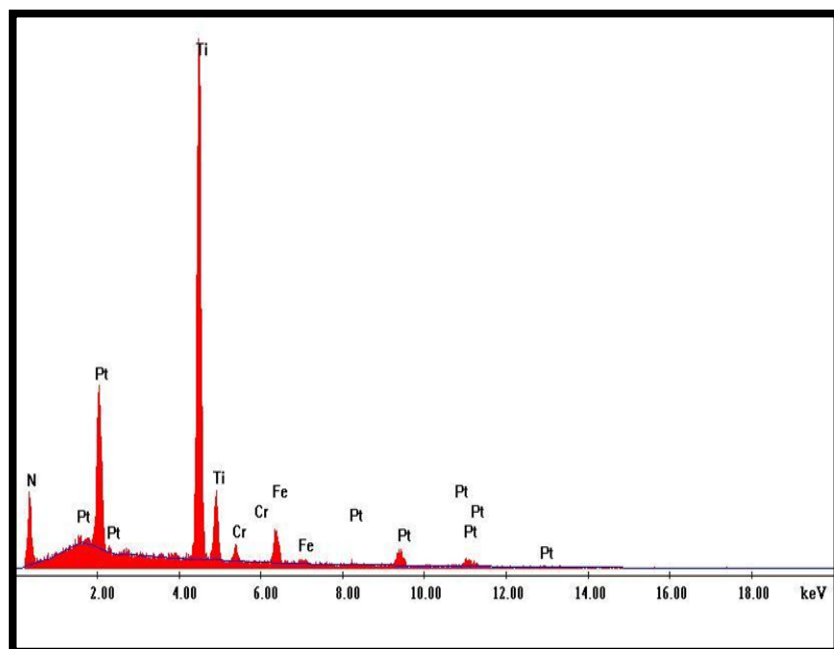
Figure S6: Peak current dependence on methanol concentration

Figure S7: RAIR spectra of Pt-TiN before and after methanol oxidation

Figure S8 EDX pattern of Pt-TiN.

References

1) Tang,Z.; Geng,D.; Lu,G. *Thin Solid Films* **2006,** *497*, 309 – 314
2) Navas, D.; Sánchez,O.; Asenjo,A.; Jaafar,M.; Baldonedo,J.L.; Vázquez,M.; Vélez,M.H. *Nanotechnology* **2007,***18*, 165302