SUPPORTING INFORMATION

Enhanced electro catalytic activity and durability of highly mono disperse Pt@PPy-PANI nanocomposites as a novel catalyst for electro-oxidation of methanol

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Materials and Methods

Polyaniline (PANI) (emeraldine salt), Polypyrrole (PPy), $PtCl_4$, Methanol (98% pure), Ethyl alcohol (%99 pure alcohol), 1-Aminopropane (pure %99), Borane dimethylamine complex (DMAB), N,N-Dimethylformamide (DMF, anhydrous %99,8), Nafion® 117 solution was purchased from Sigma Aldrich Chem. Tetrahydrofuran(THF) was purchased from Merck. The pure water for solution preparation was filtered by Millipore water purification system (18 MΩ) analytical grade.

FT-IR analyses were taken by Perkin Elmer Spectrum 2. The morphology and structure of the as-synthesized samples were characterized with transmission electron microscopy (JEOL 200 kV TEM). For TEM characterization, Pt NPs@PANI, Pt NPs@PPy and Pt NPS@PPy-PANI nanoparticuler was first dispersed into ethanol with sonication for several minutes, and was then casted on a carbon covered 400-mesh copper grid and dried in ambient condition, and then transferred into the microscope for observation. More than 300 particles were calculated to get the integrated information about the overall distribution of Pt-based catalyst sample.

A Panalytical Emperian diffractometer with Ultima+theta–theta high resolution goniometer, having an X-ray generator (Cu Kα radiation, λ = 1.54056 Å) and operating condition of 45 kV and 40 mA, were employed in X-ray diffraction (XRD) analysis.

Thermo Scientific spectrometer was used for X-ray Photoelectron Spectroscopy (XPS) measurements and the X-ray source was Kα lines of Mg (1253.6 eV, 10 mA). Samples were prepared by depositing the catalyst on Cu double-sided tape (3M Inc.). C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line.

The morphological characterization was performed by high-resolution field emission scanning electron microscope (SEM) using a FEI Quanta FEG 250 SEM operating at 10 kV.

Characterization of the Catalysts

The characteristic peaks of PANI at 1584 and 502 cm^{-1} are assigned to the C=C stretching vibration of quinoid and benzenoid rings, respectively. The bands located at 1302, 1145 and 1240 cm^{-1} belonged to C–N, C=N, and C–N+ (polaron structure of PANI), respectively. The bands at about 1041 and 834 cm^{-1} are due to the aromatic C–H in-plane bending and the out-of-plane deformation. In the spectrum of PPy, the characteristic C=C and C–N stretching vibration in the ring of PPy at 1544 and 1460 cm^{-1}, are clearly visible. The broad band from 1250 to 1100 cm^{-1} with a maximum at 1173 cm^{-1} is attributed to the breathing vibration of the pyrrole ring. The band at 1036 cm^{-1} corresponds to the C–H in plane bending. The spectrum of the PANI-PPy composites shows all of the characteristic bands of both PANI and PPy. The quinonoid phenyl ring C=C stretch band of PANI at 1584 cm^{-1} and the C=C stretching mode of PPy at 1544 cm^{-1} have amalgamated to form a broader band from 1690 to 1530 cm^{-1}.

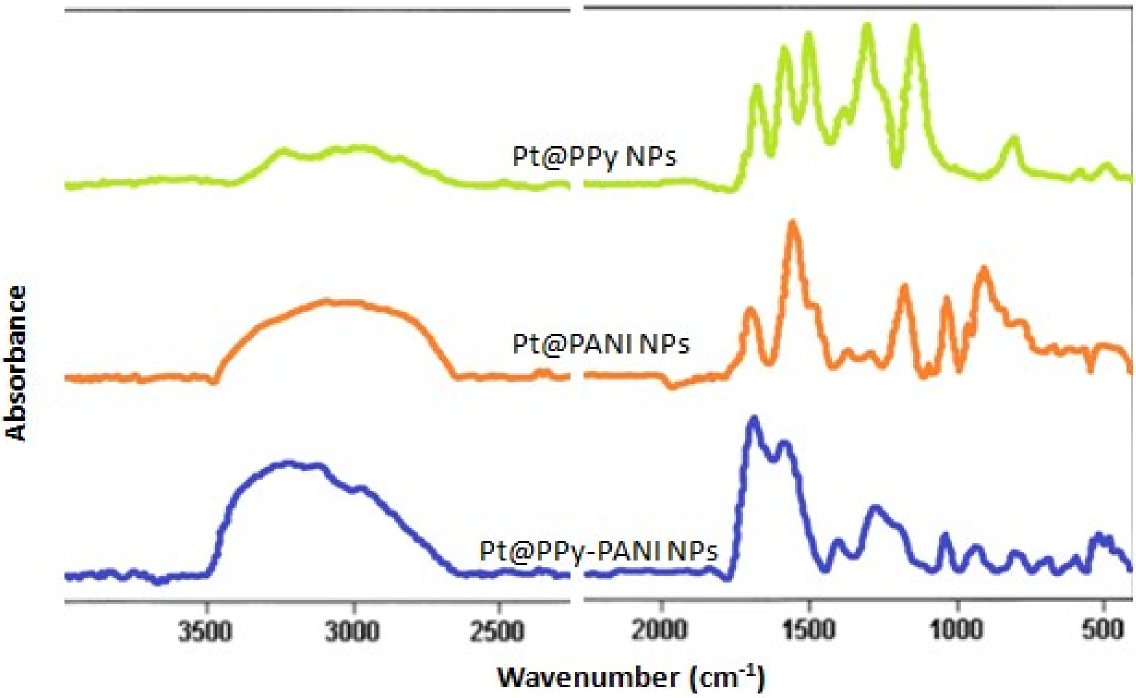


Fig. S1. Comparison of the infrared spectra of the Pt@PPy, Pt@PANI and Pt@PPy-PANI.

Table S1. Average crystallite platinum particles size determined by (a) X-ray line broadening, (b) transmission electron microscopy.

	a (nm)	**b (nm)**
Pt NPs@PPy	~3.539	~3.671
Pt NPs@PANI	~3.969	~4.235
Pt NPs@PPy-PANI	~3.176	~3.326

Table S2 Pt $4f_{7/2}$ core binding energy, eV, in the prepared catalyst. The number in the parentheses is the relative intensities of the species.

	Pt $4f_{7/2}$	**Pt $4f_{7/2}$**	
	Pt(0)	**Pt(IV)**	**Pt(0)/Pt(IV)**
Pt NPs@PPy	71.2 (77.1)	74.5 (22.9)	3.37
Pt NPs@PANI	71.1 (83.8)	74.4(16.2)	5.17
Pt NPs@PPy-PANI	70.8 (88.2)	74.1 (11.8)	7.47

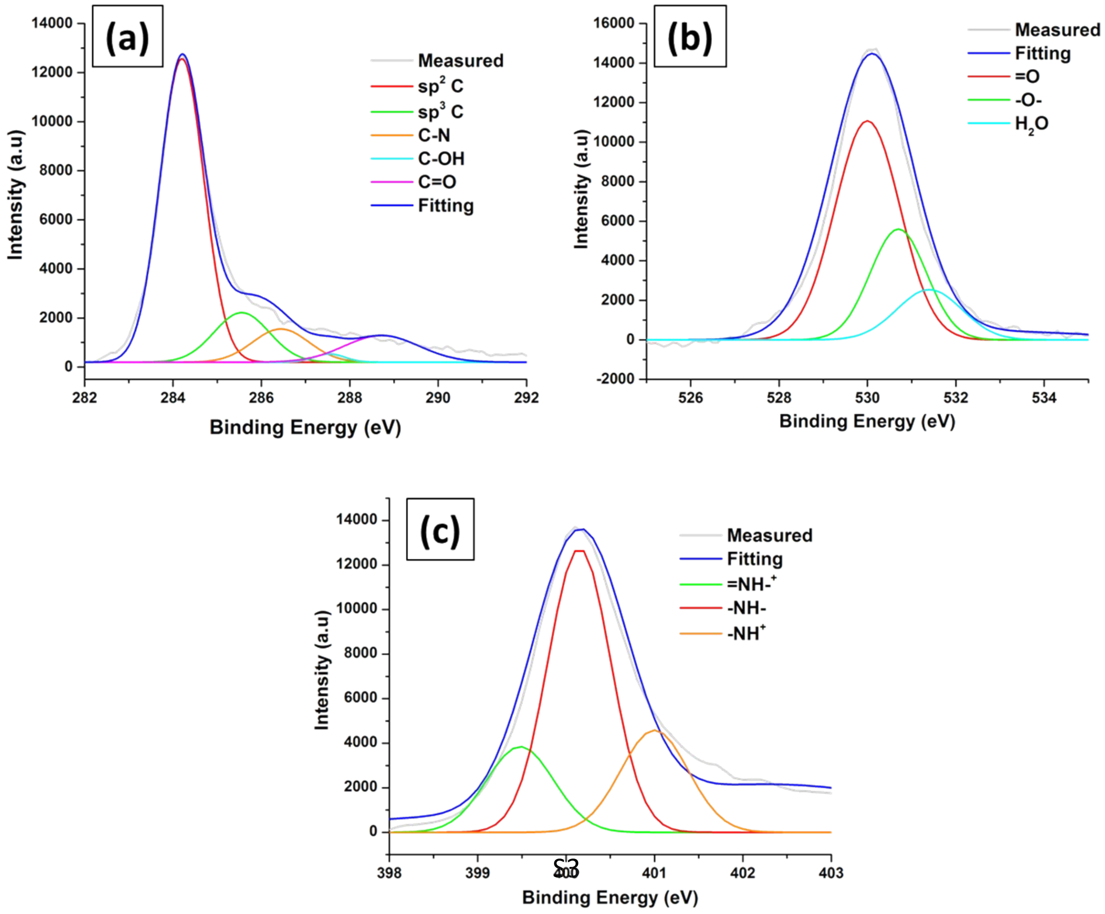
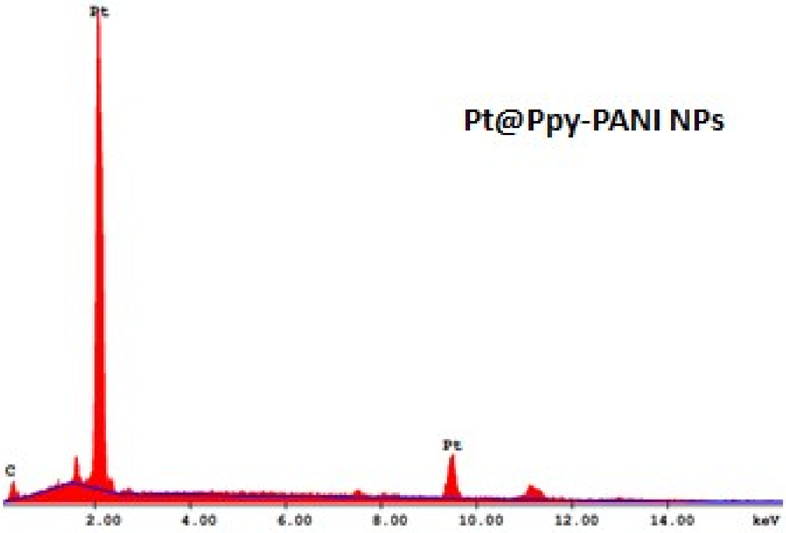


Fig. S2. The C1s (a), O1s (b) and N1s (c) XPS spectra of Pt@PPy-PANI NPs.

Table S3. The comparison of particle size, ECSA, SSA and Pt utilization for the prepared catalysts.

	Particle size (nm)	**ECSA (m^2 g^{-1})**	**Roughness factor (R_f)**	**SSA (m^2 g^{-1})**	**Pt utility (%)**
Pt NPs@PPy-PANI	3.176	78.13	293.56	89.68	87.12
Pt NPs@PPy	3.539	42.29	117.45	59.85	70.65
Pt NPs@PANI	3.969	68.52	187.93	80.75	84.85



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Element    Wt %    At %   K-Ratio     Z        A        F
  C K      5.39   48.06   0.0120   1.3729   0.1627   1.0000
  PtL     94.61   51.94   0.9102   0.9588   1.0034   1.0000
 Total   100.00  100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error       P/B
 C K       72.97        12.98         5.71          5.62
 PtL      487.81        53.67         2.09          9.09
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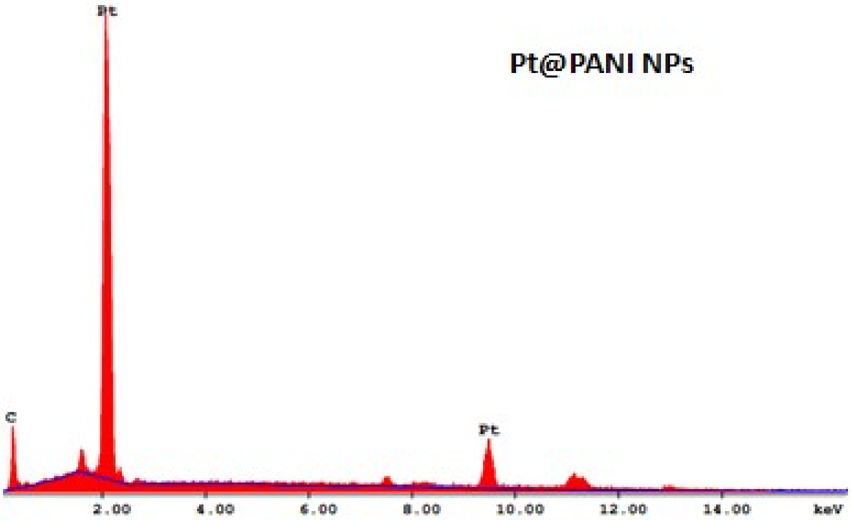

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Element    Wt %    At %   K-Ratio     Z        A        F
  C K     14.19   72.87   0.0336   1.3077   0.1812   1.0000
  PtL     85.81   27.13   0.7790   0.9002   1.0084   1.0000
 Total   100.00  100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error       P/B
 C K      206.27        12.16         2.91         16.96
 PtL      422.83        36.33         2.08         11.64
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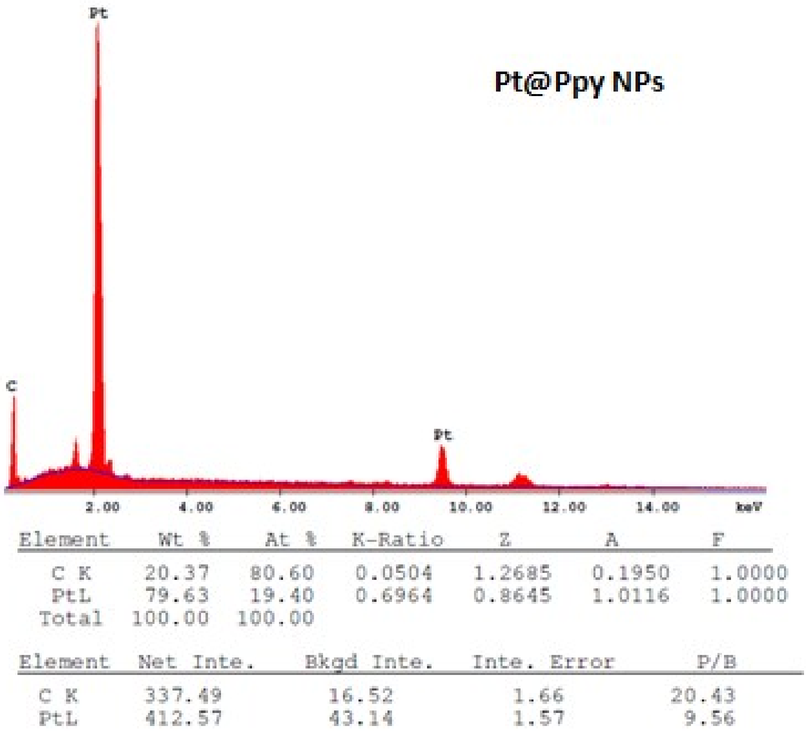

Element	Wt %	At %	K-Ratio	Z	A	F
C K	20.37	80.60	0.0504	1.2685	0.1950	1.0000
PtL	79.63	19.40	0.6964	0.8645	1.0116	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	337.49	16.52	1.66	20.43
PtL	412.57	43.14	1.57	9.56

Fig. S3. The comparison of SEM-EDAX for the prepared catalysts

Electrochemical measurements

Electrocatalytic measurements have been carried out using microcomputer-controlled potentiostat/galvanostat (Gamry Interface 1000). A glassy carbon electrode of 3 mm in diameter was carefully polished with alumina powder until a mirror finish was obtained. Then, the electrode was ultrasonically cleaned with methanol and deionized water alternant and dried in the air at room temperature. In order to prepare the catalyst ink, 1 mg of the catalyst was dispersed into 40 µL 0.5 % Nafion solution and 2 mL deionized water and ultrasonically treated for 30 min. 2 µL of the dispersion was coated on the GCE with a micropipette and let it dry in air. A conventional, three-electrode cell consisting of the GC (glassy carbon) working electrode, Pt wire, as counter electrode, and Ag/AgCl reference electrode was used for the cyclic voltammetry (CV) and chronoamperometry (CA) experiment. The CV and CA experiments were performed in 0.5 M H_2SO_4 solution in the absence and presence of 0.5 M methanol at a scan rate of 50mVs^{-1}. The cyclic voltammograms and chronoamperometry of Pt NPs@PANI, Pt NPs@PPy and Pt NPs@PPy-PANI catalysts for the electro-oxidation of methanol were recorded at a sweep rate of 50 mVs^{-1}in 0.5 M H_2SO_4 + 0.5 M methanol.

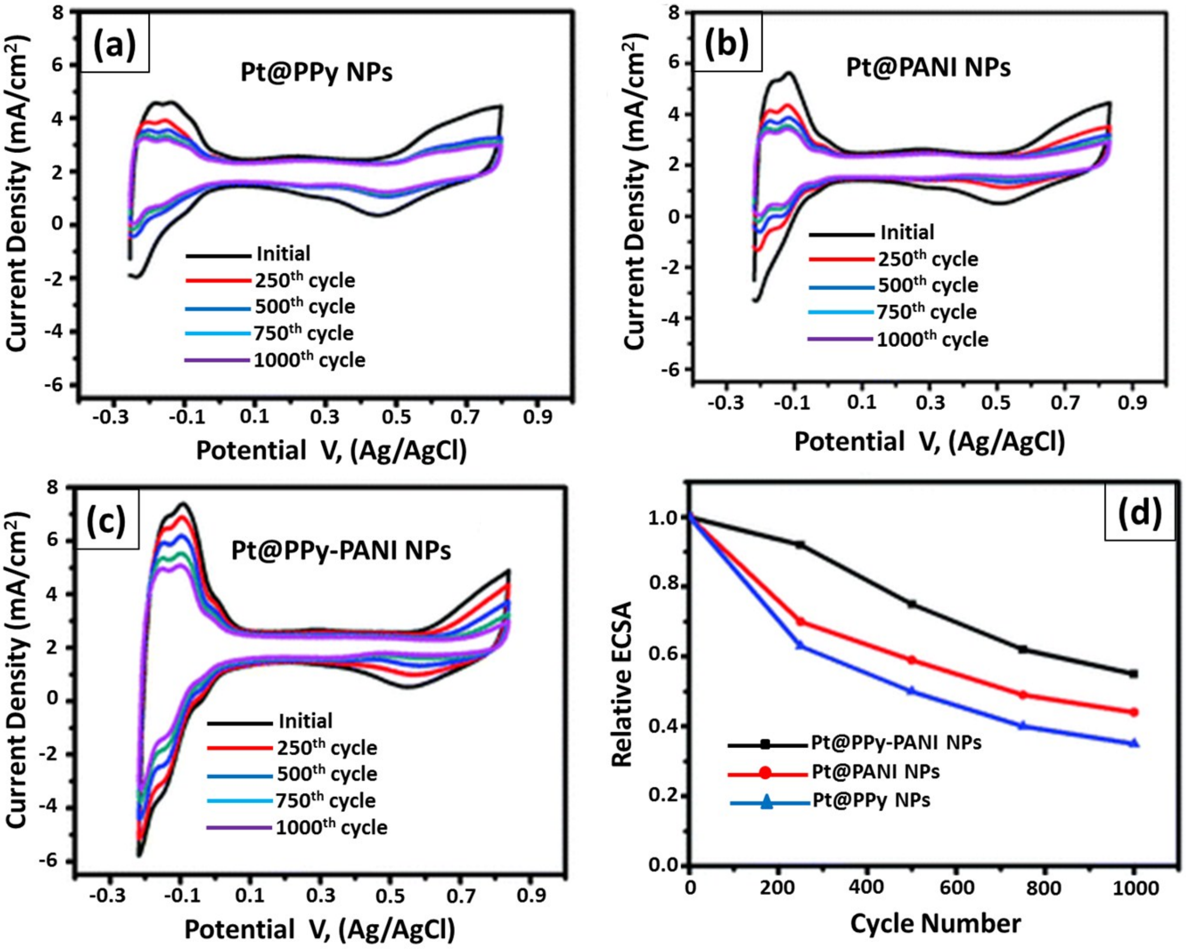

Fig. S4. Cyclic voltammograms of (a) Pt@PPy NPs, (b) Pt@PANI NPs (c) Pt@PPy-PANI NPs in nitrogen saturated solution of 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} and (d) their relative ECSA graph

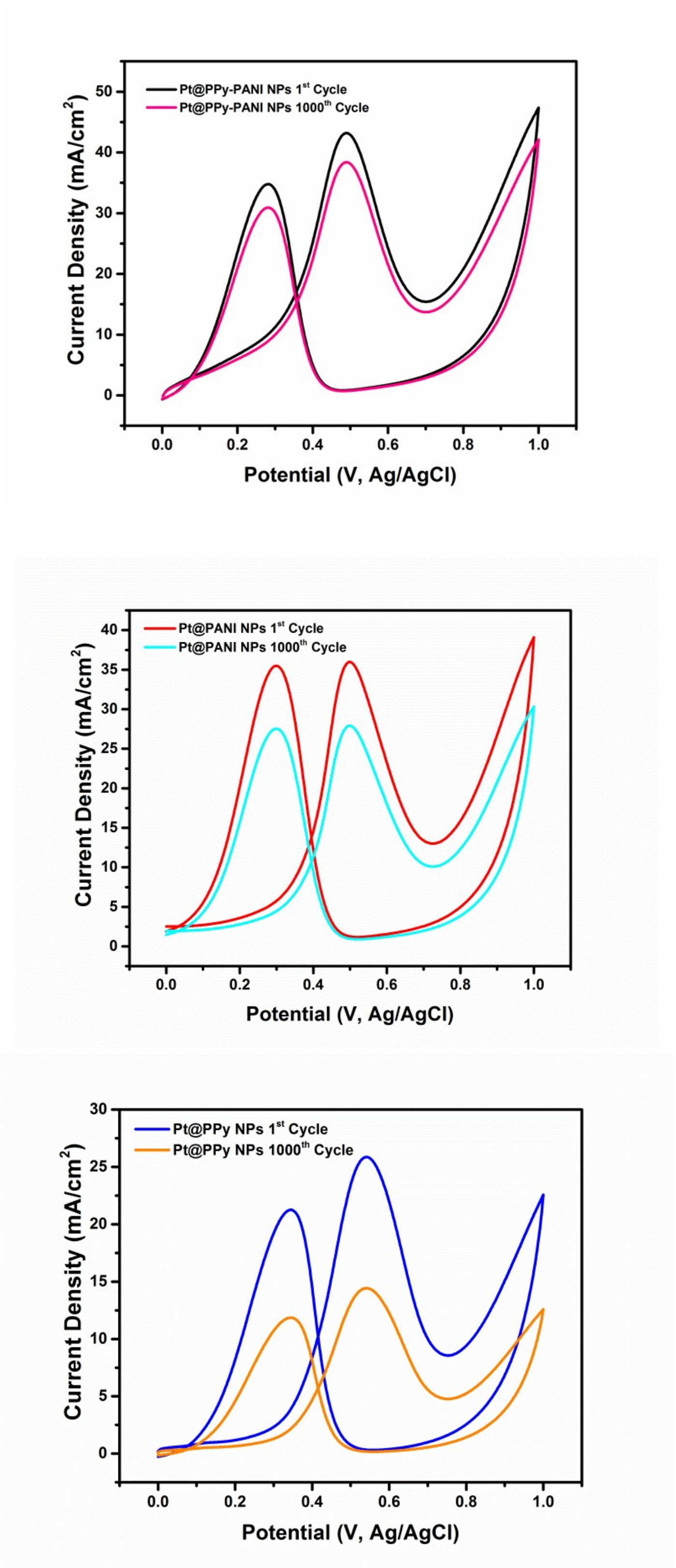

Fig. S5. Catalytic life time measurements of Pt@PPy NPs, Pt@PANI NPs and Pt@PPy-PANI NPs in nitrogen saturated solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at a scan rate of 50 mV s^{-1} at a 1st and 1000th cycle (vs. Ag/AgCl).

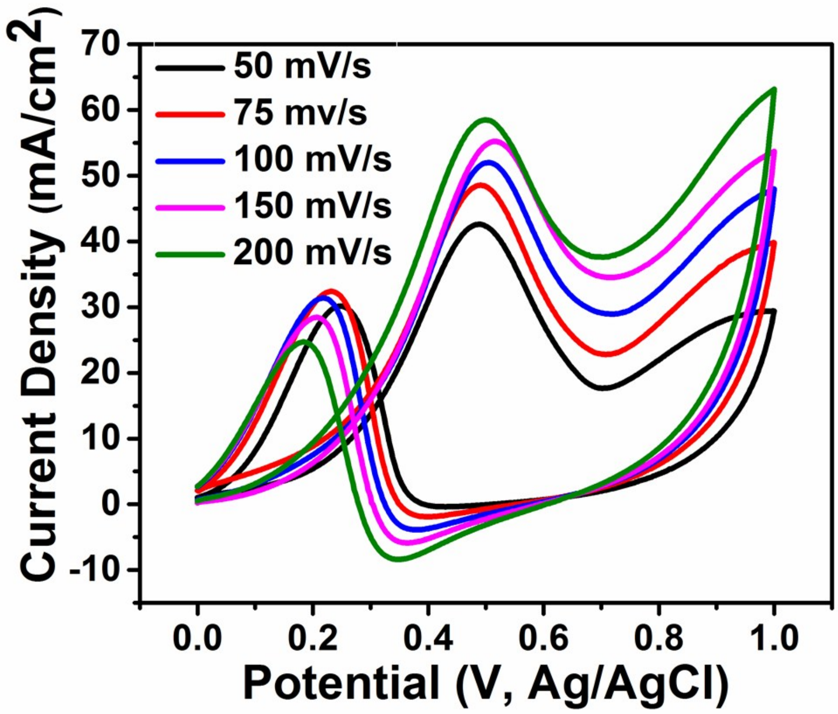

Fig. S6. Cyclic voltammograms of Pt@PPy-PANI NPs in nitrogen saturated solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at different scan rates.

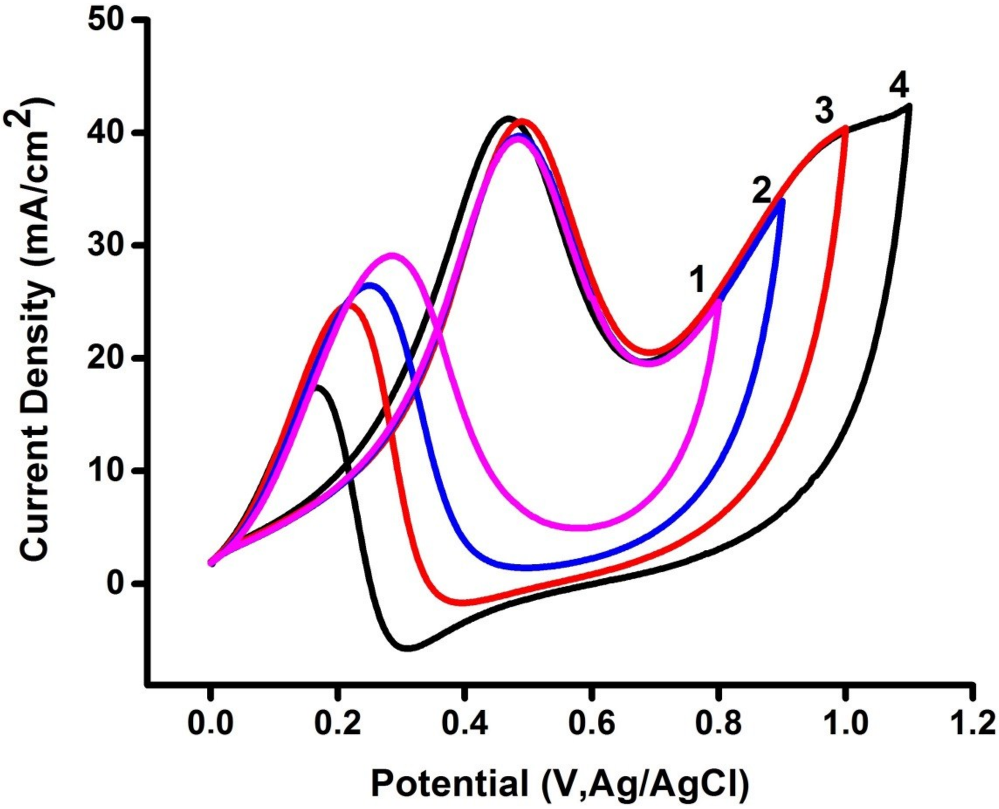

Fig. S7. Cyclic voltammograms of Pt@PPy-PANI NPs in nitrogen saturated solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at different switching potentials.