Supporting Information

Mechanistic Insight of Enhanced Hydrogen Evolution Reaction Activity of Ultra-Thin *h*-BN Modified Pt Electrodes

Anku Guha,[1#] Thazhe Veettil Vineesh,[1#] Archana Sekar,[1#] Sreekanth Narayanaru,[1#] Mihir Sahoo,[2] Saroj Nayak,[2] Sudip Chakraborty,[3,*] and Tharangattu N. Narayanan[1,*]

[1]Tata Institute of Fundamental Research - Hyderabad, Sy. No.# 36/P, Gopanapally Village, Serilingampally Mandal, Ranga Reddy District, Hyderabad 500107, India.
E-Mail: tnn@tifrh.res.inor tn_narayanan@yahoo.com (T. N. N.)

[2]School of Basic Sciences, Indian Institute of Technology, Bhubaneswar, Odisha 751013 India.

[3]Materials Theory Division, Uppsala University, Box-516, Uppsala, Sweden.
E-Mail: sudiphys@gmail.com (S.C.)

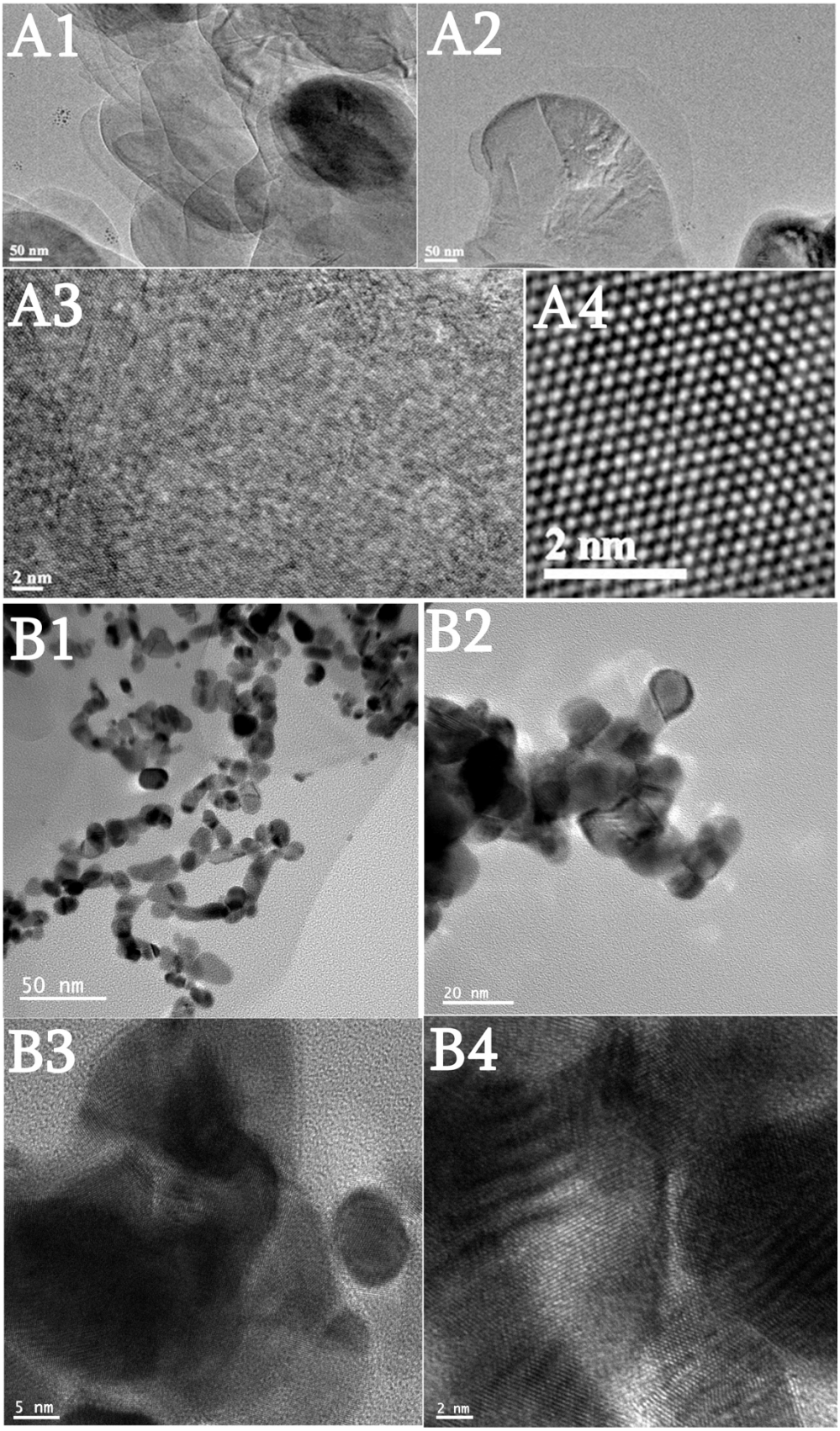
A1
50 nm
A2
50 nm
A3
2 nm
A4
2 nm
B1
50 nm
B2
20 nm
B3
5 nm
B4
2 nm

Figure S1: TEM and HR-TEM images of, (A1-A4) shear exfoliated hBN sheets, and (B1-B4) platinum nanopartcles (Pt NP, without hBN). The average size of the particles is found be 5 nm and they are spherical in shape.

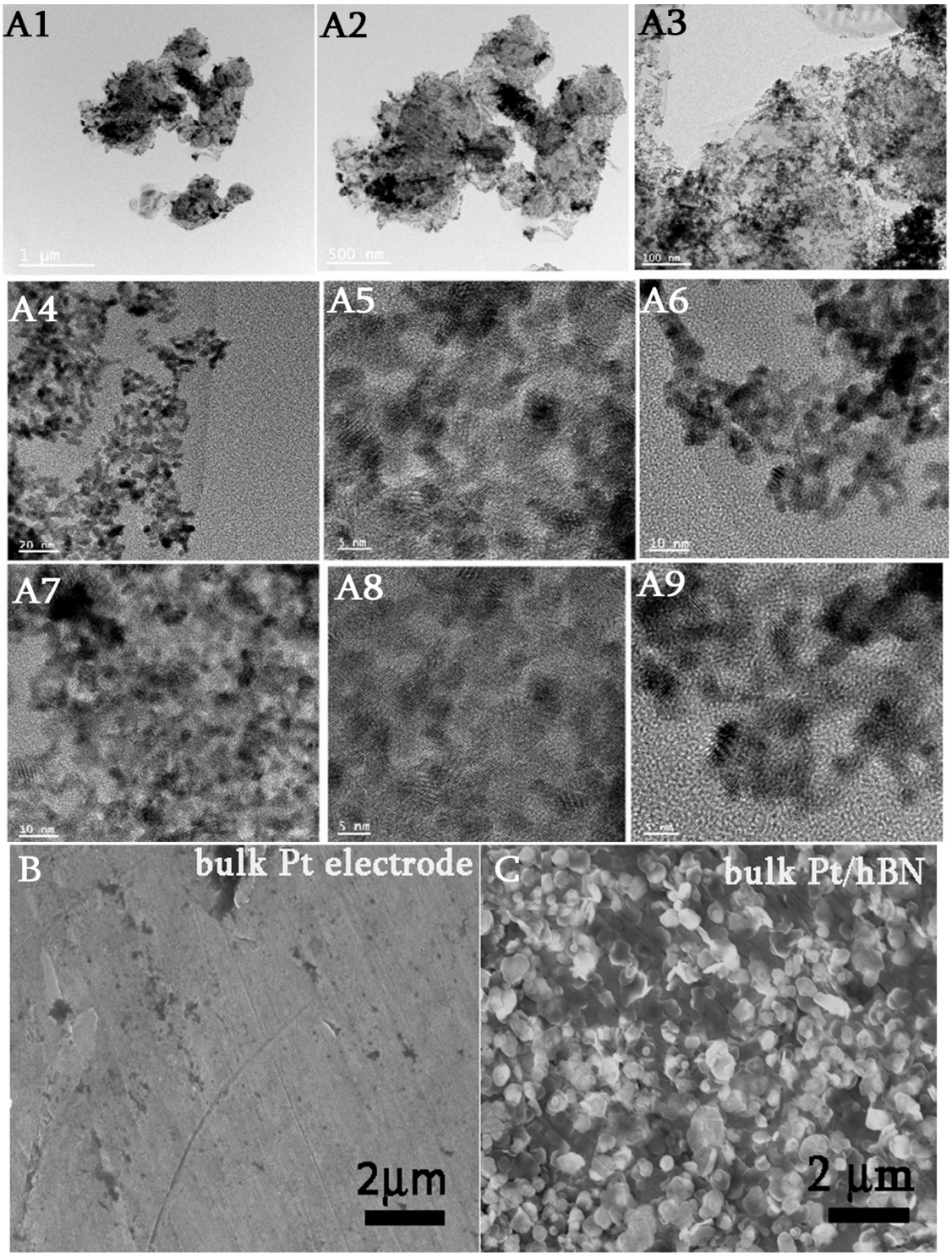

Figure S2: (A1-A9) TEM and HR-TEM images of Pt/hBN showing the presence of nanocrystalline Pt nanoparticles decorated on hBN surfaces. (B) and (C) SEM images of bulk Pt (electrode) and bulk Pt modified with shear exfoliated hBN (with Nafion binder).

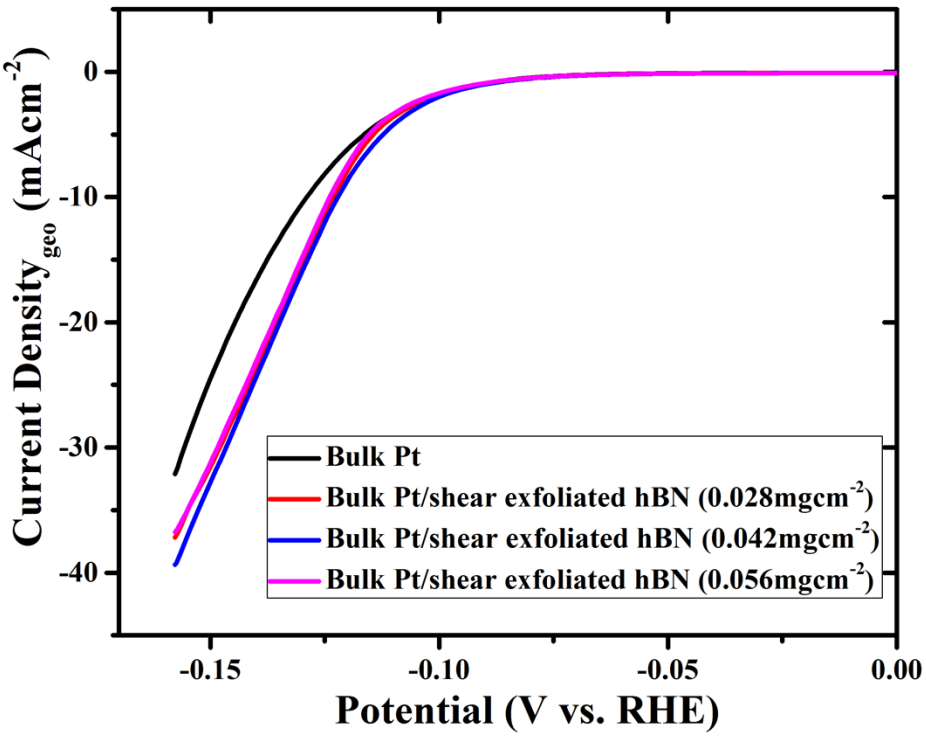

Figure S3: LSVs of different amount of hBN loaded bulk Pt electrode.

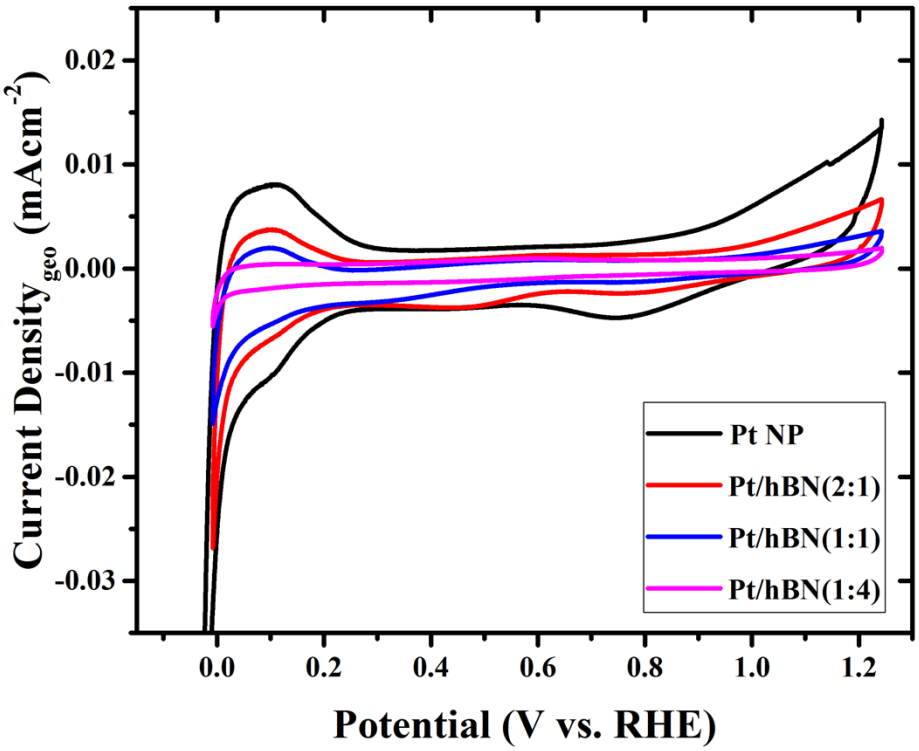

Figure S4: Pt response variation in different Pt/hBN composites.

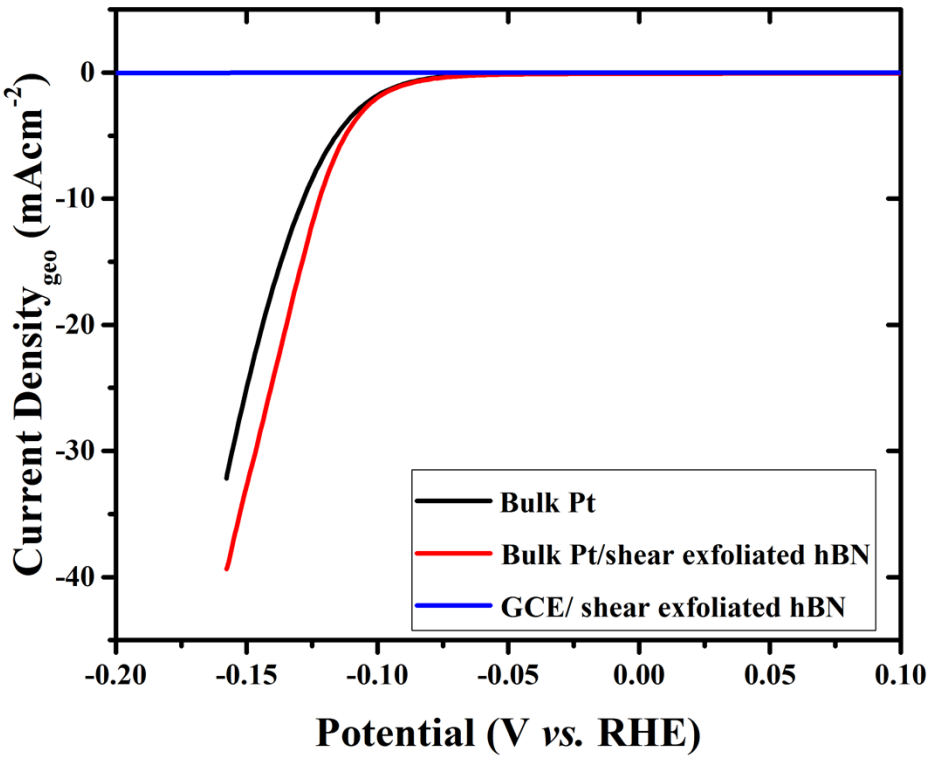

Figure S5: LSVs of bulk Pt (Pt 3mm electrode), Bult Pt/ shear exfoliated hBN and GC electrode (GCE) modified shear exfoliated hBN electrode at 50 mV/s in 0.5 M H_2SO_4.

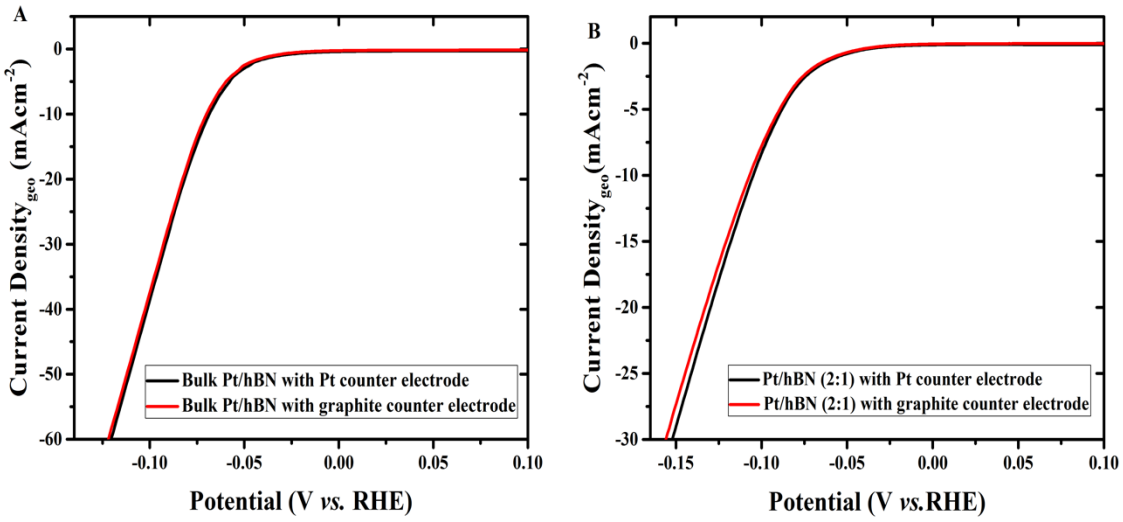

Figure S6: LSVs of Pt/hBN ((A)Pt bulk electrode, (B) Pt NP) in 0.5 M H_2SO_4 (scan rate, 50 mV/s) with both Pt electrode as counter electrode and graphite electrode as counter electrode, showing negligible variations in the current densities on onset potentials.

Geometrical and Electrochemically active surface area calculation :

The diameter of the GC/Pt electrode is 3mm. The geometrical surface area = 0.07 cm^2 (πr^2). Electrochemically active surface area (ECSA) of the catalyst was calculated based on the CVs (shown in **figure S7**) by measuring the surface area under the H_{upd} desorption area (A). Scan rate for measuring these CVs is 0.2 V/s. The following formula is used to calculate the ECSA = A/(0.2 X 210) cm^2 where 210 µC/ cm^2 is the charge associated with hydrogen adsorption on Pt surface[1, 2]. All electrochemical experiments were performed using Saturated Calomel Electrode

(SCE) as reference electrode then converted into Reverse Hydrogen Electrode (RHE) by $E_{RHE} = E_{SCE} + 0.242 + 0.0591 \text{ X pH}$, here pH = 0.

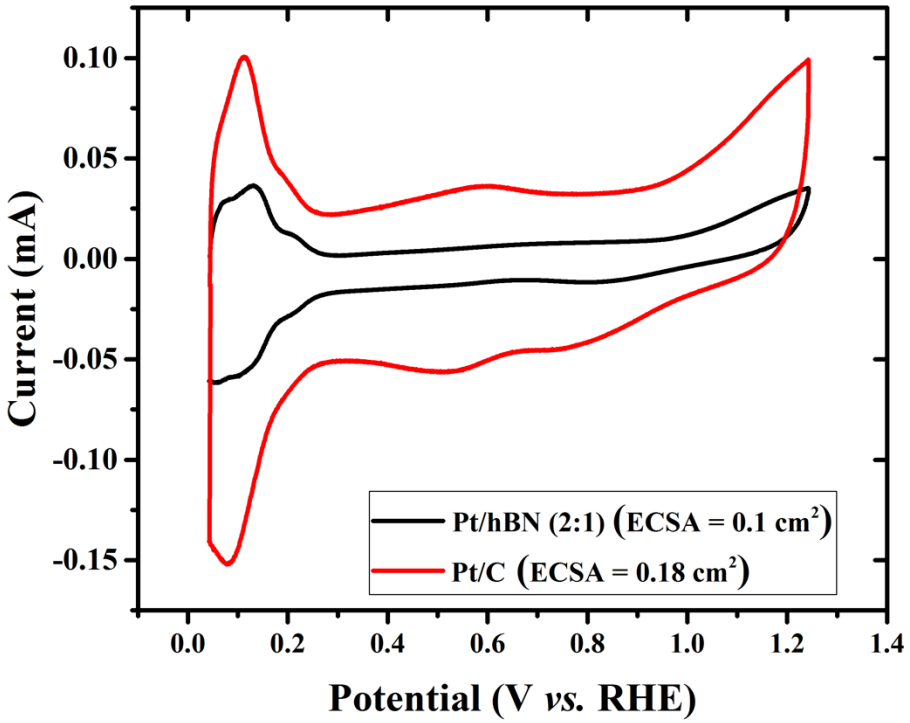

Figure S7: Scan rate for measuring these CVs is 0.2 V/s in 0.5 M H_2SO_4.

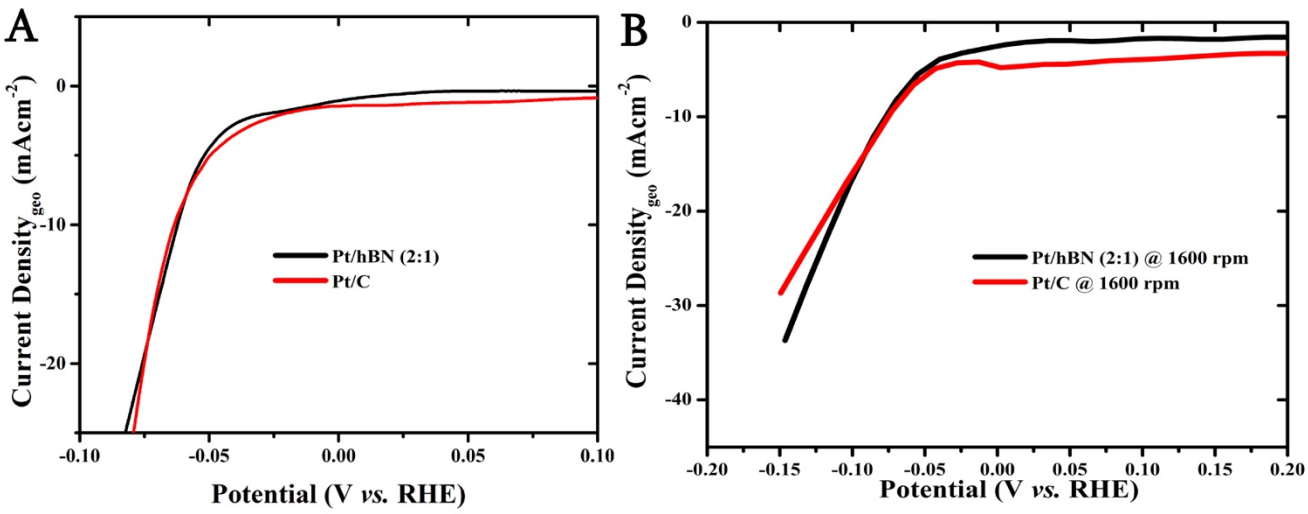

Figure S8: (A) The LSVs at 50 mV/s scan in 0.5 M H_2SO_4. (B) LSV at 50 mV/s scan in 0.5 M H_2SO_4 with rotating electrode having the rotation of 1600 rpm.

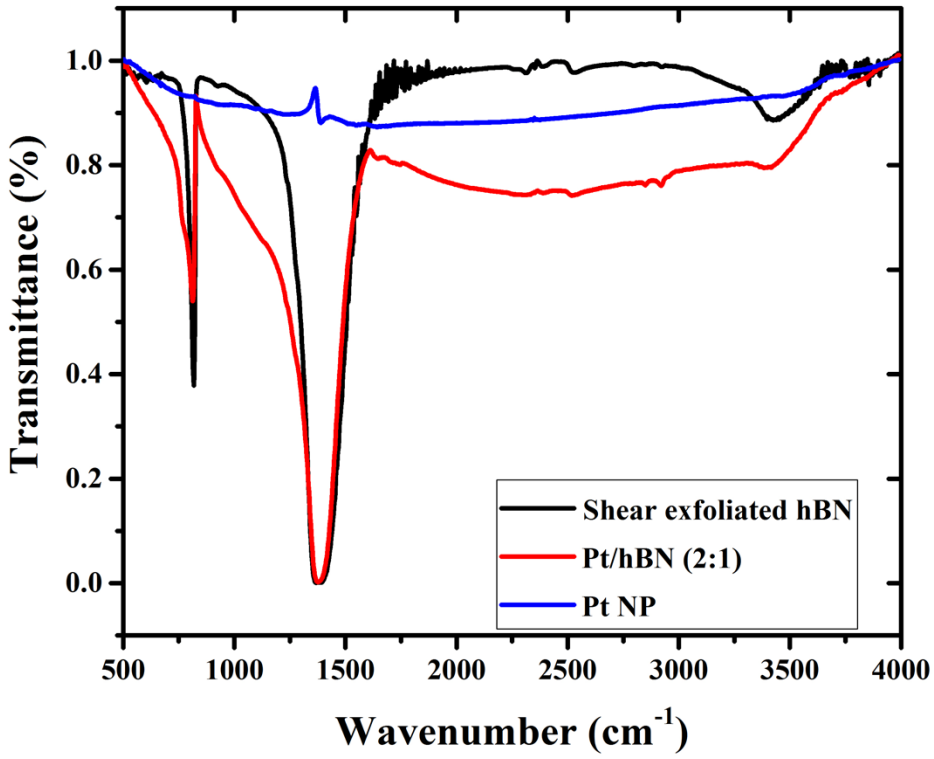

Figure S9: FT-IR spectra of Pt/hBN (2:1), Pt NP, and shear exfoliated hBN,

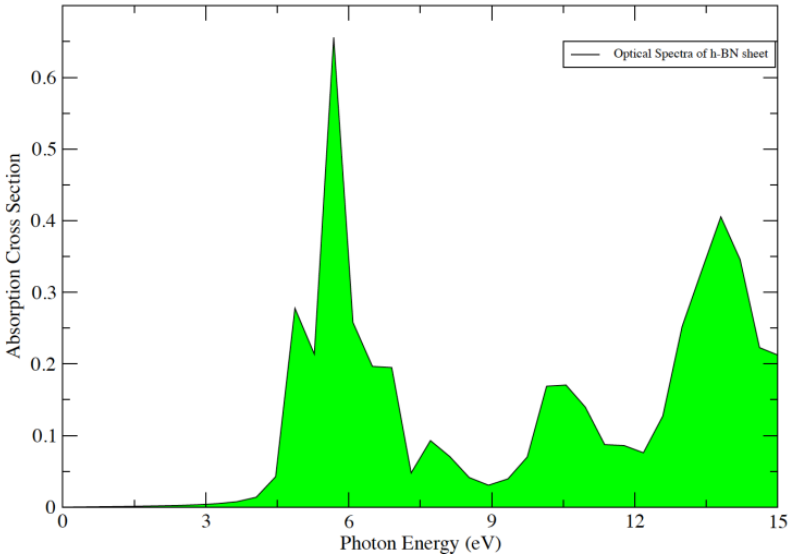

Figure S10: Optical absorption spectra of hBN.

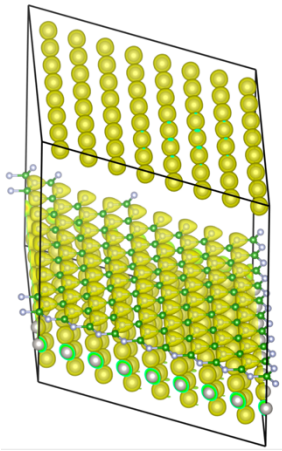

Figure S11: The charge distribution for Pt/hBN system from DFT calculation, where it indicates a uniform charge distribution between Pt and hBN sheet.

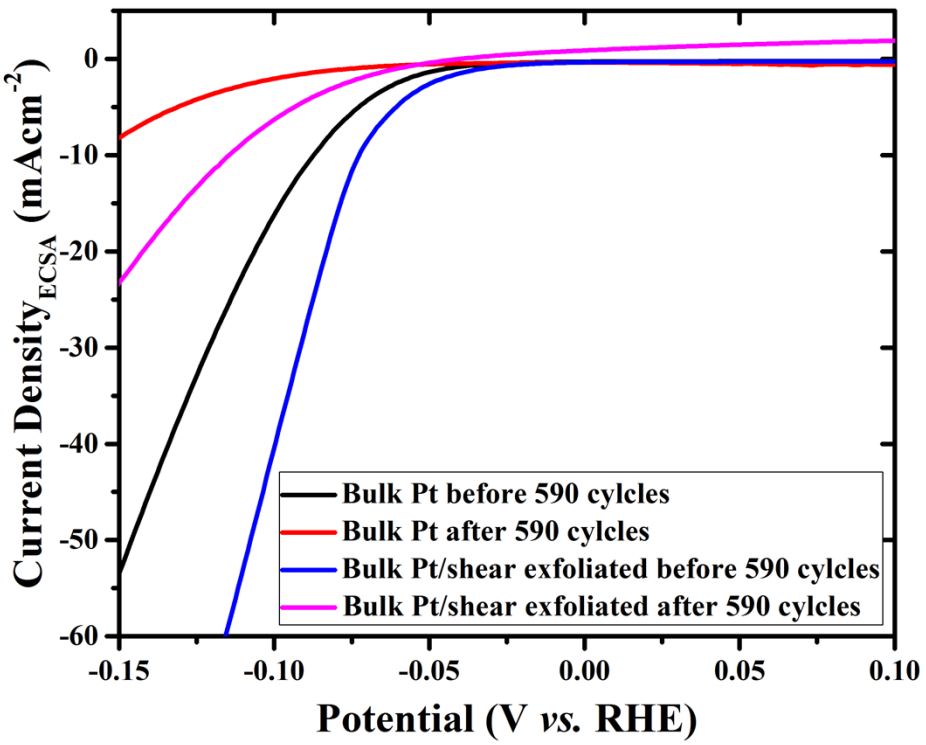

Figure S12: The electrochemical stability performance of the bulk Pt (Pt 3mm electrode) and bulk Pt modified with shear exfoliated electrode. The current densities are based on ECSA, while similar results can be obtained with geometrical area based calculations too.

References:

(1) Biegler, T.; Rand, D. A. J.; Woods, R. Limiting Oxygen Coverage on Platinized Platinum; Relevance to Determination of Real Platinum Area by Hydrogen Adsorption. J. Electroanal. Chem. 1971, 29, 269–277.

(2) Bett, J.; Kinoshita, K.; Routsis, K.; Stonehart, P. A Comparison of Gas-Phase and Electrochemical Measurements for Chemisorbed Carbon Monoxide and Hydrogen on Platinum Crystallites. J. Catal. 1973, 29, 160–168.