Supplementary Information

Tuning Palladium(II)Phthalocyanine Embedded Hybrid Electrocatalyst for Hydrogen Evolution Reaction

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S1. Experimental section

S1.1. Materials: Palladium chloride (Pd(II)Cl₂,99.9%), 4- nitrophthalonitrile (>98%), 1pentanol (C₅H₁₂O,>98%), 1,8-diazabicyclo[5,4,0] undec-7-ene (DBU), dimethyl sulfoxide (DMSO,C₂H₆OS), methanol (CH₃OH, 99.8%), ethanol (C₂H₅OH,99.5%), chloroform (CHCl₃,99.5%), acetone (C₃H₆O,99.5%), hexane (C₆H₁₄,98.5%), tetra-butylammonium perchlorate (TBAP), potassium hexacyanoferrate(II) [K₄Fe(CN)₆] were purchased from Sigma-Aldrich, India. Double-distilled water was used for all the experiments. All chemical reagents were of analytical grade and used in the work with no further purification.

S2. Characterization

The synthesized Pd(II)TNPc complex was analyzed by a Vario EL III (C,H,N & S) elemental analyzer to determine the elemental composition (%) of C, H and N elements. The UV-visible absorption spectrum of Pd(II)TNPc was measured by an Ocean Insight Spectrometer (FLAME-SUV-VIS-ES; Serial no. FLS 04808). The Pd(II)TNPc complex in DMSO (0.1 mM) was used for recording the electronic absorption spectrum in the region of 280-850 nm. The FT-IR spectra of the precursor 4-NPN and Pd(II)TNPc complex were recorded on a PerkinElmer Spectrum in the wavenumber range of 400-4000 cm⁻¹ using the KBr pellet method. The stability of palladium(II) phthalocyanine is studied in the temperature range of 50-800 °C with an STA 6000 simultaneous thermal analyzer (PerkinElmer) with a scan rate of 20 °C.min⁻¹ under air flow (20 mL.min⁻¹). The surface morphology was imaged using a field-emission scanning electron microscope (FE-SEM, Scanning Electron Microscope, Carl Zeiss, Germany, Model: EVO LS 15) at 30kV. The FE-SEM was coupled with energy-dispersive X-ray spectroscopy (EDX) to identify the elemental composition of the complex. The transmission electron microscope (HR-TEM) and HAADF-STEM images were recorded using instrument TALOS 200FG2 at 200 kV. The mass spectra (2.5 kV, electron impact

mode) were measured with an instrument Mass spectrometer-MS model: Waters; Synapt G2 High detection Mass spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a SPECSMXPS system. The deconvolution of the high-resolution XPS spectral peaks was obtained using origin 8.5 software and XPS peak 4.1.

S3. Proposed mechanism for the synthesis of palladium(II) tetranitrophthalocyanine:

The reaction involves the nucleophilic attack of the chloride anion formed by the deprotonation of the DBU (Scheme-I) on the electron-deficient carbon of one of the nitrile groups of 4-NPN, resulting in the formation of the intermediate 1-chlorate-3-iminoisoindolenine, which further undergoes coordination with Pd. Then, a sequential cyclic nucleophilic attack by the anionic nitrogen of iminoisoindolenine intermediate on the nitrile group of another 4-NPN leads to the formation of Pc complex (II, III steps in Scheme I) with Pd(II) as a central metal core, i.e, 4-NPN undergoes tetramerization at high temperature with Pd²⁺ via coordination bond to form Pd(II)TNPc complex. The Pc macrocycle formation involves a number of bond formations and transformations including –C-C & -C-N, cyclization, tetramerization, and coordination of the chelate with Pd²⁺ metal ion to form palladium(II)tetranitrophthalocyanine complex.



Scheme S1. Mechanism for the synthesis of Pd(II)TNPc

a. 4-Nitrophthalonitrile



Figure S1. Mass spectrum of precursor 4-nitrophthalonitrile with m/z of 191.06 [M+H₂O]

b. $Pd(II)TNPc (C_{32}H_{12}N_{12}O_8Pd)$



Figure S2. Mass spectrum of Pd(II)TNPc with m/z at 815.17 $[M+H_2O]^{-2}$



Figure S3. SEM image of pristine Pd(II)TNPc on Torey carbon



Figure S4. (a,b) HR-TEM images of hybrid Pd(II)TNPc+KB at 200 nm and 10 nm scale, and (c,d) respective FFT image, location of crystal plane is shown in HR-TEM image of Fig. S4 (b)

Figure S5. LSV polarization curves of Pd(II)TNPc+KB at different ratios for HER in 0.5 M

H₂SO₄.

Figure S6. LSV polarization curves for TNPc and TNPc+KB (3.5:1.5 ratio) modified

electrodes for HER studies in 0.5 M H_2SO_4 at 5 mV/s scan rate.

Figure S7. Cyclic Voltammograms measured in the non-Faradaic region of 0.3 to 0.5 (V vs RHE)for a) bare GCE, b) GCE/Pd(II)TNPc, c) GCE/Pd(II)TNPc+KB, and d) GCE/Pt/C electrodes.

Figure S8. The exchange current densities for a) bare GCE, b) GCE/Pd(II)TNPc, c) GCE/KB, d) GCE/Pd(II)TNPc+KB, and e) GCE/Pt/C electrodes.

Figure S9. Chronoamperometric (i-t) curve for HER activity at Pd(II)TNPc+KB hybrid in $0.5 \text{ M H}_2\text{SO}_4$ at an applied potential of -0.187 V for 22 hours.

The long-term stability of the hybrid Pd(II)TNPc+KB was assessed using the chronoamperometry technique by holding the potential at -0.187 V (vs RHE) in 0.5 M H₂SO₄. Figure S10 represents the chronoamperometric (I-t) response for HER activity and the designed Pd(II)TNPc+KB hybrid electrode demonstrated superior stability for 22 hours on a continuous potential hold. The SEM image recorded for the stability performed electrode was compared with the fresh electrode.

Figure S10. SEM images of Pd(II)TNPc+KB composite for fresh and after

chronoamperometric (i-t) study.

Figures S10. (a) & (b) display the SEM images of the fabricated hybrid Pd(II)TNPc+KB electrode before and after the chronoamperometric study. The SEM images of both the electrodes displayed uniform adherence of the palladium phthalocyanine macrocycle with KB in a cage-like chain connectivity. The morphology of the stability performed electrode surface indicated that Pd(II)TNPc+KB does not undergo any degradation in structure or leaching during chronoamperometric study and is found to be extraordinarily stable even after 22 hours. The excellent stability of the composite may be ascribed to effective π - π interaction and electrochemical stability.

| Table S1. Comparison of Pd(II)TNPc with reported N-4 macrocyclic derived | | | | |
|--|--------------------------------------|-----------------------------|-------------------|------|
| electrocatalysts for HER. | | | | |
| Electrocatalysts | Electrolyte | Overpotential | Stability | Ref |
| | | $(\eta_{10}, V vs RHE)$ | | |
| | | at 10 mA cm ⁻²) | | |
| Co@NG-800 | 0.5 M H ₂ SO ₄ | 286 mV | 3000 cycles | 1 |
| n-Pd@NDCDs | 0.5 M H ₂ SO ₄ | 291 mV | 3500 s | 2 |
| Co-NHPC-900 | 0.5 M H ₂ SO ₄ | 230 mV | 10 h | 3 |
| Ni(PO ₃) ₂ /CNT | 0.5 M H ₂ SO ₄ | 87 mV | 10,000 cycles | 4 |
| Pt/C | 0.1 M HClO ₄ | 23.5 mV | 29.7% loss in | 5 |
| | | | mass activity | |
| | | | after 2000 cycles | |
| WS ₂ -ZnPc | 0.5 M H ₂ SO ₄ | 233 mV | 24 h | 6 |
| WS ₂ -CuPc | 0.5 M H ₂ SO ₄ | 285 mV | - | 6 |
| GCE/Pd(II)TNPc | 0.5 M H ₂ SO ₄ | 187 mV | 80 h | This |
| + KB | | | | work |

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