

Efficient hydrogen evolution electrocatalysis using nitrogen doped carbon dots decorated palladium copper nanocomposites in acid medium

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Experimental

Materials

The *M. citrifolia* fruit was purchased from the local market. Aqueous NH₃ (25%), CuSO₄·5H₂O, ethylene glycol (EG), sulphuric acid (H₂SO₄), and KOH were procured from Central Drug House (CDH) PdCl₂, and potassium ferricyanide purchased from Sigma-Aldrich were used. All electrolytic solutions were prepared with double distilled (DD) water. The electrodes purchased from Sinsil International Pvt. Ltd., Bengaluru, India were used.

Synthesis of NDCDs from *M. citrifolia* extract

100 g of *M. citrifolia* fruit was washed and ground well with 50 mL of DD water, the resultant extract was filtered. In a typical hydrothermal process, 58 mL of extract and 2 mL of aq.NH₃ were taken in 100 mL autoclave and kept at 180 °C for 12 h. Then it was cooled naturally and filtered by Whatmann No. 40 paper. The final brown colored solution was centrifuged to remove the larger particles and was kept in the refrigerator for future studies.

Synthesis of n-PdCu@NDCDs composite

In typical synthesis, an aqueous solution of PdCl₂ (3.3 mg/mL, 3.8 mL), 20 mg of CuSO₄·5H₂O, and 50 mg of glutamate were mixed with 40 mL of ethylene glycol (EG). The pH of the mixture was adjusted to ca. 11 by the addition of 8 wt% KOH/EG solution under constant stirring. Subsequently, 30 mg of NDCDs were added to the solution and sonicated for 2 hr to obtain a homogeneous suspension. The resultant solution was subjected to solvothermal process at 160° C for 6 hr. After the reaction was completed, the product was filtered and washed several times with DD water and dried at 40° C for 8 hr. The final product was denoted as n-PdCu@NDCDs. For comparative study, similar procedure of n-PdCu@NDCDs was followed for synthesizing PdCu alloy without adding NDCDs.

Characterization of n-PdCu@NDCDs

The surface morphology of the synthesized catalyst were analyzed by the FEI Tecnai G² 20 S-TWIN HR-TEM operating at 200 kV available at Madurai Kamaraj University, Madurai, India. The elemental composition of synthesized n-PdCu@NDCDs was analyzed using a BRUKER Nano, GmbH, D-12489 Energy dispersive X-ray spectroscopy with an accelerating voltage of 30 keV. The XRD pattern of the prepared catalyst was investigated by PANalytical X'Pert diffractometer equipment using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) operating at 45 kV and 40 mA. The Raman spectrum of the synthesized n-PdCu@NDCDs was acquired using STR 500 nm focal length laser Raman spectrometer. The FT-IR spectrum was recorded over the wavenumber range of 400–4000 cm^{-1} using Jasco FT- IR 460 Plus. The electronic states present over n-Pd@NDCDs were analyzed using PHI 5000 Versa Probe II XPS analyzer.

Electrochemical measurements

Electrocatalytic activity of n-PdCu@NDCDs towards HER was investigated by linear sweep voltammetry (LSV), Tafel and electrochemical impedance spectroscopy (EIS) measurements in 0.5 M H₂SO₄. The electrochemical measurements were carried out with Princeton Applied Research versa STAT 3 electrochemical workstation with a standard three electrode system. The glassy carbon (GC) (or) n-PdCu@NDCDs/GC (or) NDCDs/GC (or) Pt sheet (1 cm^2), Ag/AgCl, and Pt wire were used as the working electrode, reference electrode, and counter electrode, respectively.

Catalyst ink preparation

20 mg of synthesized catalyst were dispersed in a mixed solvent of 1.6 mL water and 0.4 mL ethanol and combined with 40 μL of 5% nafion solution to make a homogenous ink and it was coated on the GC electrode by drop casting method. Before coating the GC, it was polished by different micro polished alumina powders (1, 0.3, 0.05 micron) for several times until it reached the standard oxidation/ reduction potential of Fe²⁺/Fe³⁺ in cyclic voltammetry. This was performed in potassium ferricyanide (5.0 mM, containing 0.2 M KCl) solution using polished GC electrode as working electrode, Ag/AgCl as a reference electrode and platinum wire as a counter electrode, respectively. The calculated loaded amount of n-PdCu@NDCDs was about 0.05 mg.

Linear sweep voltammetry and Tafel slope measurements

The LSV measurement was carried out from 0 to -1.0 V_{RHE} with the scan rate of 10 mV/s for all three electrodes. Based on the equation (S2), all the potentials were converted into a reversible hydrogen electrode (RHE) without iR drop compensation.

$$E \text{ (vs.RHE)} = E \text{ (vs. Ag/AgCl)} + E_{\text{Ag/AgCl (ref)}} + 0.0591 \text{ V X pH (EAg/AgCl (ref) = 0.1976 V)} \quad (\text{S1})$$

$$\eta = a + b \log |j| \quad (\text{S2})$$

The Tafel slope was aroused from the eqn. (S2) where η was the overpotential, b and j were Tafel slope and current density, respectively.

EIS measurements

Electrochemical impedance spectroscopic (EIS) studies were made in the range of 10⁵ to 0.1 Hz at 5 mV of amplitude with different bias potentials and the results were fitted through a proper circuit.

Calculation of electrochemically active surface area

The electrochemically active surface area (ECSA) was calculated by the double layer capacitance (C_{dl}) and it was determined by cyclic voltammetry measurements. The potential window of 0.251 – 0.258, 0.257-0.259, and 0.261- 0.264 V_{RHE} was chosen for NDCDs, PdCu, and n-PdCu@NDCDs, respectively for cyclic voltammetric measurements at different scan rates from 10 – 100 mV/s in the non-faradic region, where the electrode was completely polarized. From this measurement, the double layer capacitance was derived from the slope of average current density versus scan rate from the linear fit values and it was directly related to the ECSA. Equation (S4) shows the relation between double layer charging current density (j_{dl}), scan rate (ν), and the double layer capacitance (C_{dl}).

$$j_{dl} = \nu C_{dl} \quad (\text{S3})$$

$$ECSA = C_{dl} / C_s \quad (\text{S4})$$

From equation (S5), the ECSA was calculated using the double layer capacitance (C_{dl}) and C_s , where C_s is specific capacitance of the sample in identical electrolyte solution.

Results and discussion

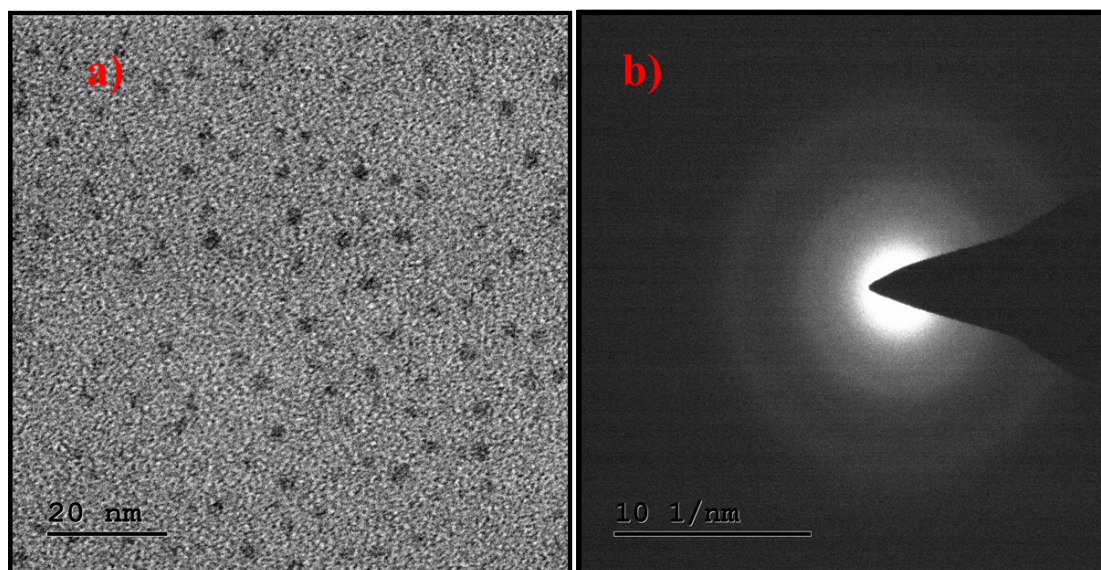


Fig. S1 (a) HR-TEM image of synthesized NDCDs at 20 nm scale (b) SAED pattern for synthesized NDCDs.

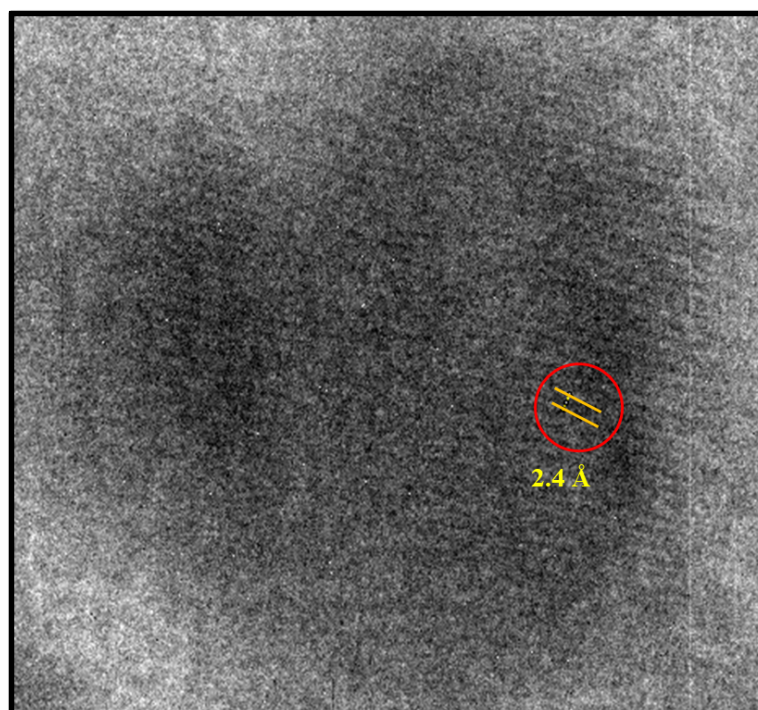


Fig. S2 HR-TEM image of synthesized n-PdCu@NDCDs at 5 nm scale

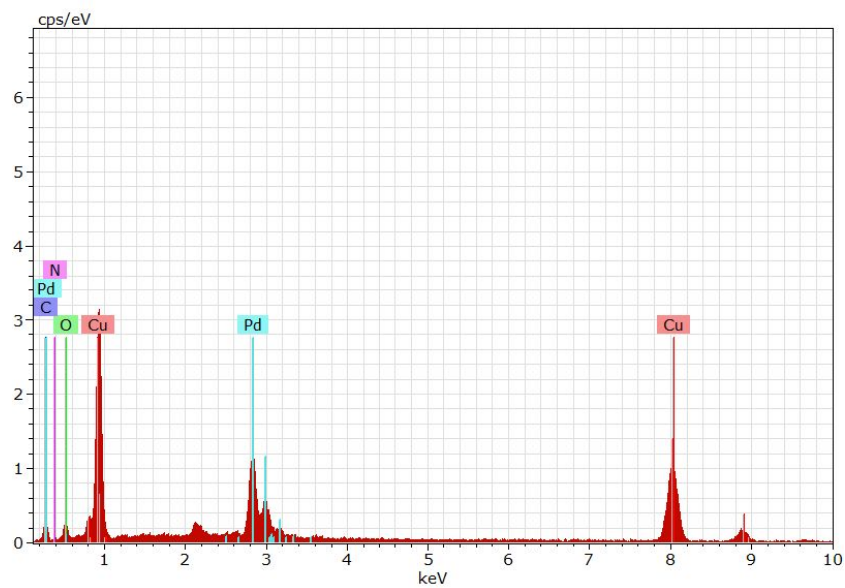


Fig.S3 EDS spectrum for the prepared n-PdCu@NDCDs composite

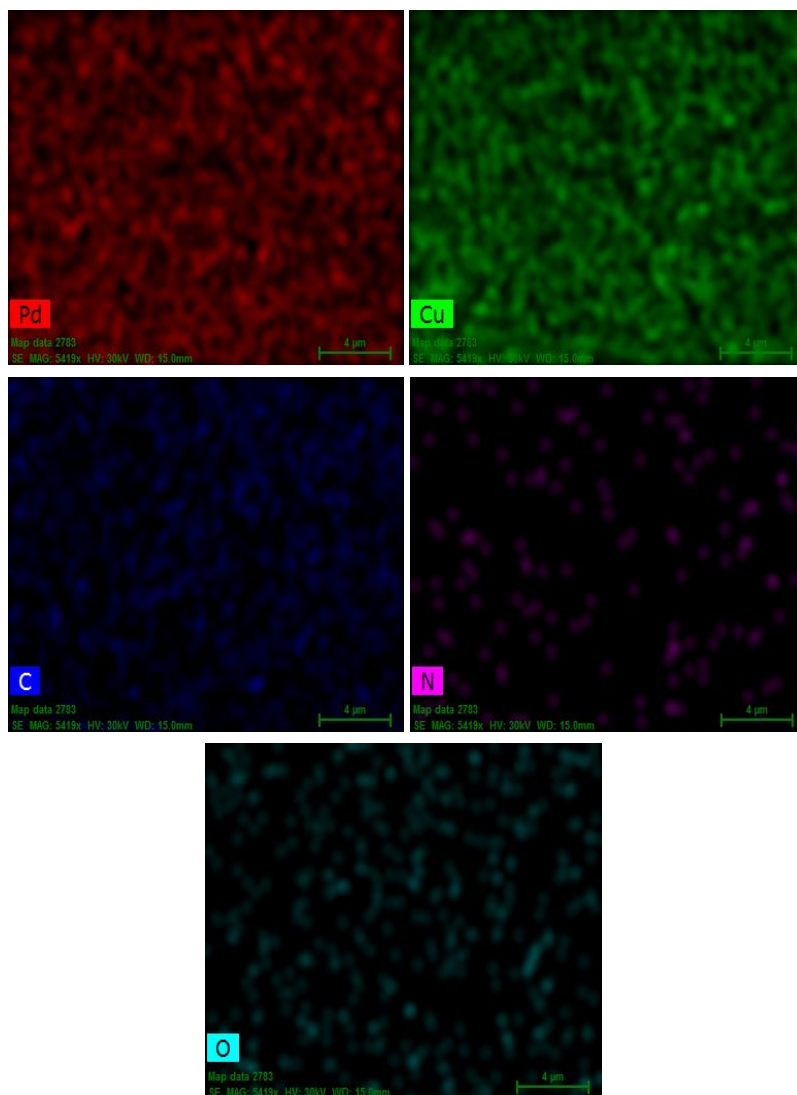


Fig S4. EDS mapping of the synthesized n-PdCu@NDCDs

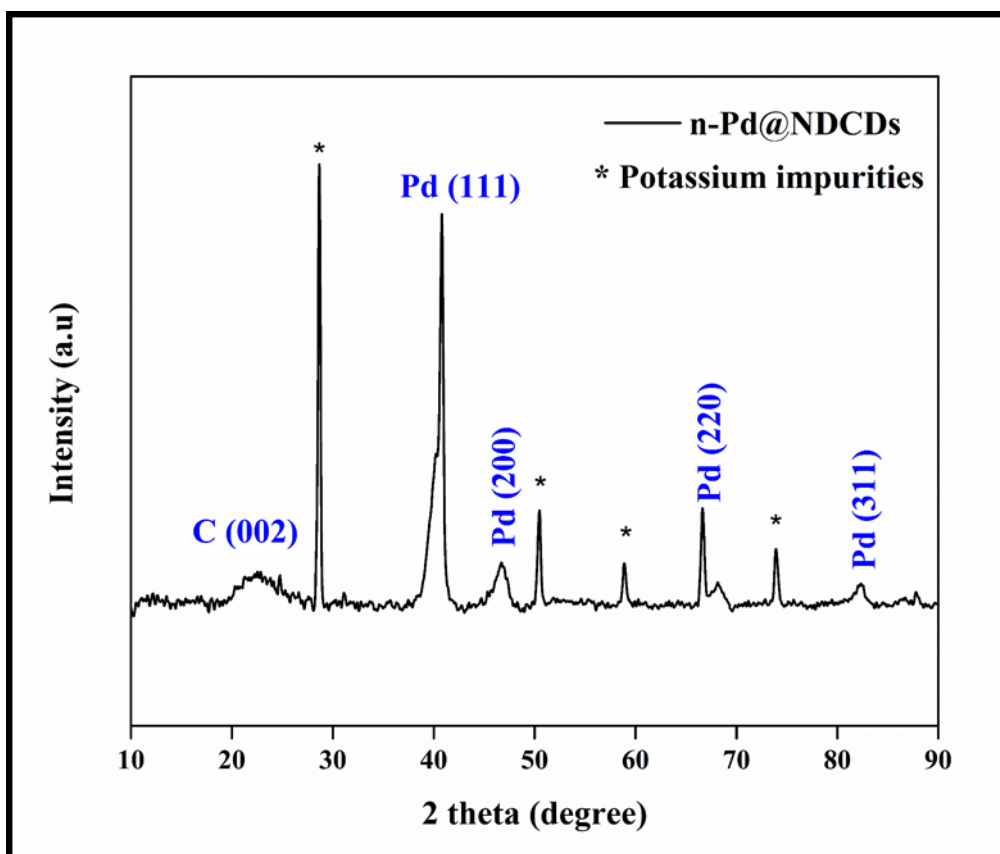


Fig S5. XRD pattern for n-Pd@NDCDs

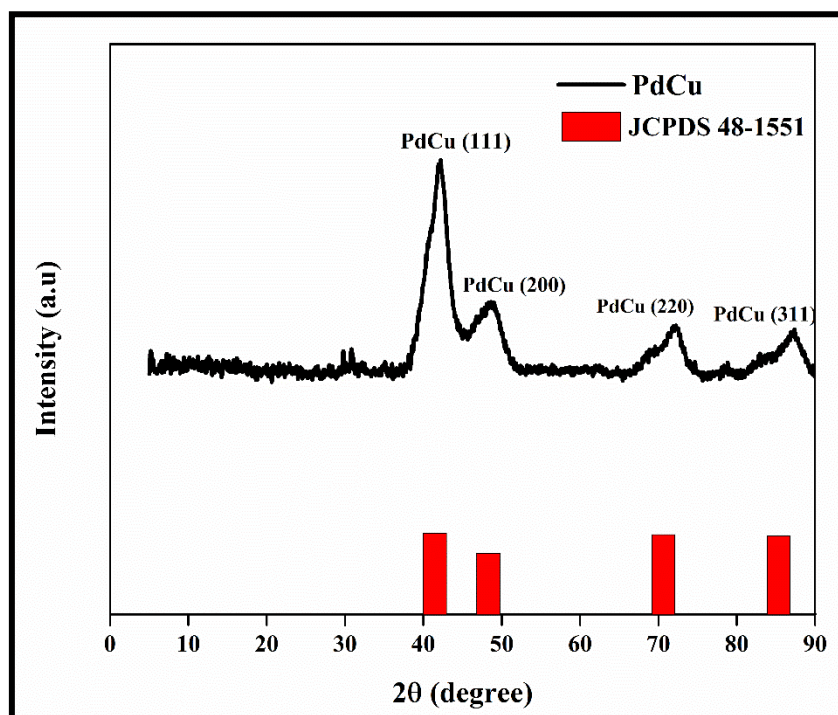


Fig S6. XRD pattern for PdCu

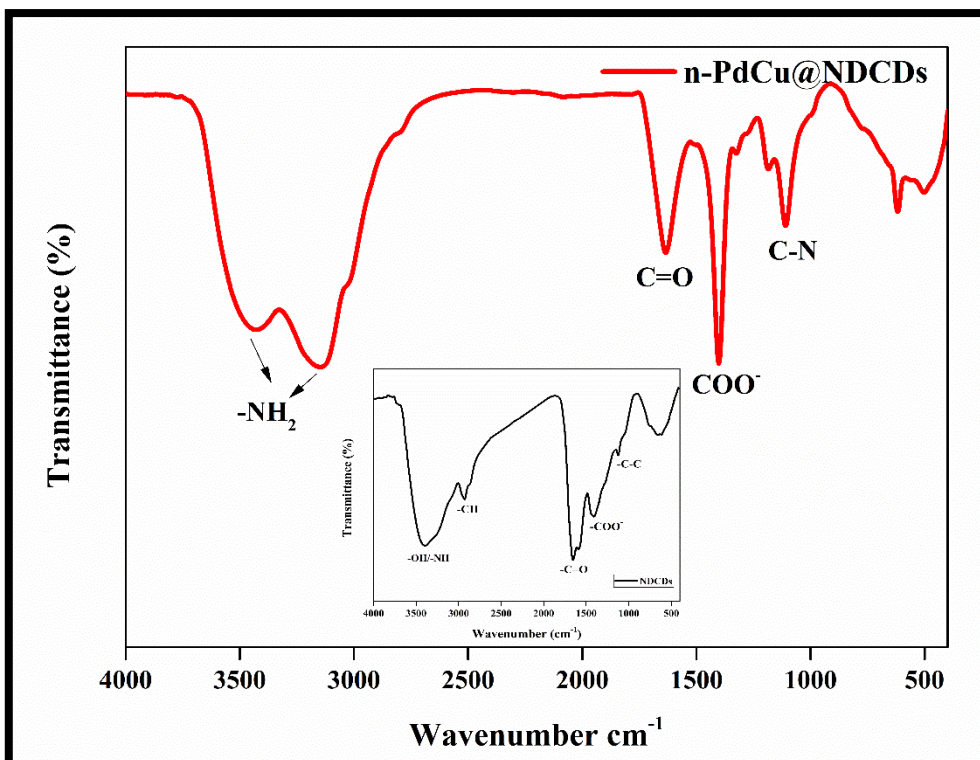


Fig S7 FT-IR spectra of the synthesized n-PdCu@NDCDs and NDCDs (inset)

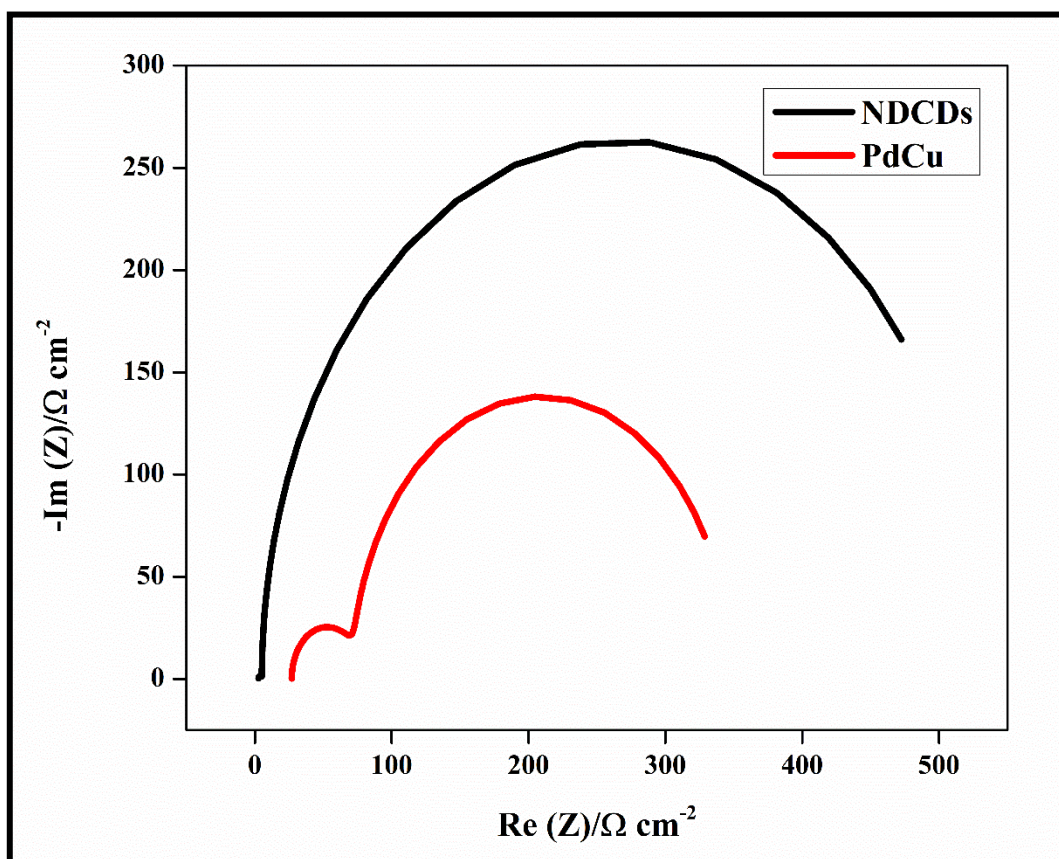


Fig S8. Nyquist plots for NDCDs and PdCu

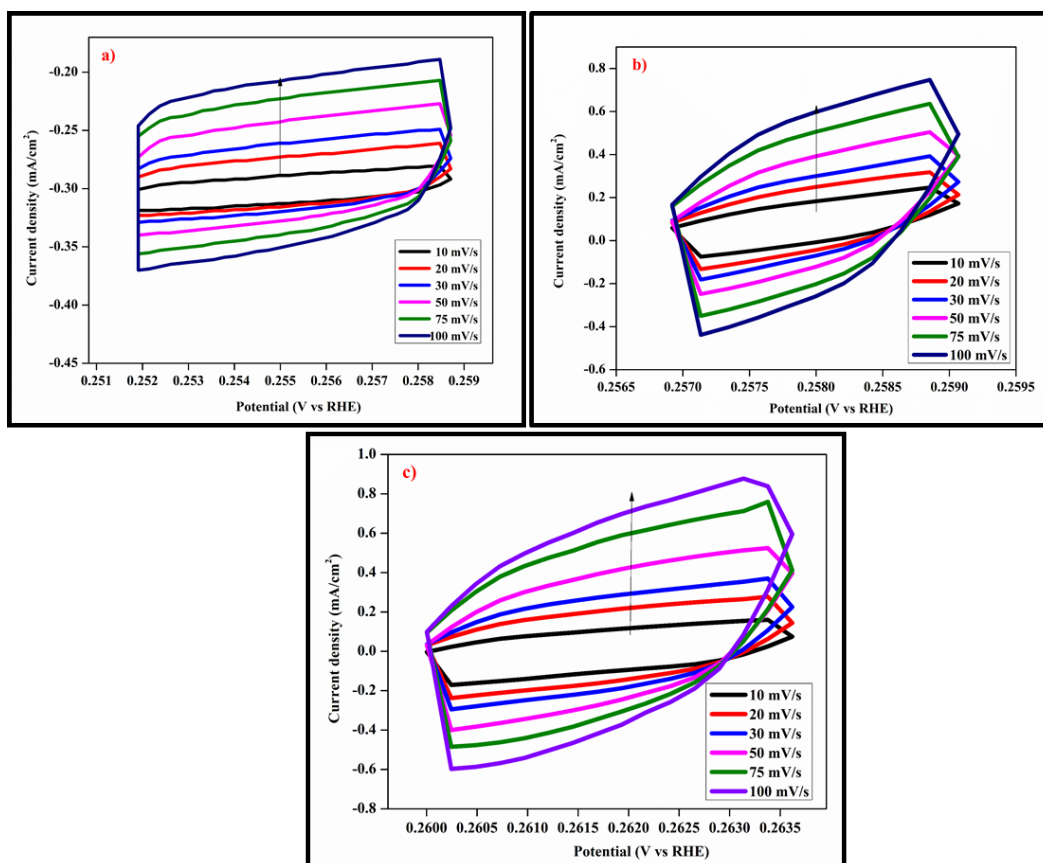


Fig S9. ECSA curves for a) NDCDs, b) PdCu and c) n-PdCu@NDCDs in 0.5 M H₂SO₄ electrolyte at different scan rates

UV-Visible spectroscopy

The optical properties of synthesized NDCDs can be scrutinized by the UV-Visible and Fluorescence spectroscopy. Figure. S10 a showed the UV-Visible spectrum and depicts two typical (268 and 302 nm) shoulders which correspond to π - π^* and n- π^* electronic transitions.

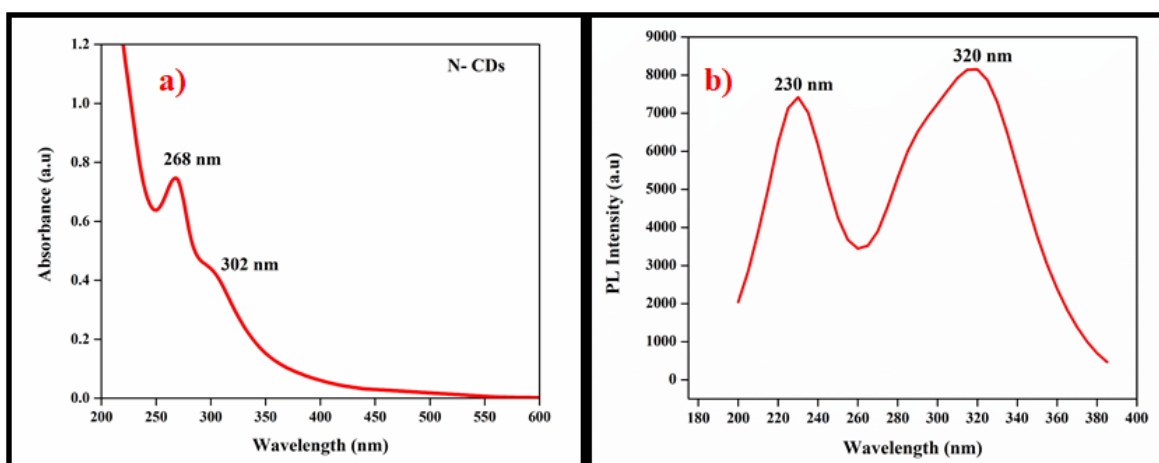


Figure. S10 (a) UV-Vis spectrum of synthesized NDCDs, and (b) Fluorescence excitation spectrum of synthesized NDCDs

The π - π^* and n - π^* transitions confirmed the sp^2 carbon (C=C) and carbonyl or amine groups present over the carbon dots ¹.

The excitation spectrum of NDCDs (Figure. S10 (b)) showed two distinct peaks at 230 and 320 nm, which corroborated the absorption spectrum (Figure. S10 (a)). This characteristic behaviour stipulated that surface of the NDCDs had at least two types of excitation energy levels ².

Fluorescence spectroscopy

Figure. S11a shows the photoluminescence spectrum of NDCDs which revealed the emission wavelength at 400 nm for different excitation wavelengths from 270 to 320 nm. The intensity of emission gradually decreased at different excitation wavelengths from 320 nm to 400 nm (Figure. S11 b) ³.

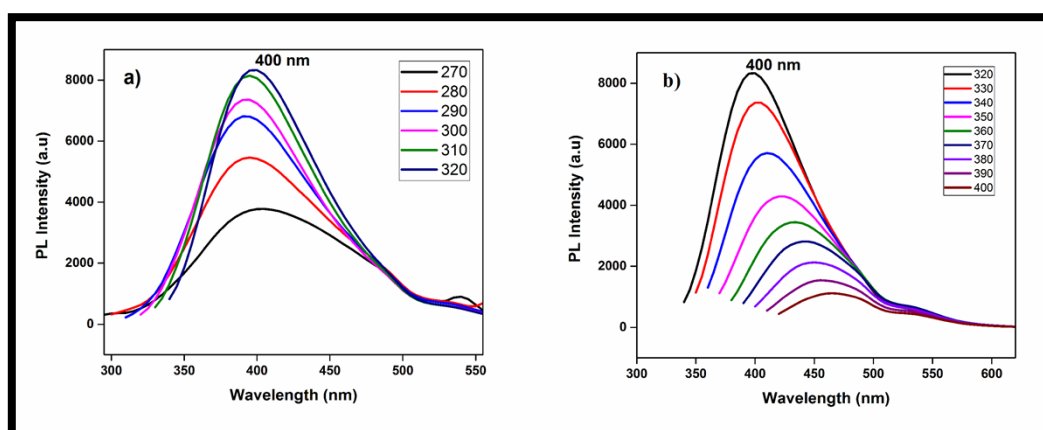


Figure.S11 a) Fluorescence spectra of NDCDs at various excitation wavelengths from 270 nm to 320 nm, b) 320 to 400 nm at 10 nm interval

The radiative recombination of the excited nonbonding electrons from the n - π^* transitions of carbonyl and heteroatom (nitrogen) part present over the NDCDs could be the reason for the fluorescence of NDCDs ⁴.

Table S1. Comparison of HER activity for the n-PdCu@NDCDs electrocatalyst with other reported non-Pt based highly efficient electrocatalyst in acid aqueous solution.

Catalyst	Electrolyte	Overpotential at 10 mA/cm ² (V)	Ref
MoSe ₂ /Pd	0.5 M H ₂ SO ₄	0.231	5
Pd/WS ₂	0.5 M H ₂ SO ₄	0.130	6
(Ni/Pd) ₁₇ Se ₁₅	0.5 M H ₂ SO ₄	0.197	7
AgPd (20:80)/CILE	0.1M H ₂ SO ₄	0.331	8
Pd ₂ Si	0.5 M H ₂ SO ₄	0.192	9
MoS ₂ /rGO	0.5 M H ₂ SO ₄	0.150	10
Defect-rich MoS ₂	0.5 M H ₂ SO ₄	0.190	11
n-PdCu@NDCDs	0.5 M H ₂ SO ₄	0.115	Present study

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