

## Self-supported amorphous TaN<sub>x</sub>(O<sub>y</sub>)/Nickel foam thin film as an advanced electrocatalyst for hydrogen evolution reaction

Ganesh Babu Thiyagarajan<sup>1,§</sup>, Raghunath Sharma Mukkavilli<sup>1</sup>, David Graf<sup>2</sup>, Thomas Fischer<sup>2</sup>, Michael Wilhelm<sup>2</sup>, Silke Christiansen<sup>3,4</sup>, Sanjay Mathur<sup>1,2,§\*</sup>, and Ravi Kumar<sup>1,§\*</sup>

<sup>1</sup>Laboratory for High Performance Ceramics, Department of Metallurgical and Materials Engineering, Indian Institute of Technology-Madras (IIT Madras), Chennai 600036, India

<sup>§</sup>Ceramic Technologies Group-Center of Excellence in Materials and Manufacturing for Futuristic Mobility, Indian Institute of Technology-Madras (IIT Madras), Chennai 600036, India

<sup>2</sup>Department of Chemistry, Institute of Inorganic Chemistry, University of Cologne, Cologne 50939, Germany

<sup>3</sup>Department Correlative Microscopy and Materials Data, Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Forchheim, Germany

<sup>4</sup>Physics Department, Freie Universität Berlin (FU), Berlin, Germany

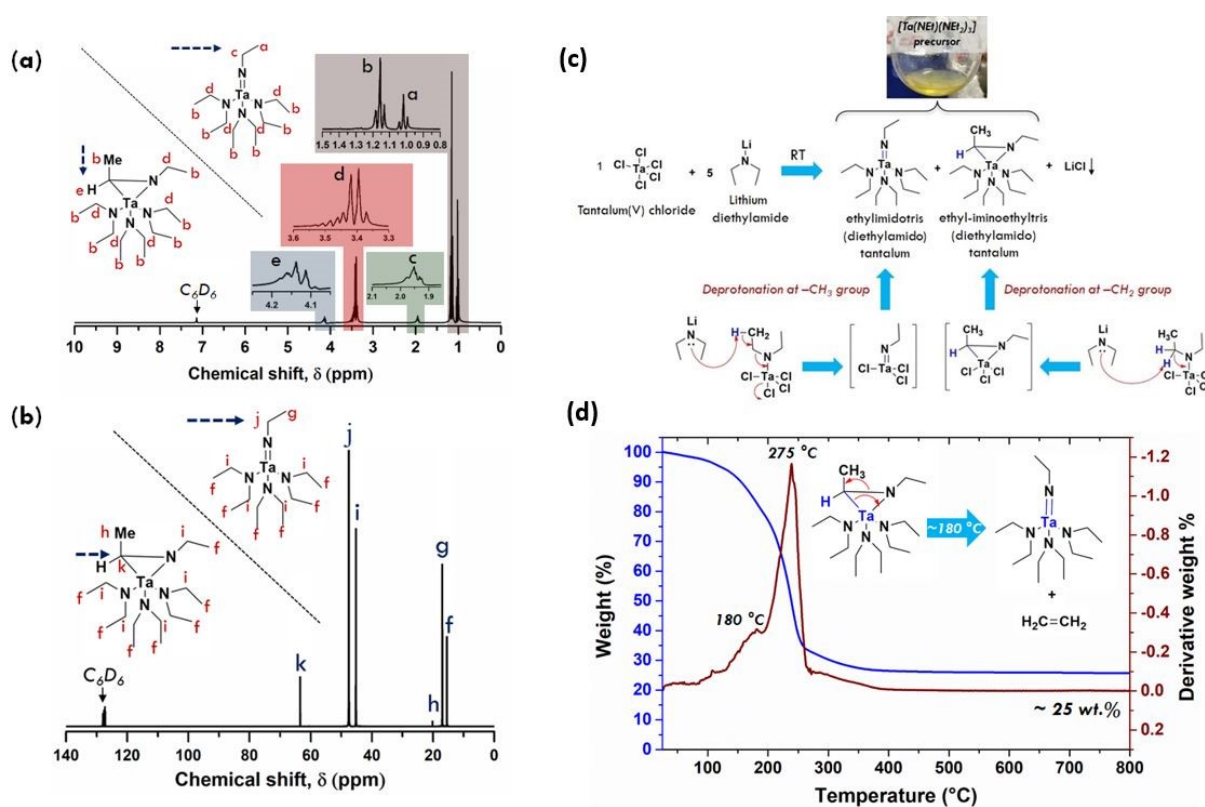
\*E-mail: [sanjay.mathur@uni-koeln.de](mailto:sanjay.mathur@uni-koeln.de) (Sanjay Mathur); [nvrk@iitm.ac.in](mailto:nvrk@iitm.ac.in) (Ravi Kumar)

### Supporting Information:

#### S1. Materials and Methods

All the reactions were conducted in carefully dried glass apparatus under oxygen-free dry nitrogen atmosphere of using Stock-type all glass assemblies. Diethylamine and tetrahydrofuran (THF) were stored over sodium wire and distilled from freshly cut sodium as required. Commercially available tantalum pentachloride (TaCl<sub>5</sub>) and n-butyllithium (n-BuLi) solution of 2.5 M in hexanes were used without further purification. NMR spectra were recorded on a Bruker Avance II spectrometer operating at 300 MHz; chemical shifts are denoted in parts per million (ppm) and coupling constants (J) are given in Hz. Thermogravimetric (TG) measurements were performed on a TGA/DSC1 (METTLER-TOLEDO GmbH, Germany) apparatus. The surface morphology of TaN<sub>x</sub>(O<sub>y</sub>) thin films on 3D NF, uniform distribution of the elements and thickness of the coating were examined using

field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 430). The surface elemental composition, oxidation state and bonding configuration of  $\text{TaN}_x(\text{O}_y)/\text{NF}$  was investigated using X-ray photoelectron spectroscopy (XPS) which was carried out with an ESCA M-Probe (Al  $K\alpha$  rays,  $\lambda = 8.33 \text{ \AA}$ ) in a detector range of 0–1000 eV. The detector pass energies were 158.28 eV for survey spectra and 55.22 eV for high-resolution (HR) spectra. HRTEM images were obtained on JOEL JEM-2200FS with 200 KV accelerating voltage.

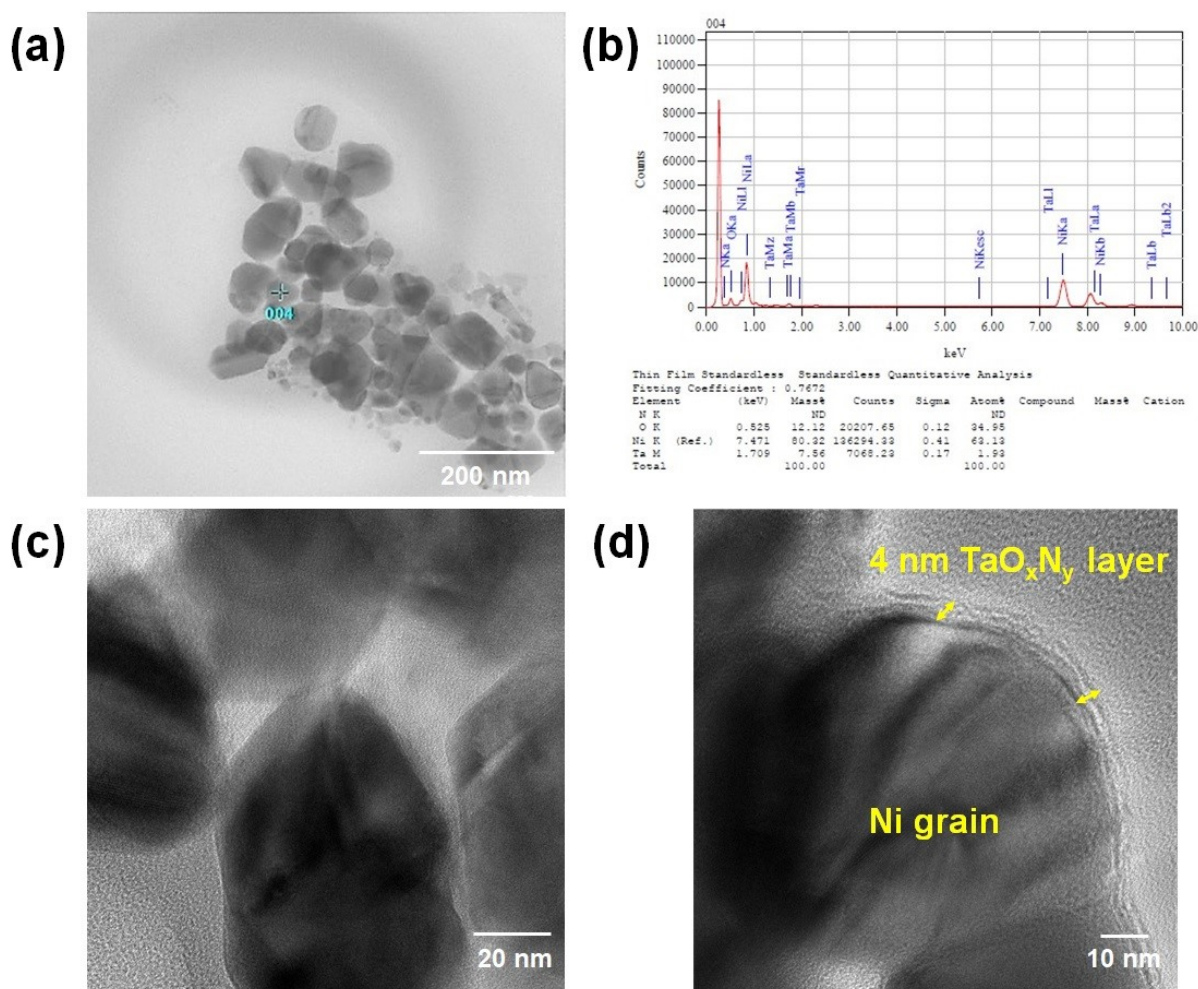


**Figure S1** a)  $^1\text{H}$  NMR & b)  $^{13}\text{C}$  spectra of  $([\text{Ta}(\text{NEt})(\text{NEt}_2)_3])$  precursor. c) Schematic representation of the proposed  $\text{S}_\text{N}2$  mechanism for the formation of mixed ethylimidotris(diethylamido)tantalum and ethyl-iminoethyltris(diethylamido)tantalum complexes via deprotonation at  $-\text{CH}_3$  group and deprotonation at  $-\text{CH}_2$  group of tantalum diethylamido complex, respectively. b) TGA of the precursor with a yield of 25 wt %.

## S2.Synthesis

### 2.1 Tantalum diethylamide $([\text{Ta}(\text{NEt})(\text{NEt}_2)_3])$ precursor:

[Ta(NEt)(NEt<sub>2</sub>)<sub>3</sub>] precursor was synthesized *via* three step reaction as per the previously reported procedure. Typically, in the first step, lithium diethylamide was prepared by reacting n-BuLi (0.1346 M) with diethylamine (0.1346 M) in THF at -78°C. In the second step, TaCl<sub>5</sub> (0.0269 M) in THF was added dropwise to the obtained lithium diethylamide. A slow reaction occurred with the development of a red viscous liquid. The mixture was kept stirred at room temperature for 24 h and insoluble LiCl was separated out. In the third step, the product was vacuum distilled (10<sup>-3</sup> mbar) at 120 °C to yield 56 wt.% of TaNEt as pale yellow low viscous liquid and was stored under nitrogen atmosphere. <sup>1</sup>H NMR (300.1 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>), δ (ppm) = 1.01 (t, CH<sub>2</sub>CH<sub>3</sub>N=, J= 15 Hz), 1.15 (t, CH<sub>2</sub>CH<sub>3</sub>N-, J= 40 Hz), 1.95 (m, CH<sub>2</sub>CH<sub>3</sub>N=, J= 16 Hz), 3.39 (q, CH<sub>2</sub>CH<sub>3</sub>N-, J= 40 Hz) and 4.23 (q, CH<sub>3</sub>CH(N)Ta, J= 26 Hz). <sup>13</sup>C NMR (75.5 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>) δ (ppm) = 15.3 [(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>N-], 16.8 (CH<sub>3</sub>CH<sub>2</sub>N=), 20.5 (CH<sub>3</sub>CH=), 45.1 [(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>N-], 48.0 (CH<sub>3</sub>CH<sub>2</sub>N=), and 63.5 ppm (CH<sub>3</sub>CH=)



**Figure S2** (a), (c) & (d) HRTEM images indicating a thin layer  $\sim 4$  nm of  $\text{TaO}_x\text{N}_y$  on nickel obtained due to aerial oxidation of TaN film and (b) EDS of  $\text{TaO}_x\text{N}_y$ -Nickel exemplifying the elemental composition of the catalyst.

## 2.2 Electrochemical Characterization

The electrochemical characterizations were conducted in three-electrode configuration with bare NF and  $\text{TaN}_x(\text{O}_y)$ -coated NF as working electrodes with active area of  $2.64 \text{ cm}^2$ , saturated calomel electrode as reference electrode and graphite as counter electrode in  $0.5 \text{ M H}_2\text{SO}_4$  aqueous electrolyte. All the measurements were carried out using a potentiostat (Biologic Instruments). All the potentials are reported with respect to reversible hydrogen electrode

(RHE). The HER activity was evaluated through linear sweep voltammetry (LSV) experiments carried out in the potential range of -0.4-0.1 V at scan rate of 5 mV s<sup>-1</sup>. The electrode-electrolyte interface was studied through electrochemical impedance spectroscopy (EIS). The EIS spectra was recorded at an over-potential of 300 mV in the frequency range of 10 kHz to 0.05 Hz at an alternating current amplitude of 5 mV.

**Table S1.** Comparison of onset potential values reported for HER on TaN<sub>x</sub>(O<sub>y</sub>)/NF with previously reported TaN<sub>x</sub> based materials

| Sl. No | Materials                                     | Onset potential vs. RHE (mV) | Electrolyte                                 | References |
|--------|---|------------------------------|---|------------|
| 1.     | Ta <sub>3</sub> N <sub>5</sub> microparticles | 530                          | 0.1 M H <sub>2</sub> SO <sub>4</sub>        | 1          |
| 2.     | Ta <sub>3</sub> N <sub>5</sub> /Ta foil       | 540                          | 0.1 M H <sub>3</sub> PO <sub>4</sub> (pH 4) | 2          |
| 3.     | Mesoporous TaN                                | 160                          | 0.05 M H <sub>2</sub> SO <sub>4</sub>       | 3          |
| 4.     | Ta <sub>3</sub> N <sub>5</sub> nano rods      | 115                          | 0.5 M H <sub>2</sub> SO <sub>4</sub>        | 4          |
| 5.     | Ta <sub>5</sub> N <sub>6</sub> single crystal | 84                           | 0.5 M H <sub>2</sub> SO <sub>4</sub>        | 5          |
| 6.     | TaN <sub>x</sub> (O <sub>y</sub> )/NF         | 50                           | 0.5 M H <sub>2</sub> SO <sub>4</sub>        | This work  |

**Table S2.** Impedance parameters calculated from the equivalent circuit

| Materials                             | R <sub>s</sub> (Ω) | R <sub>ct</sub> (Ω) | R <sub>mt</sub> (Ω) |
|---------------------------------------|--------------------|---------------------|---------------------|
| NF                                    | 0.6                | 2.3                 | 22.3                |
| TaN <sub>x</sub> (O <sub>y</sub> )/NF | 0.8                | 0.9                 | 6.4                 |

#### References:

1. Wirth, S., Harnisch, F., Weinmann, M. & Schröder, U. Applied Catalysis B : Environmental Comparative study of IVB – VIB transition metal compound electrocatalysts for the hydrogen evolution reaction. *Applied Catal. B, Environ.* **126**, 225–230 (2012).
2. Ishikawa, A., Takata, T., Kondo, J. N., Hara, M. & Domen, K. Electrochemical Behavior of Thin Ta<sub>3</sub>N<sub>5</sub> Semiconductor Film. *J. Phys. Chem. B* **108**, 11049–11053 (2004).
3. Alhajri, N. S. *et al.* Synthesis of tantalum carbide and nitride nanoparticles using a reactive mesoporous template for electrochemical hydrogen evolution. *J. Mater. Chem. A* **1**, 12606–12616 (2013).

4. Yan, Y. *et al.* Simultaneous electrochemical ozone production and hydrogen evolution by using tantalum-based nanorods electrocatalysts. *Appl. Catal. B Environ.* **266**, (2020).
5. Zhang, F. *et al.* Metallic Porous Iron Nitride and Tantalum Nitride Single Crystals with Enhanced Electrocatalysis Performance. *Adv. Mater.* **31**, (2019).