

## Supplementary Materials

### On substrate, self-standing hollow-wall Pt and PtRu-nanotubes and their electrocatalytic behavior

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#### 1. Reagents.

Hexamethylenetetramine (HTMA), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), hexachloroplatinum (IV) acid ( $\text{H}_2\text{PtCl}_6$ ), sodium hydroxide (NaOH), ruthenium (III) chloride hydrate ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich, Germany. Methanol ( $\text{CH}_3\text{OH}$ ), Ti(IV)-isopropoxide ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ), acetylacetone ( $\text{C}_5\text{H}_8\text{O}_2$ ), copper sulfate ( $\text{CuSO}_4$ ) and acetic acid ( $\text{CH}_3\text{COOH}$ ) were obtained from Fluka, Germany. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was supplied by Roth, Germany. All chemicals were of analytical grade purity. All solutions were prepared with deionized water ( $\geq 18 \text{ M}\Omega$ ).

#### 2. Preparation of substrates and ZnO templates.

$2 \times 2 \text{ cm}^2$  mil-finish stainless steel substrates were ultrasonically cleaned in a mixture of ethanol and acetone followed by drying at  $60^\circ \text{C}$ . Pre-coating with a nanocrystalline anatase  $\text{TiO}_2$  film was performed using spin-coating of a precursor solution in ambient atmosphere and final annealing at  $500^\circ \text{C}$  for 30 minutes, as described previously by Es-Souni et al.<sup>S1</sup> These substrates were taken for growing ZnO-NRs.

ZnO-NTs were grown as described by Chu et al.<sup>S2</sup> The steel substrate mentioned above was inserted in a flask containing 20 ml of the ZnO-NRs growth solution (aqueous solution of 60 mM HMTA and 60 mM  $\text{Zn}(\text{NO}_3)_2$ ). Initial pH of this solution was tuned to 5.75-5.85 by adding  $\text{CH}_3\text{COOH}$ . Then the covered flask was placed for 3 hours in an oil bath that was preheated to  $72\text{-}75^\circ \text{C}$ . Subsequently, the ZnO-NRs coated substrate was washed with deionized water and immersed into NaOH solution (0.3 M) at  $80^\circ \text{C}$  for 1.5h, followed by rinsing with deionized water and drying in air at  $60^\circ \text{C}$ .

Prior to electrochemical deposition of Pt or PtRu films, the ZnO-NTs were sputter coated with approximately 3 nm thin gold film to achieve a good electrical contact.

Furthermore, to form a desirable geometrical surface area of the electrode and to avoid deposition on the back and lateral steel surfaces, the steel sheet was isolated with a nonconductive lack.

### 3. Electrochemical deposition of Pt and PtRu.

Pt, PtRu deposition and all electrochemical measurements were carried out at room temperature in a standard three-electrode cell using an electrochemical workstation (IM6e, ZAHNER, Germany). All solutions were saturated with nitrogen (N<sub>2</sub>) before each experiment. A Pt mesh and Ag/AgCl (in saturated KCl) electrode were used as counter and reference electrodes, respectively. All potentials in this study were referred to the standard hydrogen electrode (SHE). Substrates with ZnO-NTs sputter coated with ca. 3nm Au were used as working electrodes. The electrodeposition of Pt and PtRu was performed potentiostatically within 200 s. Pt was deposited at 0.2 V from a H<sub>2</sub>PtCl<sub>6</sub> (20 mM) aqueous solution and PtRu at 0.01 V from an aqueous solution containing H<sub>2</sub>PtCl<sub>6</sub> (10 mM) and RuCl<sub>3</sub> (6 mM). After deposition, working electrodes were removed from the electrolyte and thoroughly rinsed with deionized water.

### 4. Real surface area (S<sub>R</sub>) determination.

The real surface area, S<sub>R</sub>, of catalysts was estimated via copper underpotential deposition (Cu-UPD).<sup>S3</sup> For this purpose, reference voltammograms were first recorded in H<sub>2</sub>SO<sub>4</sub> (0.1 M) aqueous solution between 0 and 0.9 V for PtRu and between 0 and 1.1 V for Pt electrodes at a scan rate of 10 mVs<sup>-1</sup> until a stable voltammogram was obtained. Electrodes were then transferred in to a H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.1 M) containing CuSO<sub>4</sub> (2 mM) and polarized at 0.3 V for 150s. This leads to the deposition of a Cu-monolayer on the surface of the electrode. Subsequently, a linear voltammetric scan with 10mVs<sup>-1</sup> was performed between 0.3 and 0.9 V for PtRu and between 0.3 and 1.1 V for Pt for the removing of the Cu monolayer. Integration of the Cu-UPD stripping peak after subtracting the reference scan in the same potential range was used to determine S<sub>R</sub> using Equation 1:

$$S_R = Q_{Cu} / \nu \cdot c \quad (1)$$

where  $Q_{Cu}$  denotes the corrected integrated area of the Cu-UPD stripping peak (in V·A),  $\nu$  is the scan rate (in Vs<sup>-1</sup>) and  $c = 420 \mu\text{Ccm}^{-2}$  is the charge density corresponding to the adsorption of a single copper atom on each surface metal atom.<sup>S4</sup>

### 5. Methanol electrooxidation study.

The electrocatalytic activity of Pt-based NSs towards methanol electro-oxidation was evaluated using cyclic voltammetry in an aqueous solution containing CH<sub>3</sub>OH (0.5 M) and H<sub>2</sub>SO<sub>4</sub> (0.5 M). The potential was swept at a rate of 50 mVs<sup>-1</sup> between 0 and 1.4 V for Pt and between 0 and 0.9 V for PtRu electrodes. All CV measurements were performed for multiple cycles until obtaining a stable curve. The current (i) in methanol electro-oxidation measurements was normalized with respect to the real surface area of the electrodes.

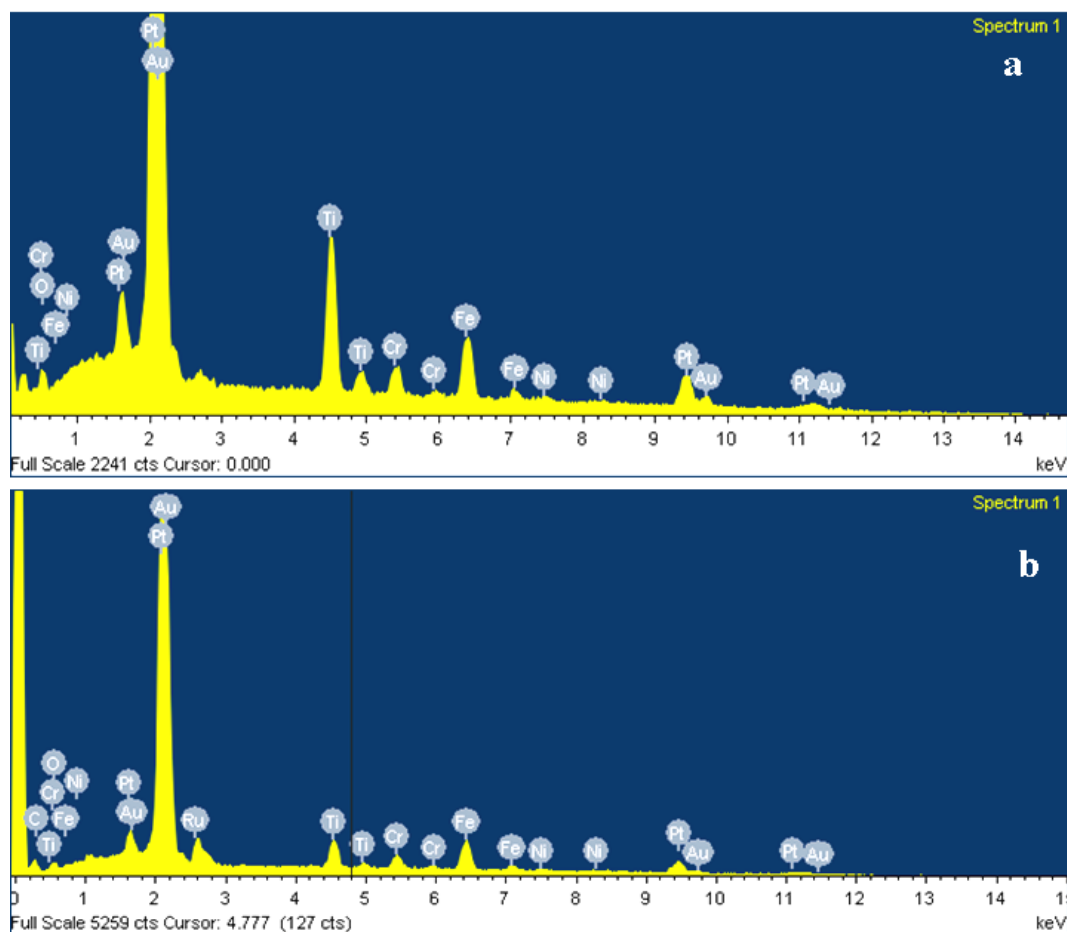
## 6. Characterization of microstructure.

The samples were investigated by X-ray diffraction (XRD) (X'Pert Pro, PanAnalytical, Holland) in grazing incidence diffraction geometry with constant  $\theta = 1^\circ$  using monochromatic Cu K $\alpha$  radiation with  $\lambda = 1.5418 \text{ \AA}$  and a scanning range 2 $\theta$  = 24 – 90°.

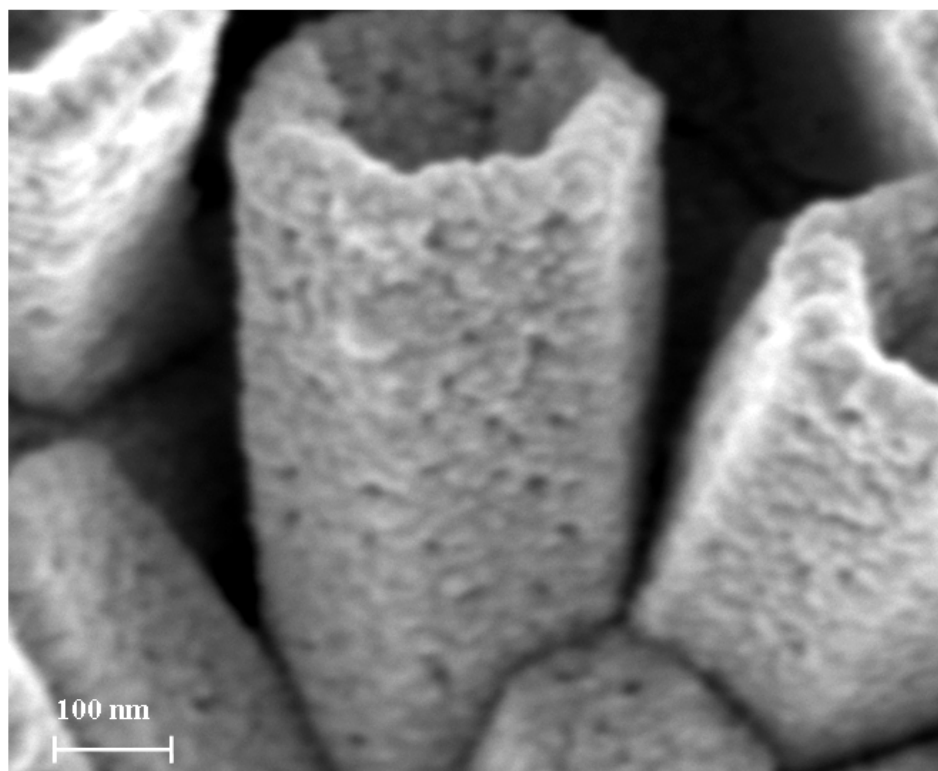
A high-resolution scanning electron microscope (Ultra Plus, ZEISS, Germany), equipped with an energy dispersive spectroscopy (EDS) package (Oxford, UK) was used to investigate microstructure and morphology of samples, and to verify elemental composition.

## References

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**Fig. 1S** EDS spectrum of Pt- (a) and PtRu-NTs (b). The substrate peaks, including those of stainless steel (Fe, Ni, Cr), TiO<sub>2</sub> and gold layers are present but none of the Zn peaks can be seen.



**Fig. S2** SEM image of PtRu-NTs array after 200s deposition time. Notice the porous character of the NTs.