

## Supplementary materials

### **Preparation and thermal treatment influence on Pt-decorated electrospun carbon nanofiber electrocatalysts**

Igor I. Ponomarev,<sup>\*a</sup> Olga M. Zhigalina,<sup>b,c</sup> Kirill M. Skupov,<sup>a</sup> Alexander D. Modestov,<sup>d</sup> Victoria G. Basu,<sup>b</sup> Alena E. Sufiyanova,<sup>b,c</sup> Ivan I. Ponomarev<sup>a</sup> and Dmitry Y. Razorenov<sup>a</sup>

<sup>a</sup>A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, GSP-1, Vavilova St., 28, Moscow, 119991, Russia.

<sup>b</sup>Shubnikov Institute of Crystallography of Federal Scientific Research Centre “Crystallography and Photonics” of Russian Academy of Sciences, Leninsky Av., 59, Moscow, 119333, Russia.

<sup>c</sup>Bauman Moscow State Technical University, 2-ya Baumanskaya St., 5, Moscow, 105005, Russia.

<sup>d</sup>Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Leninsky Av., 31, Moscow, 119071, Russia

#### **Additional electron microscopy data**

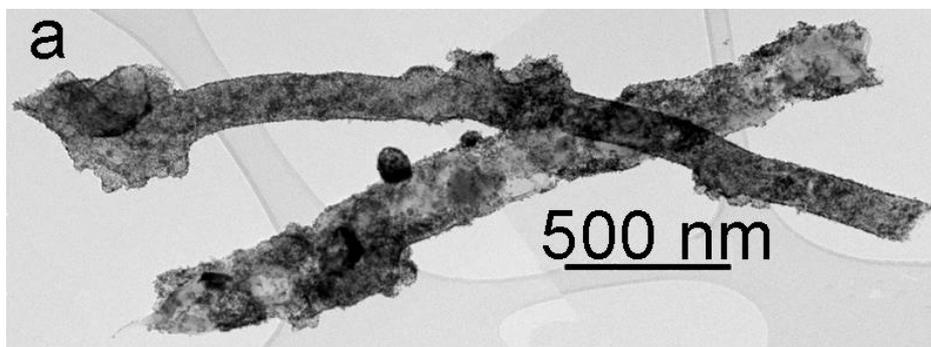


Fig. S1. Structure of **1**: (a) general view.

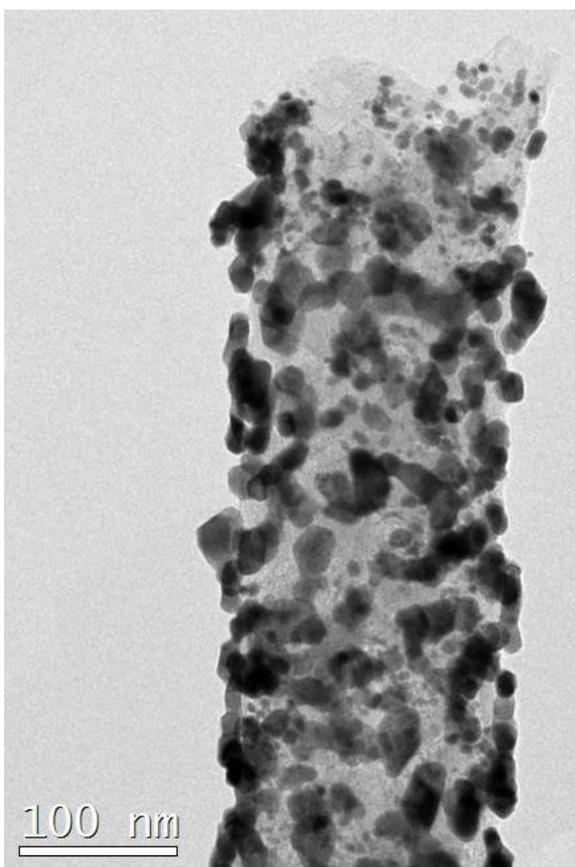


Fig. S2. Structure of 4: TEM image of a nanofiber fragment.

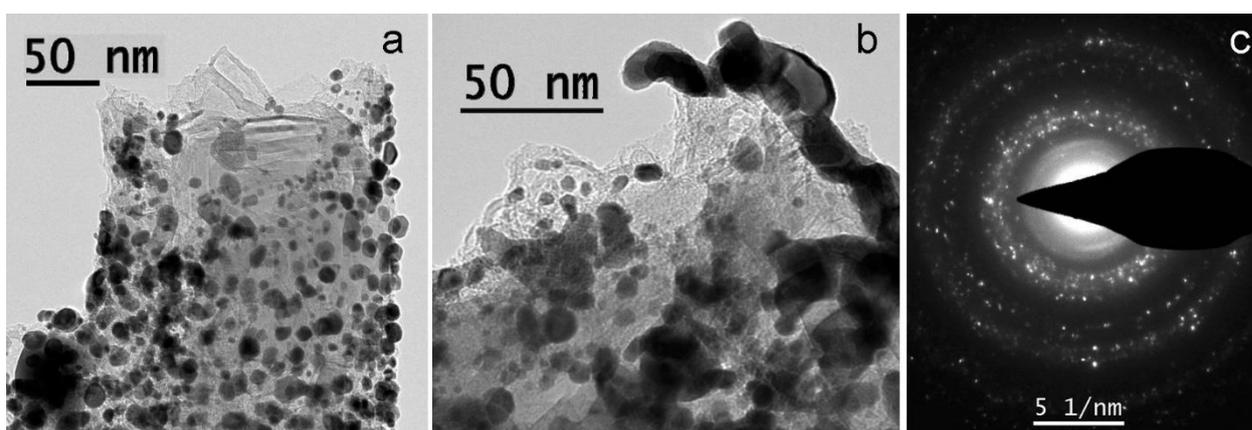


Fig. S3. Structure of 7: (a) TEM image of the fiber; (b,c) enlarged image of Pt heavily sintered particles and corresponding SAED pattern.

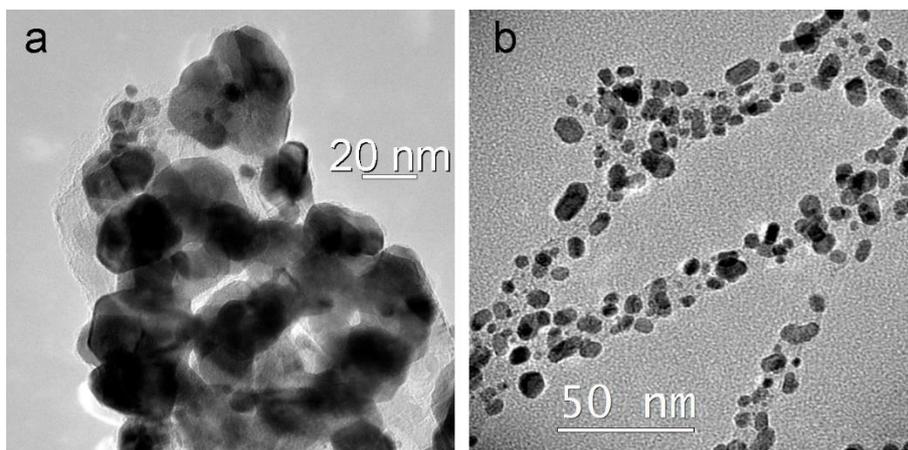


Fig. S4. Structure of **8**: (a) Pt conglomerates; (b) enlarged image of the Pt crystals.

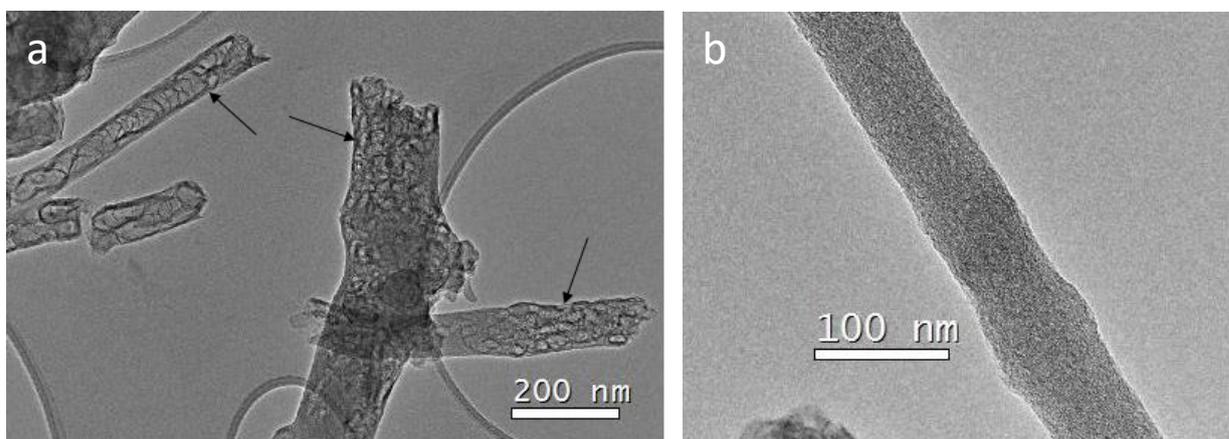


Fig. S5. Examples of nanofiber fragments with different porosity. (a) large pores, (b) small pores.

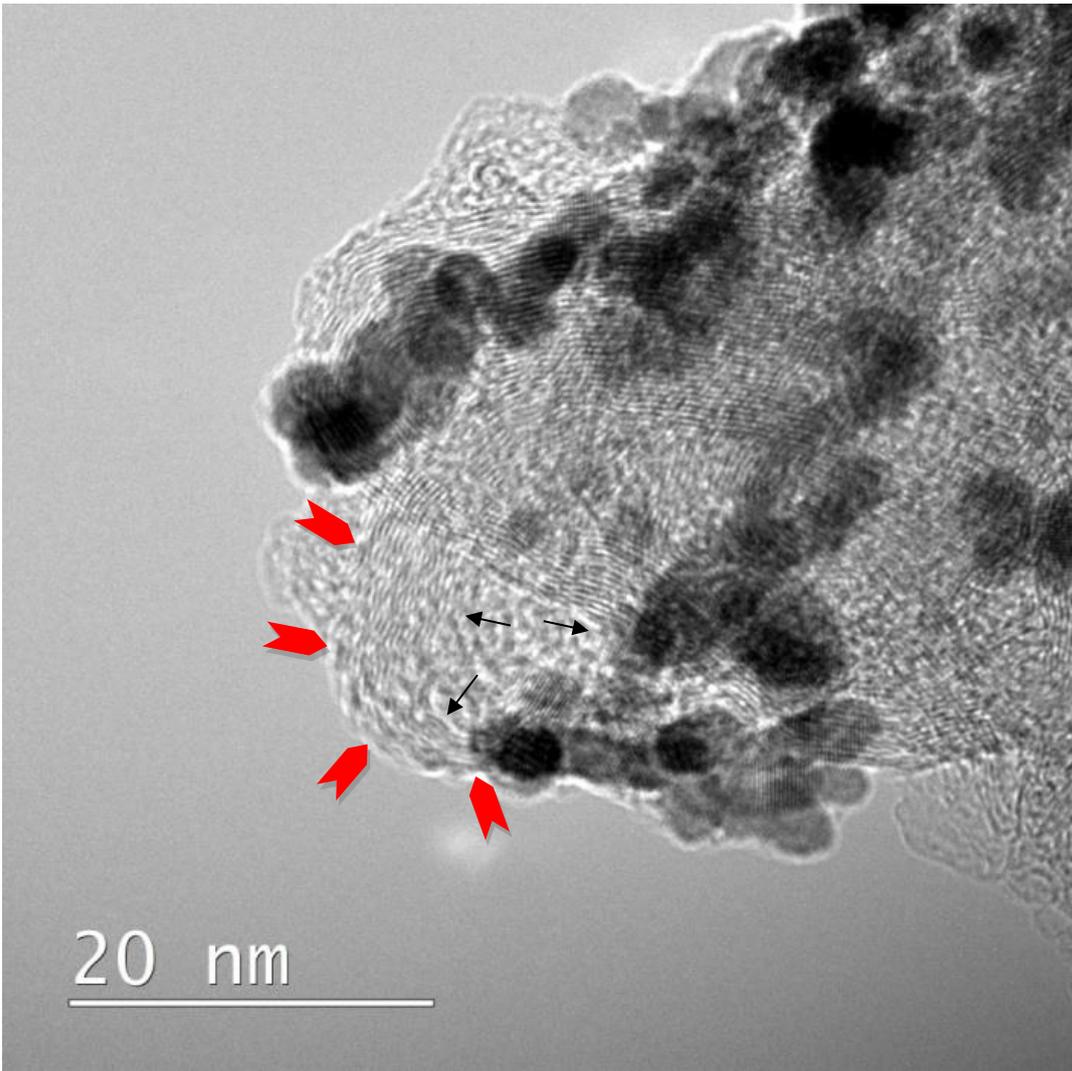


Fig. S6. TEM image of platinumized nanofiber fragment (sample 5) with pores which are made by the loops of parallel graphene planes. Red arrows indicate to an external border of the loop, red arrows indicate to an internal border.

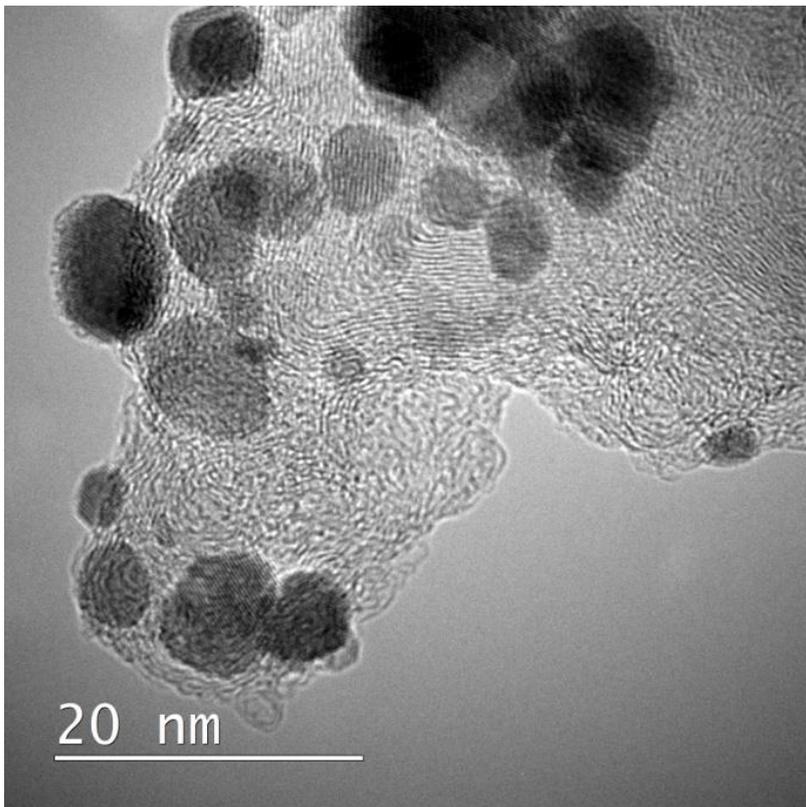


Fig. S7. TEM image of platinized nanofiber fragment with pores formed by the large loops of parallel graphene planes (sample 8)

Zirconium oxide particles increase in size with the increase of heat-treatment temperature according to EDX-mapping (Fig.S8)

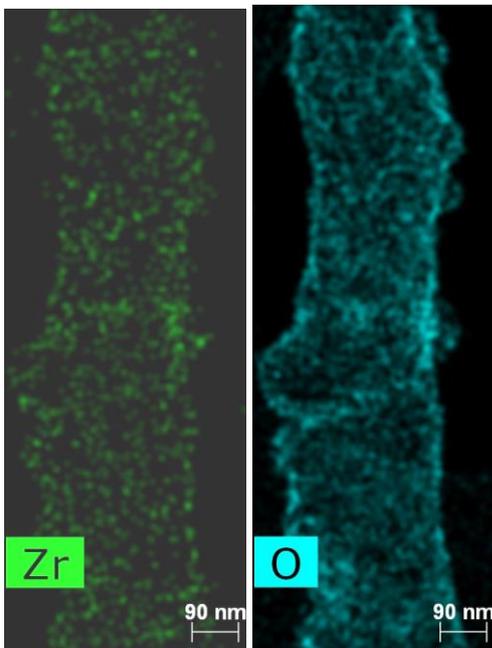


Fig. S8. EDX maps of element distribution on carbon nanofiber. Zr correlate with O, particle size of individual zirconium oxide particles is around 10 nm (sample 3).

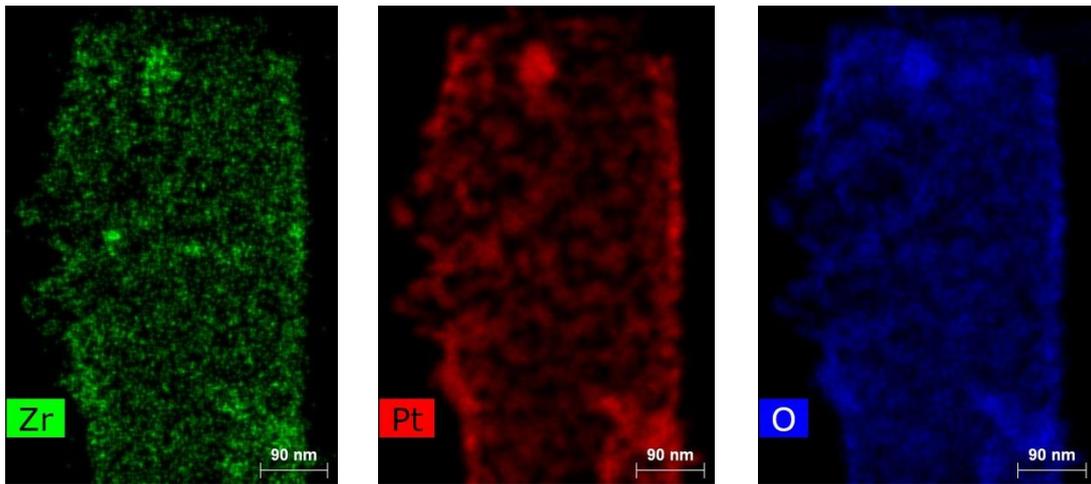


Fig. S9. Zirconium oxide – platinum correlation (sample 7)

**Additional XRD data**

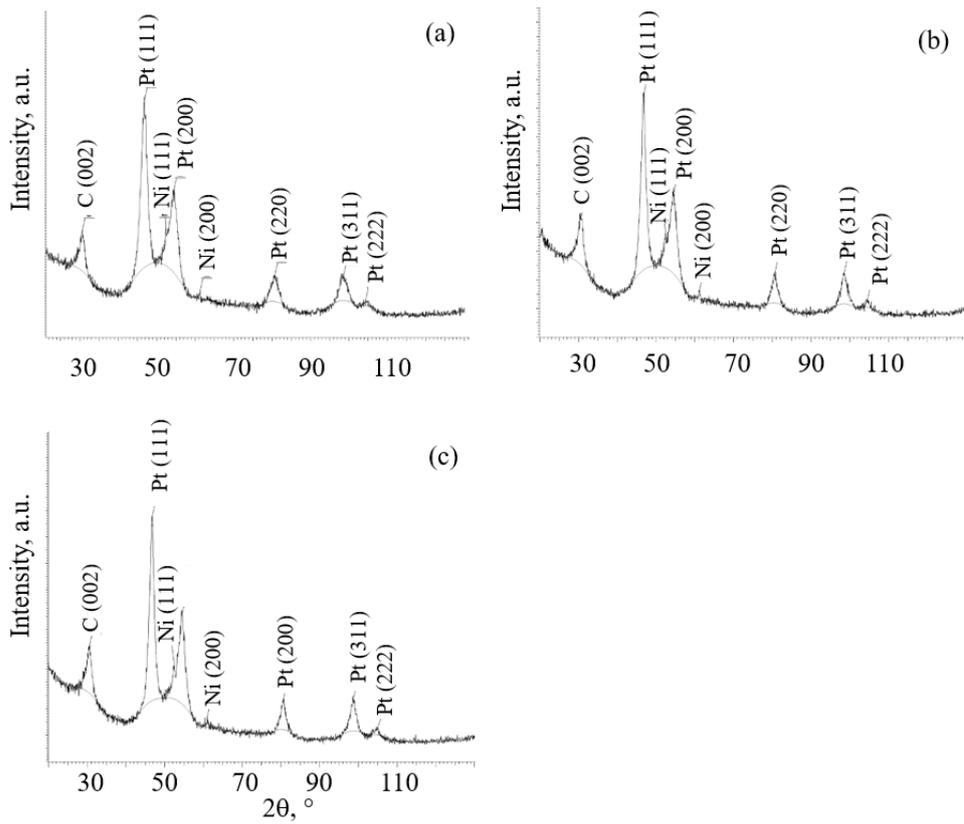


Fig. S10. XRD data for samples **6** (a), **7** (b), **8** (c).

## Fuel cell performance

Primary HT-PEMFC tests using PBI-OPht as proton conducting membrane, Celtec ® P1000 as anode and material **3** which possessed the highest ECSA value (after heat treatment at 500 °C under vacuum; 0.9 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathode at 180 °C: open-circuit voltage (V<sub>oc</sub>) 0.887 V; 0.612 V at 0.2 mA cm<sup>-2</sup>; 0.539 V at 0.4 mA cm<sup>-2</sup>; 0.475 V at 0.6 mA cm<sup>-2</sup>.

## BET data

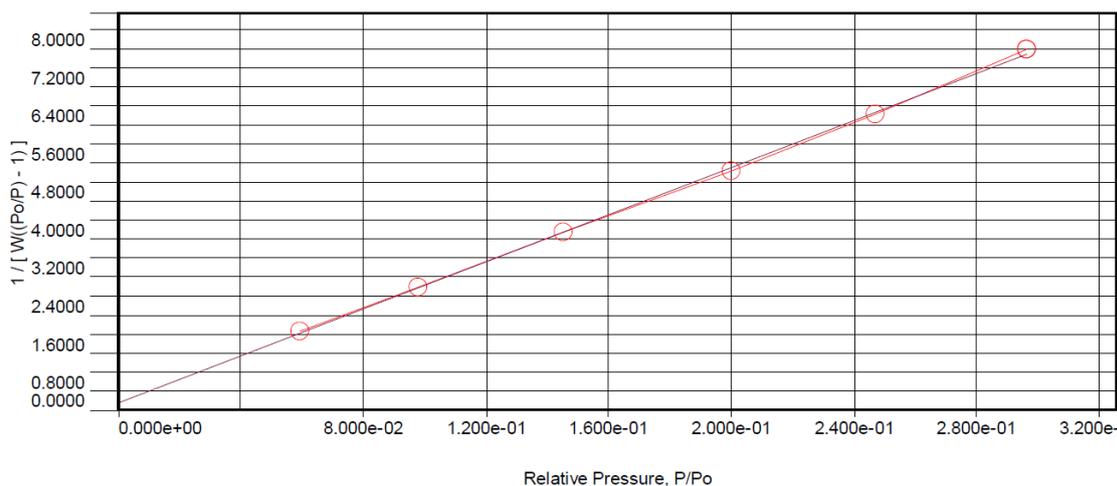


Fig. S11. BET data for CNF sample before platinization.

Slope 24.811

Intercept 0.1466

Correlation coefficient, r 0.999653

C constant 170.239

Surface Area 139.535 m<sup>2</sup>g<sup>-1</sup>

To compare, specific surface area for carbon black Vulcan®XC-72 is 213 m<sup>2</sup> g<sup>-1</sup> according to T. Chen, et al. *Sci. Rep.*, 2016, 6, 23289.

### EDX spectrum

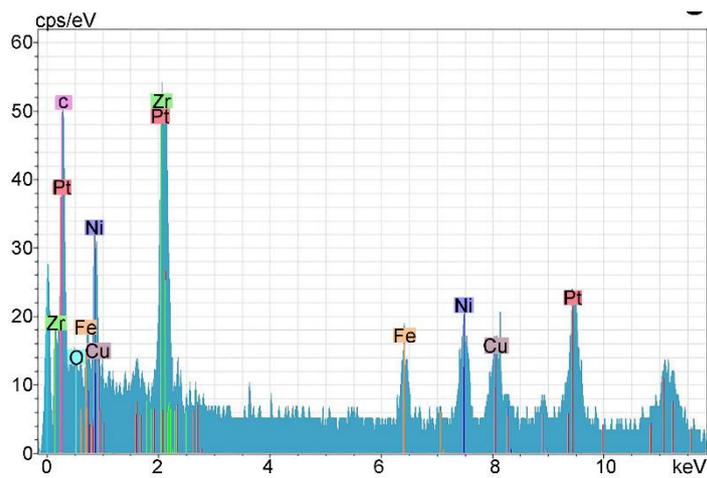


Fig. S12. EDX spectrum for a mapping on Figs. 5 and 6.

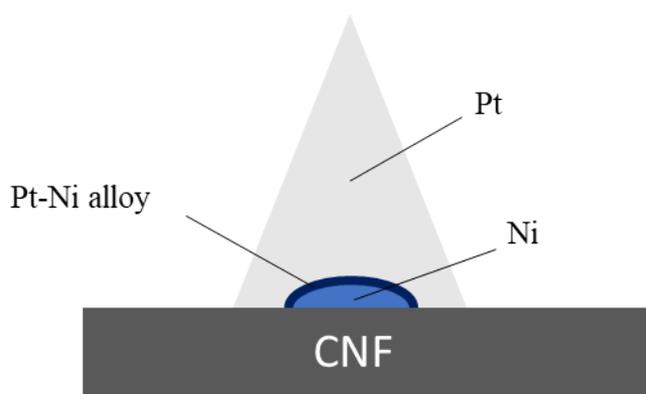


Fig. S13. Schematic representation of a nanoneedle platinum crystal structure. Pt-Ni alloy assuming form on the contact Pt-Ni surface.