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Du, Shangfeng; Lu, Yaxiang; Steinberger-wilckens, Robert

DOI:

[10.1016/j.carbon.2014.07.076](https://doi.org/10.1016/j.carbon.2014.07.076)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Du, S, Lu, Y & Steinberger-wilckens, R 2014, 'PtPd nanowire arrays supported on reduced graphene oxide as advanced electrocatalysts for methanol oxidation', *Carbon*, vol. 79, pp. 346-353.  
<https://doi.org/10.1016/j.carbon.2014.07.076>

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Eligibility for repository checked October 2014

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## Accepted Manuscript

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PII: S0008-6223(14)00714-3

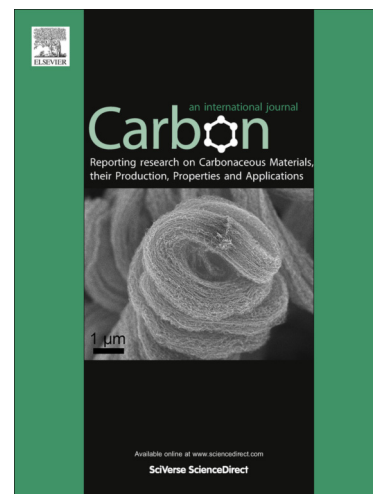
DOI: <http://dx.doi.org/10.1016/j.carbon.2014.07.076>

Reference: CARBON 9197

To appear in: *Carbon*

Received Date: 30 May 2014

Accepted Date: 28 July 2014



Please cite this article as: Du, S., Lu, Y., Steinberger-Wilckens, R., PtPd Nanowire Arrays supported on Reduced Graphene Oxide as Advanced Electrocatalysts for Methanol Oxidation, *Carbon* (2014), doi: <http://dx.doi.org/10.1016/j.carbon.2014.07.076>

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# PtPd Nanowire Arrays supported on Reduced Graphene Oxide as Advanced Electrocatalysts for Methanol Oxidation

Shangfeng Du,<sup>\*</sup> Yaxiang Lu and Robert Steinberger-Wilckens

School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

## Abstract

Novel reduced graphene oxide (RGO) nanosheet/PtPd nanowire hybrids were prepared by a mild wet chemical approach. Uniform Pt nanowire arrays are successfully supported on functionalized RGO nanosheets with Pd nanoparticles as growing seeds. The whole deposition process was achieved in aqueous solution at room temperature. TEM and HR-TEM analysis indicated the single-crystal feature of the Pt nanowires with a diameter of ca. 4 nm in average and a length of 20-200 nm. Electrochemical characterization demonstrated that the hybrid nanostructures have a higher catalytic activity and stability than commercial state-of-the-art platinum black catalysts (Hispec1000) toward the methanol oxidation reaction (MOR). An initial mass activity of 0.51 A mg<sup>-1</sup> and a degradation ratio of 17.2% after 1000 potential sweeping cycles were achieved for the hybrid nanostructures, compared with 0.44 A mg<sup>-1</sup> and 27.5% for Pt black, respectively, demonstrating a great potential of this RGO/PtPd hybrids for DMFC applications.

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<sup>\*</sup> Corresponding author. E-mail: [s.du@bham.ac.uk](mailto:s.du@bham.ac.uk)

## 1. Introduction

Pt nanowires, as one-dimensional (1D) nanostructure, have been demonstrated as high performance catalyst for various catalysis applications, benefiting from their anisotropic structure and unique surface properties [1, 2]. For practical applications, Pt nanowires can be grown on various supports, e.g. metal gauzes [3, 4], carbon paper [5, 6], carbon black [7], carbon fibre [8] or nanotubes [9], or even directly in water [2]. Recently, graphene has also attracted tremendous attention for the utilization in electrochemical conversion and storage applications, in particular as catalyst support in fuel cells, due to its high conductivity ( $10^3$ – $10^4$  S m<sup>-1</sup>), large surface area (calculated value, 2630 m<sup>2</sup> g<sup>-1</sup>), unique graphitized basal plane structure, and potentially low manufacturing cost [10-12]. To improve the Pt utilization and enhance the catalytic activity, Pt nanoparticles and nanodendrites have been dispersed on graphene surfaces to achieve high performance fuel cell catalysts [13]. However, with these graphene-based hybrids, the drawback from Pt nanoparticle or nanodendrite themselves can still not be overcome, e.g. Ostwald ripening and dissolution [14-16], in addition with the serious stacking and folding of graphene nanosheets in catalyst preparation caused by their 2-dimensional morphology and soft feature [10, 17], thus the poor catalyst performance and stability can still not be effectively improved in practical applications. To address these issues, the synthesis of graphene/Pt nanowires has been demonstrated with reduced graphene oxide (RGO) as initial supports [10, 11, 18]. However, although some functional groups existed on GO surface, the inert surface properties of the framework make it very difficult to grow uniform Pt nanowires to produce a high performance catalyst. Fig. 1 shows SEM and TEM images of Pt nanowires grown directly on RGO surface with formic acid as the reducing agent at room temperature, by an approach as reported in the literature [18]. It can be seen that, similar to the reported results, Pt nanowires grew only on some RGO nanosheets, and due to the limited nucleation sites on the surface, most Pt nanowires

assembled each other to form large superstructures with a size of 50-500 nm, and even some huge aggregates with a diameter of 1  $\mu\text{m}$  or larger (Fig. 1d). Recently, Chen and coworkers have demonstrated the synthesis of Pt nanowire arrays on sulfur-doped graphene which was achieved by heating graphene with phenyl disulfide (PDS) at a high temperature of 1000  $^{\circ}\text{C}$  [12]. But it still remains a grand challenge to synthesize graphene nanosheet/Pt nanowire hybrids via a mild chemical route.

Motivated by need, in this work, we demonstrate a new facile wet-chemical approach for the synthesis of uniform Pt nanowire arrays supported on reduced graphene oxide nanosheets. The whole preparation strategy is displayed in Fig. 2. After partially reducing and a surface functionalization of graphene oxide nanosheets, Pd nanoparticles were first introduced as growing seeds on the nanosheet surface. Then by controlling the growth reaction kinetics of the chemical synthetic process, single crystal Pt nanowires were grown with Pd nanoparticles as seeds, thus a hybrid nanostructure of RGO/PtPd nanowires were achieved. Formic acid was used as reducing agent for the deposition of Pd nanoparticles and the growth of Pt nanowires. Both deposition processes were achieved in aqueous solution at room temperature, without using any template, surfactant or organic solvent.

## 2. Experimental

### 2.1 Materials:

Poly(*N*-vinyl-2-pyrrolidone) (PVP-K30, molecular weight = 30 000–40 000),  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{PdCl}_2$ ,  $\text{HCOOH}$ , ascorbic acid (AA), and ethanol were purchased from Sigma-Aldrich UK and used as received without further purification. Single layer graphene oxide water dispersion (thickness 0.43 - 1.23 nm, diameter 1.5 - 5.5  $\mu\text{m}$ , dispersed in water with 2 wt%) was purchased from US Research Nanomaterials, Inc. The state-of-the-art

Johnson-Matthey HiSpec™ 1000 Pt black was purchased from Alfa Aesar for comparison with the as-prepared catalyst. Water used throughout all experiments was purified with the Millipore system.

## 2.2 Sample preparation

### 2.2.1 Preparation of PVP-Functionalized RGO

In a typical procedure for chemical conversion of graphene oxide to PVP-functionalized RGO, 400 mg of PVP was added into 1.25 mL of GO dispersion with 87.5 mL water, followed by stirring for 12 h. Then, to the resulting dispersion were added 100 mg of ascorbic acid and stirred for 1 h at 95 °C. Finally, the stable black dispersion was centrifuged one time and dissolved in 12.5 mL of water.

### 2.2.2 Preparation of RGO nanosheet/Pd nanoparticle hybrids

Amounts of 1.25 mL of PVP-functionalized RGO aqueous dispersion were diluted with water (the final total volume of water is 10 mL), followed by the addition of 5 mg PdCl<sub>2</sub> and 0.6 mL of formic acid (HCOOH). The mixture was stored at room temperature until the Pd precursor was reduced completely. Then, the dispersion was centrifuged and washed 3 times with water and finally dispersed in 15 mL of water.

### 2.2.3 Preparation of RGO nanosheet/PtPd nanowire hybrids

The as-prepared suspension of RGO/Pd nanoparticle hybrids (15 mL), 53.10 mg H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, and 1.66 mL of HCOOH were filled into a 100 mL flask. The mixture was stored at room temperature for 72 hours until the Pt precursor was reduced completely. The product was collected by centrifugation and washed several times with water for further electrochemical measurements.

## 2.3 Electrochemical measurement and physical characterization

All electrochemical experiments were performed in a standard three-electrode system, using an Autolab PGSTAT302N potentiostat (Eco-Chemie) and a glassy carbon rotating disc electrode (RDE, a geometric area of  $0.196 \text{ cm}^2$ ) setup (ED101, Radiometer Analytical). To prepare the working electrode, the as-prepared RGO/PtPd hybrids or Pt black catalyst were dispersed to make  $0.4 \mu\text{g}_{\text{Pt}} \mu\text{L}^{-1}$  solution (based on Pt mass) by using water, iso-propanol (IPA) and 10 wt% Nafion aqueous solution (D1021, Ion Power) with a ratio of water:IPA:Nafion solution at 3:1:0.02. 10  $\mu\text{L}$  of the dispersion was transferred onto the RDE. The loading amount of Pt for all catalysts was 4  $\mu\text{g}$ . The working electrodes were dried overnight at  $40^\circ\text{C}$  in a vacuum oven.

The background electrolyte was 0.1 M  $\text{HClO}_4$ , prepared from 70% (AR, Fisher), purged with  $\text{N}_2$  gas for at least 20 minutes before testing. Potentials are reported against the RHE and the counter electrode was a platinum mesh attached to a platinum wire. The working electrode was first activated using cyclic voltammetry (CV) between 0.05 V to 1.1 V with a scan rate of  $100 \text{ mV s}^{-1}$  in  $\text{N}_2$ -purged 0.1 M  $\text{HClO}_4$  solution until a steady CV was obtained. Then the electrolyte was changed to 0.1 M  $\text{HClO}_4$  contained 1M methanol. CV scan was conducted between 0.3 V and 1.2 V with a scan rate of  $25 \text{ mV s}^{-1}$ . The electrochemical stabilities of the catalysts were investigated by an accelerated durability test (ADT), which was carried out at  $25^\circ\text{C}$  by applying cyclic potential sweeps for 1000 cycles between 0.3 and 1.2 V versus RHE at a sweep rate of  $50 \text{ mV s}^{-1}$ .

The as-prepared RGO/PtPd hybrids were characterized by field emission scanning electron microscope (FE-SEM, JEOL 7000F, operating at 20 kV) and transmission electrolyte microscopy (Philips CM200 FEGTEM). X-Ray diffraction (XRD) patterns were obtained with a Siemens 5005 X-ray diffractometer using  $\text{Cu } K\alpha$  radiation at  $\lambda = 1.5418 \text{ \AA}$ . X-Ray photoelectron spectroscopy (XPS) characterization was performed on an XPS spectrometer (AXIS Nova, Kratos Analytical) by using high power monochromatized  $\text{Al } K\alpha$  radiation

(1486.6 eV). XPS spectra were fitted using CasaXPS V2.3.16 software in which a Shirley background was assumed, and fitting the peaks of the experimental spectra was completed by considering a combination of Gaussian (90%) and Lorentzian (10%) distributions.

### 3. Results and discussion

Fig. 3 shows typical TEM images and the corresponding diffraction pattern of Pd nanoparticles loaded on PVP-functionalized RGO nanosheets. It is observed that small Pd nanoparticles have a size of ca. 5 nm in average. The high-resolution (HR) TEM image in Fig. 3c indicates that they are single crystal with many (111) facets. Due to the very small lattice mismatch (only 0.77%) between Pd and Pt, these Pd nanoparticles on RGO nanosheets would work as seeds to direct the growth of Pt nanowires upon the following reduction of  $\text{H}_2\text{PtCl}_6$  by formic acid in aqueous solution at room temperature [13, 19]. The microstructure and morphology of the as-prepared RGO/PtPd hybrids were investigated by SEM and TEM analysis. Fig. 4a and 4b show the SEM images of RGO/PtPd hybrids at two different magnifications. We can see that, Pt nanowires grow uniformly through the entire surface of the RGO nanosheets, which have a length of 20-200 nm and a diameter of several nanometers. All the nanowires project outwards from the support surface although the orientations are random. An edge area TEM image and HR-TEM images are shown in Fig. 4c and 4d, respectively. It can be seen the nanowires possess relatively uniform diameter of ca. 4 nm. The HR-TEM image demonstrates the single-crystal feature of these Pt-nanowires growing along the  $\langle 111 \rangle$  direction. The lattice spacing between the  $\{111\}$  planes was measured to be 0.23 nm, which agrees with that of bulk Pt crystal. XRD analysis (Fig. 5) confirmed the face-centered-cubic (fcc) structure of these Pt nanowires.



For a complete view of the RGO/PtPd nanowire hybrid formation process, a time dependent study was conducted to the Pt nanowire growing procedure. Products were collected from the reaction solution at various times, and their morphologies were evaluated by TEM. As shown in Fig. 6, when the sample is collected after 2 h of reaction, the product is composed of PtPd nanoparticles (Fig. 6b). Compared with Fig. 3a and Fig. 6a, it can be seen that the distribution density PtPd nanoparticles is similar to the Pd nanoparticles on RGO surface, and there is no obviously increase observed to the particle number. This similar particle distribution indicates that Pt grow on Pd nanoparticle on RGO, not directly grow on the surface of RGO. After 5 h, some short nanowires (mean length, 10 nm) are formed (Fig. 6c,d). A comparison of Fig. 6c with 6a, and Fig. 6d with 6b, respectively, further confirms that Pt nanowire grow on Pd nanoparticles. With a longer time, these Pt nanowires will grow up to 20-200 nm in length, finally forming the RGO/PtPd nanowire hybrid structures shown in Fig. 4.

The PtPd nanowire arrays grown on RGO nanosheets were further characterized by energy-dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS). The corresponding EDX spectrum (Fig. S1) shows the peaks corresponding to C, Pd and Pt elements, confirming the existence of bimetallic Pd-Pt and RGO nanostructures. XPS pattern (Fig. 7) shows significant Pt4f signals that are compared with the commercial state-of-the-art Johnson-Matthey HiSpec<sup>TM</sup> 1000 Pt black. The Pt4f<sub>7/2</sub> and Pt4f<sub>5/2</sub> peaks lie at 71.18 and 74.58 eV, showing about 0.2 eV shift as compared with those of pure Pt black at 70.98 and 74.38 eV, which generally arises from the synergistic effects in the hybrids. It reflects the alteration of the electronic properties of the RGO/PtPd hybrids. According to former research, this shift is beneficial for oxygen and CO desorption from the catalyst surface, thus allowing a high catalytic performance and CO tolerance [20, 21].

This better catalytic activity of the hybrid nanostructures was further approved by electrochemical measurement towards methanol oxidation reaction (MOR). Fig. 8a shows the CV comparison of RGO/PtPd nanowire hybrids and Pt black in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solution at a scan rate of 25 mV s<sup>-1</sup>. The ECSA obtained are close for both samples, they are 19.07 and 22.99 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> for RGO/PtPd hybrids and Pt black, respectively. The ECSA for Pt black is nearly the same as that reported in the literature, where the Pt black, with a particle size of ca. 6.5 nm in average, showed an ECSA of 24 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> [14]. Considering the diameter of 3-5 nm of the as-prepared Pt nanowires in this work, the ECSA obtained here for the hybrids agrees very well with their geometry, further confirming the uniform distribution of Pt nanowires on RGO nanosheet surfaces, with very few aggregates formed. Fig. 8b further shows the CV comparison of RGO/PtPd nanowire hybrids and Pt black toward MOR. The RGO/PtPd hybrids exhibited a higher catalytic performance with a peak current density of 0.51 A mg<sup>-1</sup>, higher than 0.44 A mg<sup>-1</sup> of Pt black. Regarding the CV scan with methanol, it has been reported that the anodic peak in the reverse scan may be attributed to the removal of the incomplete oxidized carbonaceous species, such as CO, HCOO<sup>-</sup> and HCO<sup>-</sup>, which accumulated on the surface of the catalyst during the forward scan. The ratio of the forward oxidation current peak (*I<sub>f</sub>*) to the reverse current peak (*I<sub>b</sub>*), *I<sub>f</sub>*/*I<sub>b</sub>*, can be used to infer the CO tolerance of the catalyst [13, 18]. A lower *I<sub>f</sub>*/*I<sub>b</sub>* value usually indicates poor oxidation of methanol to CO<sub>2</sub> during the forward anodic scan and an excessive accumulation of residual carbon species on the catalyst surface. On the other hand, a higher *I<sub>f</sub>*/*I<sub>b</sub>* ratio is indicative of improved CO tolerance. In our study, the *I<sub>f</sub>*/*I<sub>b</sub>* of the RGO/PtPd hybrids is 1.29, which is higher than that of Pt black (*I<sub>f</sub>*/*I<sub>b</sub>* = 1.16), suggesting that methanol molecules can be more effectively oxidized on the hybrids during the forward scan, generating relatively fewer poisoning species compared to Pt black, indicating a better CO tolerance. The accelerated degradation tests (ADT) were conducted to check the catalyst stability, which was performed

by cycling potential sweeps at  $50 \text{ mV s}^{-1}$  between 0.3 and 1.2 V vs RHE for 1000 cycles. The mass activity comparison between the 1<sup>st</sup> and 1000<sup>th</sup> cycle is shown in the inset of Fig. 8b. After 1000 cycles, the mass activity of RGO/PtPd nanowire hybrids and Pt black degrade from 0.54 to 0.44  $\text{A mg}^{-1}$  and 0.46 to 0.34  $\text{A mg}^{-1}$ , retaining 82.8% and 72.5% of their original mass activity, respectively.

This higher MOR activity and stability observed for RGO nanosheet/PtPd nanowire hybrids can be attributed to the hybrid nanostructures and the graphene support used: i) better distribution of Pt nanowires on the RGO nanosheet surface reduces the aggregates formed between catalysts and the stack of RGO support, leading for a high surface area [6, 12, 22]; ii) the synergistic effect between Pt, Pd and graphene potentially contributes to the higher MOR activity [23, 24]; iii) while the higher chemical and structure stability of the single-crystal Pt-nanowires [2, 15] and the RGO support [10, 11, 17], as compared with commercial Pt black catalyst, reduce catalyst degradation and loss.

#### 4. Conclusions

We have developed a facile wet-chemical approach to prepare RGO nanosheet/PtPd-nanowire hybrid nanostructures. The whole deposition process was achieved in aqueous solution at room temperature. Uniform Pt-nanowire arrays were successfully grown on RGO nanosheet surfaces, led to a large ECSA close to the conventional Pt black. Most importantly, the hybrid nanostructures exhibited a higher catalytic activity and stability toward the methanol oxidation reaction (MOR), where a mass activity of 0.51  $\text{A mg}^{-1}$  and an  $I_p/I_b$  ratio of 1.29 were achieved, respectively. After the durability test, RGO/PtPd nanowire hybrids retained 82.8% of its original activity compared with 72.5% for Pt black. This new and powerful approach can open new possibilities for enhancing the performance for DMFCs,

and this structure combining graphene-based nanostructure and Pt-based nanowires may also be useful in other electrochemical applications.

### Acknowledgements

YX Lu was sponsored by a joint Li Siguang Scholarship from the University of Birmingham (UoB) and the China Scholarship Council (CSC). X-ray photoelectron spectra were obtained at the National EPSRC XPS User's Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility (NEXUS). TEM analysis was performed at Leeds EPSRC Nanoscience and Nanotechnology Research Equipment Facility funded by EPSRC Grant EP/F056311/1 and the University of Leeds (LENNF).

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Figure captions:

**Fig. 1 – (a) SEM and (b-d) TEM images of Pt nanowires grown on pristine reduced graphene oxide (RGO) nanosheets. Images (c) and (d) are taken from the white squares 1 and 2 in image b), respectively.**

**Fig. 2 - Procedure to grow PtPd nanowire arrays on the reduced graphene oxide nanosheets.**

**Fig. 3 - TEM images and the corresponding diffraction pattern of Pd nanoparticle supported on RGO nanosheets. Image (c) shows one single crystal Pt nanoparticles revealing the 0.23 nm  $\{111\}_{\text{Pd}}$  lattice fringes.**

**Fig. 4 - (a-b) SEM, (c) TEM and (d) HR-TEM images of PtPd nanowire arrays on RGO nanosheets.**

**Fig. 5 - XRD pattern of RGO/PtPd nanowire hybrids. The strong peaks at 69.4° and 62° come from the doped silicone chip substrate used.**

**Fig. 6 - TEM images of (a) RGO/Pd, and RGO/PtPd nanowire hybrids collected at (b) 2 and (c,d) 5 h after mixing the two solutions.**

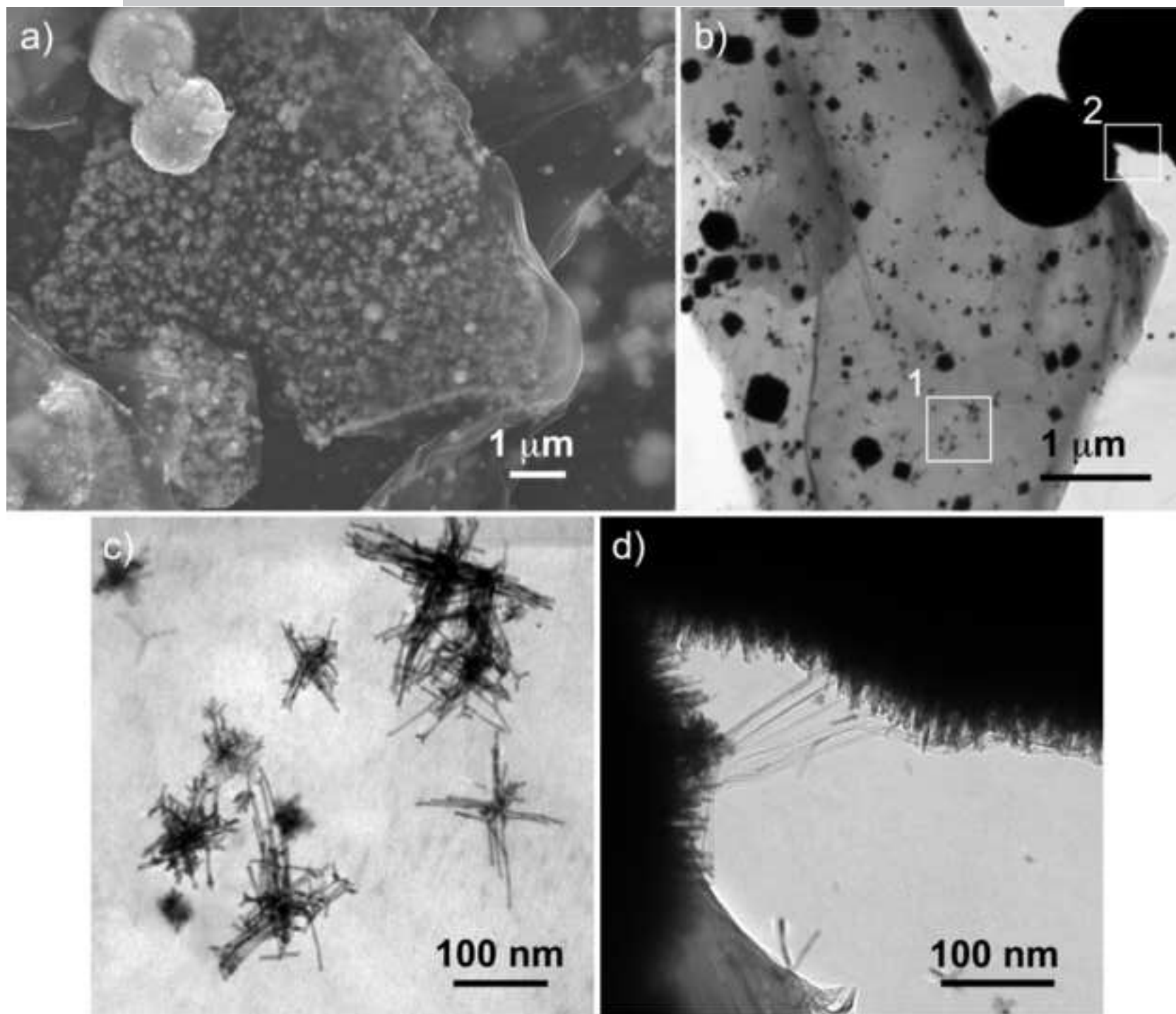
**Fig. 7 - Pt 4f XPS pattern of Pt black (Johnson-Matthey HiSpec™ 1000) and RGO/PtPd nanowire hybrids.**

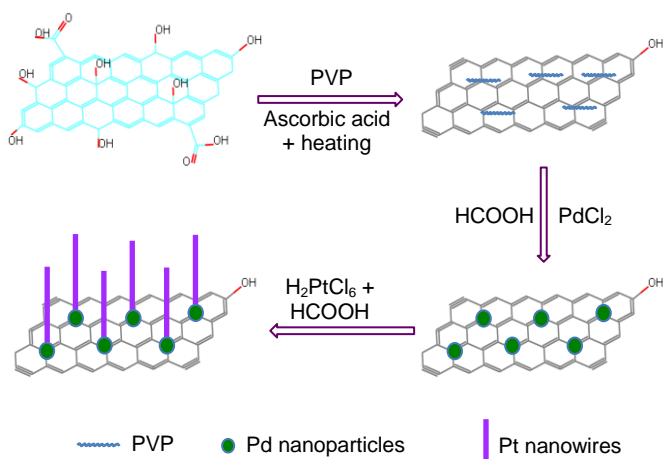


**Fig. 8 - Electrocatalytic activity comparison between RGO nanosheet/PtPd-nanowire hybrids and Pt black catalysts: (a) CVs in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solution at a scan rate of 25 mV s<sup>-1</sup>. (b) CVs in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solution containing 1.0 M methanol at a scan rate of 25 mV s<sup>-1</sup>. Inset: mass activities at the 1<sup>st</sup> and 1000<sup>th</sup> cycles during accelerated degradation test by applying cyclic potential sweeps for 1000 cycles between 0.3 and 1.2 V versus RHE at a sweep rate of 50 mV s<sup>-1</sup>.**

Fig. 1

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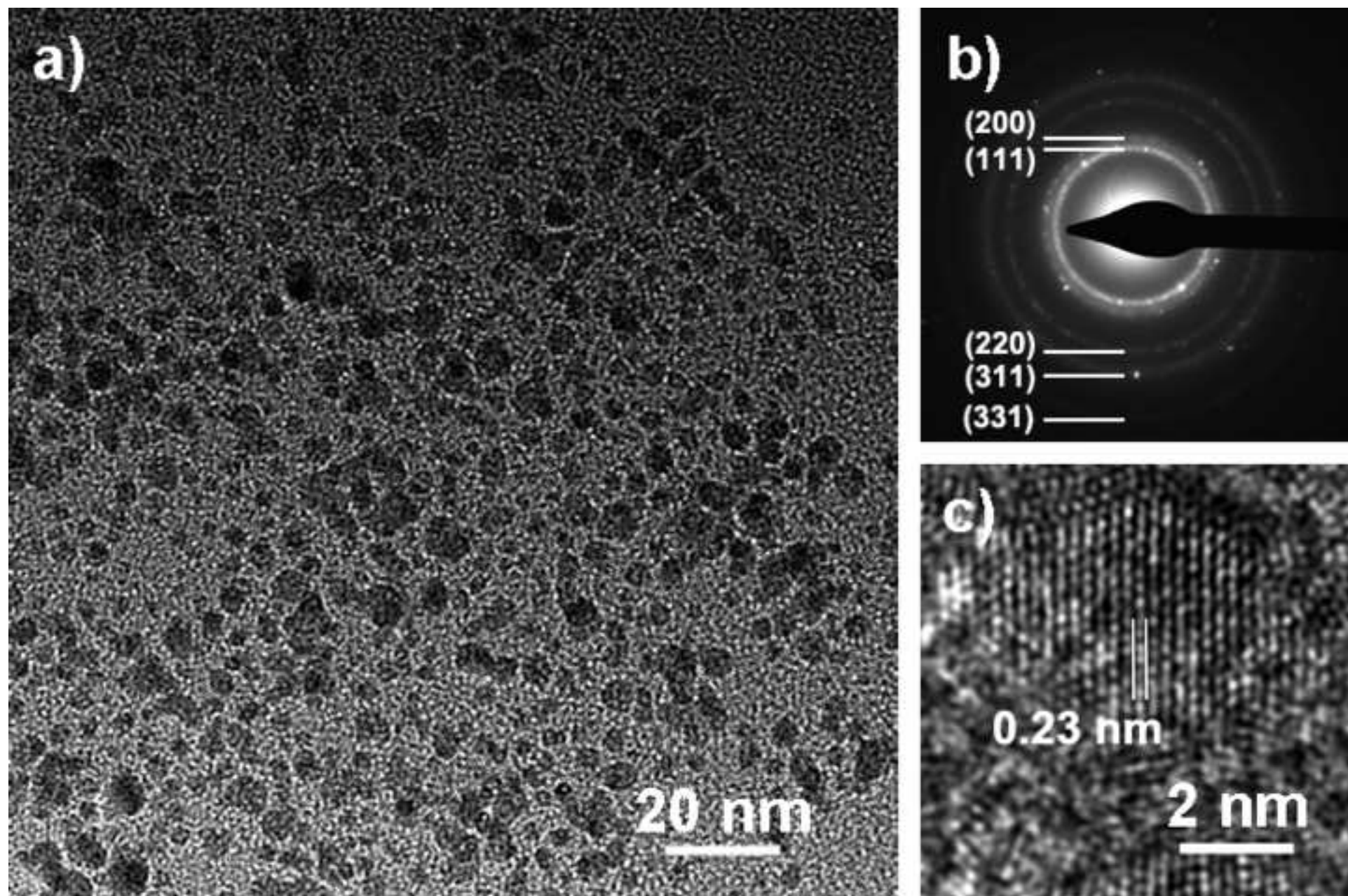


Fig. 4

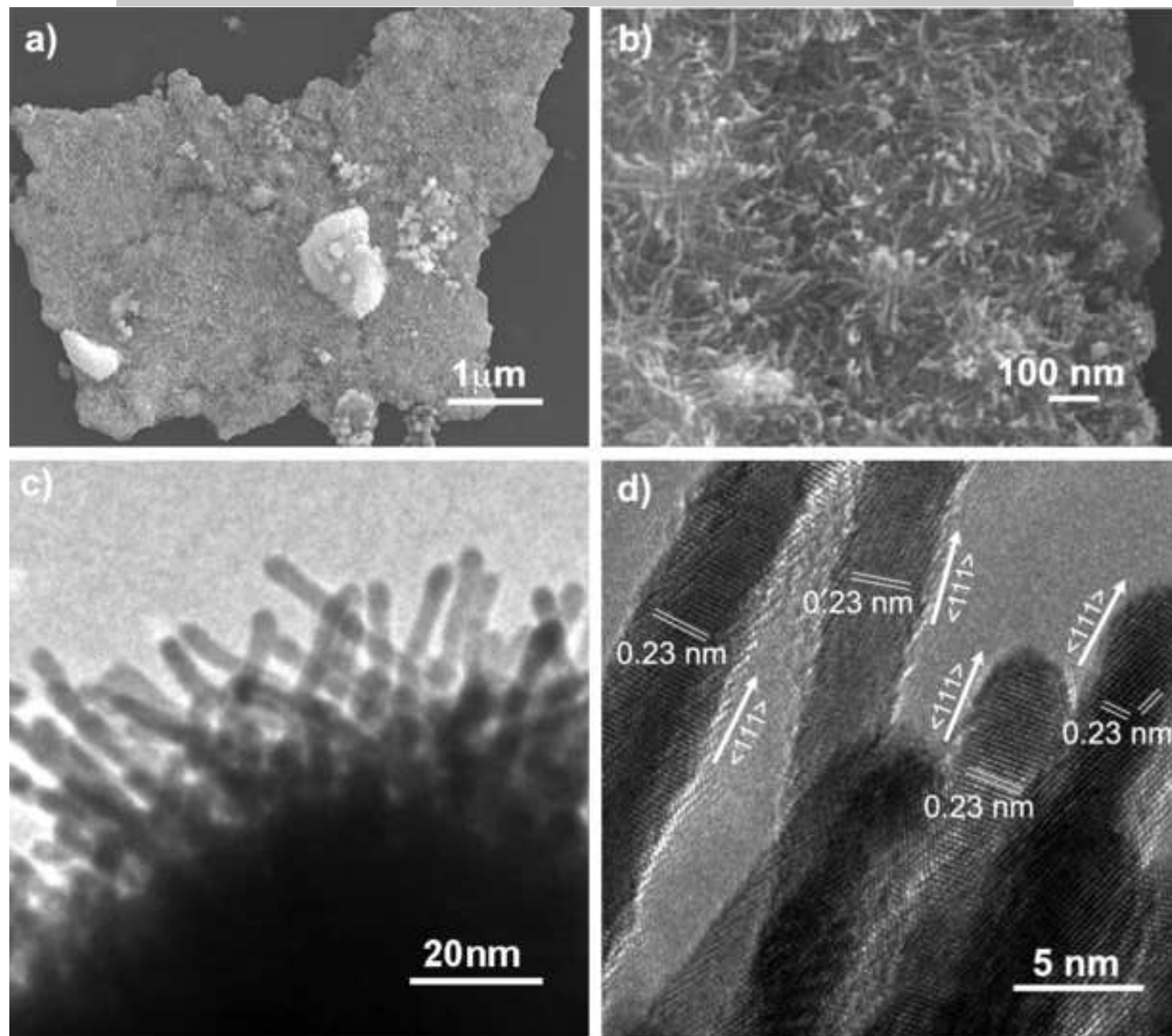


Fig. 5

