Oxygen Electroreduction on Pt Nanoparticles Deposited on Reduced Graphene Oxide and N-doped Reduced Graphene Oxide Prepared by Plasma-assisted Synthesis in Aqueous Solution

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Platinum nanoparticles were deposited on reduced graphene oxide (rGO) and nitrogen-doped rGO (rGO–N) by He/H₂ plasma jet treatment of H₂PtCl₆ aqueous solution for electroreduction of oxygen. Physical characterization of the prepared catalysts was performed by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. Electrochemical characterization was carried out by cyclic voltammetry and CO-stripping techniques. The oxygen reduction reaction (ORR) activity of the prepared Pt/rGO and Pt/rGO–N catalyst materials was investigated using the rotating disk electrode method in 0.1 M KOH and 0.05 M H₂SO₄. In both acidic and alkaline electrolytes, the catalyst materials prepared by the plasma jet method demonstrated superior electrocatalytic properties compared to that of commercial 20 wt% Pt/C catalyst. Specific activity values for the ORR in acid electrolyte were 2-fold and in alkaline media more than 3-fold higher than that obtained for commercial Pt/C catalyst.

1. Introduction

Development of the next-generation composite materials based on graphene is gaining tremendous attention in both scientific and industrial communities. Due to their unique electrical, electronic and chemical properties, graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO) are used in a wide range of applications e.g. fuel cells, supercapacitors, batteries, and related devices. Being perfect mechanically, thermally and chemically stable two-dimensional platform for metal nanoparticles (NPs), graphene has potential application in polymer electrolyte membrane fuel cells (PEMFC), where the oxygen reduction reaction (ORR) on the cathode meets strict kinetic limitations. To date, high-area carbon supported platinum or Pt-alloys have shown the highest electrocatalytic activity toward the ORR, however there is an increasing demand to minimize the amount of scarce and precious Pt in fuel cell cathode materials. Besides, to cut down the cost of fuel cell by lowering Pt loading (state-of-the-art is 0.4 mg cm⁻²) it is important to maintain the long-term stability of Pt catalysts. Pt/C composites have tendency to deteriorate during long-term operation of fuel cell. In harsh PEMFC conditions, Pt particles dissolve, migrate, and grow in size, resulting in the loss of electroactive catalyst surface area. Furthermore, Pt nanoparticles (PtNPs) enhance the corrosion of carbon support shortening the lifetime of fuel cell cathodes. To overcome these challenges, great effort has been made in order to combine PtNPs with graphene and its derivatives for enhancing their electrocatalytic performance. GO has hydroxyl, epoxy and carboxyl groups at the edges and on the basal plane, which make the GO materials hydrophilic and dispersible in aqueous solutions. Such surface functionalities favor good dispersion of catalyst nanoparticles on GO carrier increasing the electrochemically active surface area. Moreover, rGO based 2-D platform is used to stabilize supported metal NPs.

The most common preparation method of graphene-supported nanostructures is based on the reduction of GO and Pt precursors (K₂PtCl₄ or H₂PtCl₆) via different chemical and physical approaches, such as chemical reduction, photochemical method, microwave assisted preparation, electrospray deposition and thermal treatment. The use of plasma-liquid interaction, where charge transfer processes take place, is currently a rapidly developing alternative technique for preparation of catalyst nanoparticles. Plasma jet method provides good controllability, cleanliness and selectivity. It can tune optical and electronic properties of graphene, besides it is cost and time-effective. Plasma-assisted jet treatment of the aqueous solution is a simple one-step method to prepare simultaneously nanoparticles and the support material without any additional
reducing agents. Above all, it is possible to avoid surfactants, because the synthesized NPs are usually stabilized electrostatically.

In this work we report highly efficient approach to precisely design electrochemically active rGO and rGO–N supported platinum nanoparticles by using He/H₂ plasma jet treatment of aqueous solution of H₂PtCl₆. The main advantages of this one-step technique are relative simplicity, high reaction yield, fast processing rates at room temperature, and the absence of side products. Highly dispersed metal NPs on different high surface area supports have advanced properties for catalytic activity and sensor sensitivity. Moreover, using plasma jet method, catalyst nanoparticles can be deposited onto both sides of rGO monolayer sheets and integration of such two-dimensional supports with highly dispersed NPs can be an exciting material for use in future nanotechnology.

2. Results and Discussion
2.1. Physical Characterization of Catalyst Materials

The key processes for preparing of Pt/rGO and Pt/rGO–N catalysts are the reduction of PtCl₆²⁻ ions and formation of PtNPs. The detailed procedure for the plasma-assisted preparation of PtNPs in the aqueous solution of H₂PtCl₆ is described in Supporting information. Herein, we present the results of the simultaneous plasma treatment of H₂PtCl₆ water solution with rGO or rGO–N additives. The optical absorption spectra of working solutions before and after plasma processing were recorded using UV/VIS/NIR spectrophotometry and these results are presented in Figure 1.

![Figure 1. Characteristic extinction spectra of: 1 – GO solution; 2 – 0.1 mM solution of H₂PtCl₆ with NaOH and GO additives (0.1 mL of 2 mg mL⁻¹ GO solution) after 45 min of plasma processing (pH 7.6); 3 – rGO–N solution; 4 – 0.1 mM solution of H₂PtCl₆ with NaOH and rGO–N additives (0.1 mL of rGO–N solution) after 10 min of plasma processing (pH 5.7).](image)

Curve 1 in Figure 1 shows the UV-VIS absorption spectrum of GO (0.3 mg mL⁻¹) solution. The spectrum exhibits a maximum at 230 nm (attributed to π-π* transitions of the hexagonal aromatic chains of sp² bonded carbon atoms) and a shoulder at about 300 nm (ascribed to n-π* transitions of C=O bonds). It is well known that during the reduction of GO to rGO the 230 nm peak is red-shifted to about 260 nm, indicating the partial restoration of electronic conjugation in the aromatic carbon structure of GO. Curve 2 in Figure 1 shows the extinction spectrum of 0.1 mM solution of H₂PtCl₆ with NaOH and GO additives (0.1 mL of 2 mg mL⁻¹ GO solution) after 45 min of He/H₂ plasma processing. The obtained colloidal solution with pH 7.6 was stable. The shifted peak of rGO band at 262 nm was rather small due to low concentration of GO in the solution. It should be noted that 10 min of plasma processing is enough for the total reduction of PtCl₆²⁻ anions, however additional processing during 35 min is necessary mainly due to the slow reduction process of GO to rGO.

Chemical composition of the rGO–N support and Pt/rGO–N catalyst surfaces was evaluated using X-ray photoelectron spectroscopy (XPS). C1s, N1s, and O1s XPS peaks were observed as shown in Figure 2 and Pt4d and Pt4f peaks appeared in Figure 2b for Pt/rGO–N. Insets in Figure 2 show N1s XPS spectra, which can be deconvoluted into 3 peaks located at binding energies of 401.1, 399.6 and 398.3 eV, corresponding to the graphitic, pyrrolic and pyridinic N, respectively, all three N
species can form strong interactions with Pt atoms.\textsuperscript{[21,36]} High resolution XPS spectra of Pt/rGO–N and Pt/rGO catalysts in the Pt4f and C1s regions are presented in Figure S4 and discussed in Supporting information.

PtNPs and rGO flakes extracted from the solution immediately after the plasma treatment were imaged by scanning electron microscopy (SEM). As can be seen from Figure 3a, in Pt/rGO catalyst, prepared with NaOH additives (synthesis conditions are specified in Figure 1 for curve 2) rGO flakes were not successfully covered by small nonagglomerated PtNPs. This behavior may be explained by electrostatic repulsion between PtNPs and rGO sheets. PtNPs are negatively charged in the solution of pH 7.6. The value of zeta potential of rGO prepared by plasma-assisted technique is unknown. However, according to data for rGO produced by chemical reduction methods, the rGO isoelectric point (IEP) is at about 3.5.\textsuperscript{[37,38]} Therefore, we may consider that the prepared rGO flakes were also negatively charged and they were repelled from PtNPs in solution at pH 7.6.

It was revealed earlier that the attachment of NPs is efficient if pH is higher than the IEP of the NPs and lower than the IEP of the support.\textsuperscript{[39]} Unfortunately, isoelectric points of PtNPs and rGO are very close and the pH “window” of the attachment process is very narrow if at all possible. Negatively charged PtNPs could be attached to a slightly negatively charged rGO support if weak repulsive forces may be overcompensated by van der Waals attractive forces. To trigger the Pt nanoparticle attachment, small additives of diluted HCl were admixed to the solution of PtNPs containing rGO flakes just after the plasma processing (synthesis conditions are specified in Figure 1 for curve 2). As a result, pH of the solution decreased from 7.6 to 4.0 and colloidal solution became unstable – black precipitate separated after a few hours. SEM image of Pt/rGO nanocomposite extracted from the solution is shown in Figure 3b.
Small PtNPs are highly dispersed on the surface of rGO sheets. At pH close to the IEP, three competitive processes are involved: agglomeration of small PtNPs; attachment of NPs onto rGO support; agglomeration of uncovered rGO flakes. Depending on the rates of these processes different results could be obtained. From general consideration, to achieve homogeneous loading of PtNPs over all rGO flakes the concentration of H₂PtCl₆ and rGO as well as HCl additives should be carefully optimized.

To prepare nanocomposites with improved loading of PtNPs, nitrogen-doped rGO was used as a support. According to earlier data, functionalization of graphene surface with nitrogen-containing groups will move the isoelectric points of rGO–N to the higher value comparing with rGO. The starting solution was 4 mL of 0.05 mM H₂PtCl₆ with 0.1 mL additives of rGO/C₆ and pH of the starting solution (0.1 mM H₂PtCl₆ with 0.1 mL additives of rGO/C₆ and 0.51 mM NaOH). After 10 min of plasma processing, slightly adsorbed CO was observed. SEM image of Pt/rGO–N nanocomposite extracted from the solution after the plasma treatment is shown in Figure 3c. Small PtNPs were homogeneously dispersed on the surface of rGO–N sheets, however, a number of PtNPs agglomerates were also observed. PtNPs were produced continuously in the plasma-liquid interface layer and they were ready to deposit immediately to the surface of rGO–N if it was allowed by electrostatic interaction. Therefore, in ideal deposition conditions, PtNPs are not accumulated in the solution, which prevents the creation of agglomerates.

The morphology of deposited PtNPs onto rGO–N nanocomposite and c) size distribution histogram of PtNPs in Pt/rGO–N.

![ TEM and HRTEM images of Pt/rGO–N nanocomposite and size distribution histogram of PtNPs in Pt/rGO–N.](image)

Figure 4. a) TEM and b) HRTEM images of Pt/rGO–N nanocomposite and c) size distribution histogram of PtNPs in Pt/rGO–N.

rGO–N (see curves 3 in Figure S1 and Figure 1, respectively). The peak at 270 nm is rather weak due to low concentration of rGO–N in the solution. SEM image of Pt/rGO–N nanocomposite is shown in Figure 3d, where small PtNPs without agglomerates homogeneously dispersed on the surface of rGO–N sheets. PtNPs attached to the surface of rGO nanoflakes, prevented restacking of rGO sheets, resulting in the formation of stable nanocomposites.

2.2. Electrochemical Characterization

2.2.1. CO-Stripping and CV Experiments

Electrochemical decontamination of the modified electrode surface was carried out by CO-stripping technique as shown in Figure 5. The first potential cycle (between 0.05 and 0.4 V) shows complete blockage of the electrode surface due to the adsorbed CO. The broad peak between 0.6 and 0.8 V can be observed in the second potential cycle (0.05–1.0 V), which shows oxidation of the pre-adsorbed CO while hydrogen adsorption/desorption peaks in the third cycle confirm complete removal of the CO from the electrode surface. In order to confirm surface decontamination via CO-stripping, CV curves were measured before and after the CO oxidation experiments as shown in the insets of Figure 5. It can be seen in the H⁺ region that the hydrogen adsorption/desorption peaks are well-defined on the CV curves measured after the CO-stripping as compared to the one measured before, confirming surface decontamination and availability of more adsorption sites on the electrode surface.

CO stripping is one of the well-known electrochemical techniques used for the surface characterization of the electrocatalysts. Figure 6 displays comparison of the CO-stripping profiles of all the catalysts studied in this work in 0.05 M H₂SO₄ (a) and 0.1 M KOH (b).

In acid media (Figure 6a), Pt/rGO and Pt/rGO–N catalysts showed nearly the same CO oxidation profile while in alkaline media (Figure 6b) higher currents were observed in the case of Pt supported on rGO–N. Formation of a well-defined surface oxidation peak at ca 0.85 V observed for Pt/rGO–N catalyst can
be explained by Pt oxide formation. Plasma jet treatment is considered to be a clean method, since no reducing agents and stabilizing surfactants are used during synthesis. Nevertheless, trace amount of Cl\textsuperscript{-}/CO\textsubscript{3}\textsuperscript{2−} anions may remain from precursors and further exacerbate the catalyst efficiency by blocking Pt surface active sites.\textsuperscript{[25]} Therefore, it is strongly recommended to include CO-stripping technique in electrode preparation routine. In PEM fuel cells, chloride impurities arise from the membrane electrode assembly (MEA) preparation and less than 5-ppm of chloride residues can result in a voltage loss of 50 mV and affect the open-circuit voltage.\textsuperscript{[5]}

Cyclic voltammetry measurements were carried out in Ar-saturated 0.05 M H\textsubscript{2}SO\textsubscript{4} (Figure 7a) and 0.1 M KOH (Figure 7b) solutions in the potential range between 0.05 and 1.45 V at 50 mV s\textsuperscript{-1}. Similar CV profiles of the Pt-based electrocatalysts have been reported earlier.\textsuperscript{[41–44]} Formation of the Pt surface oxides can be seen in the anodic sweep at a potential above 0.8 V in both media, which are reduced at ~0.7 V in the cathodic sweep. The hydrogen desorption peaks at ~0.14 and ~0.27 V in acidic media and at ~0.28 and ~0.38 V in alkaline media correspond to the presence of (110) and (100) adsorption sites on the Pt surface.

![Figure 5](image_url)

**Figure 5.** CO stripping voltammograms of Pt/rGO–N catalyst in a) 0.05 M H\textsubscript{2}SO\textsubscript{4} and b) 0.1 M KOH solution (v = 20 mV s\textsuperscript{-1}). The insets show cyclic voltammograms measured before and after the CO oxidation treatment (v = 50 mV s\textsuperscript{-1}). The current densities are normalized to the geometric surface area of the electrode.

![Figure 6](image_url)

**Figure 6.** CO stripping voltammograms of Pt/rGO and Pt/rGO–N catalysts in a) 0.05 M H\textsubscript{2}SO\textsubscript{4} and b) 0.1 M KOH solutions (v = 20 mV s\textsuperscript{-1}). The current densities are normalized to the geometric surface area of the electrode.

The Pt/rGO–N nanocatalyst exhibited broader peaks with higher current in the hydrogen adsorption/desorption region than the Pt/rGO. Assuming that a charge density equal to 210 mC cm\textsuperscript{-2} is required to desorb a monolayer of the adsorbed hydrogen, the real surface area of the Pt catalysts (A\textsubscript{r}) was calculated from the hydrogen desorption peaks as given in Table 1 and 2. The double-layer capacitance for the Pt/rGO–N is larger than that for Pt/rGO, showing that the rGO–N support has higher electrochemically active surface area than rGO support. Increased specific surface area of the support material is influential for mass activity enhancement for Pt based catalysts.\textsuperscript{[28,45]}

**Table 1.** Kinetic parameters for oxygen reduction on Pt/rGO, Pt/rGO–N and commercial Pt/C catalysts measured in 0.05 M H\textsubscript{2}SO\textsubscript{4} solution.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>A\textsubscript{r} [cm\textsuperscript{2}]</th>
<th>Tafel slope [mV] region I\textsuperscript{[a]}</th>
<th>Tafel slope [mV] region II\textsuperscript{[a]}</th>
<th>E\textsubscript{1/2} [V]</th>
<th>SA at 0.9 V [mA cm\textsuperscript{-2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/rGO</td>
<td>0.71</td>
<td>—70</td>
<td>—155</td>
<td>0.84</td>
<td>0.20</td>
</tr>
<tr>
<td>Pt/rGO–N</td>
<td>1.24</td>
<td>—63</td>
<td>—121</td>
<td>0.85</td>
<td>0.22</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.67</td>
<td>—59</td>
<td>—125</td>
<td>0.84</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\[a\] Region I corresponds to low current densities and region II to high current densities.
Electrochemical reduction of oxygen was investigated in O$_2$-saturated 0.05 M H$_2$SO$_4$ and 0.1 M KOH solutions using the rotating disk electrode (RDE) method. The ORR measurements were performed for Pt/rGO and Pt/rGO–N catalysts at different electrode rotation rates (360–4600 rpm) in the potential range between 0.05 and 1.0 V at a scan rate of 10 mV s$^{-1}$.

Figure 8 illustrates the electrochemical ORR behavior of the electrodes measured at various rotation rates in 0.05 M H$_2$SO$_4$ (a, b) and 0.1 M KOH (c, d) solutions. Furthermore, the insets in Figure 8 show the number of electrons transferred per O$_2$ molecule ($n$) calculated using the Koutecky-Levich (K–L) equation given below [46]:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{nFkC_O^0} - \frac{1}{0.62nFD_O^{1/2}v^{1/6}C_O^0 \omega^{1/2}}
\]

(1)

where $j$ denotes the measured current density at a specific potential, while $j_k$ and $j_d$ are the kinetic and diffusion-limited current densities, respectively. $F$ denotes the Faraday constant (96,485 C mol$^{-1}$), $k$ is the rate constant for electrochemical reduction of oxygen (cm s$^{-1}$), $C_O^0$ denotes the concentration of O$_2$ (1.2×10$^{-6}$ mol cm$^{-3}$ in 0.1 M KOH and 1.22×10$^{-6}$ mol cm$^{-3}$ in 0.05 M H$_2$SO$_4$) while $D_O$ represents the diffusion coefficient of O$_2$ (1.9×10$^{-5}$ cm$^2$ s$^{-1}$ in 0.1 M KOH and 1.93×10$^{-5}$ cm$^2$ s$^{-1}$ in 0.05 M H$_2$SO$_4$), $v$ is the kinematic viscosity of the solution (0.01 cm$^2$ s$^{-1}$) and $\omega$ is the rotation rate of the electrode (rad s$^{-1}$). It was revealed that the catalysts follow the typical 4-electron transfer pathway in both acidic and alkaline media (see insets to Figure 8).

Figure 9 shows a comparison of the RDE polarization curves measured at 1900 rpm. Figure 9a displays the electrocatalytic ORR behavior of the catalysts in acidic media, while Figure 9b presents the ORR polarization curves recorded in alkaline media. Compared with commercial Pt/C catalyst in acid media, both catalysts showed lower current density in diffusion-limiting potential region, indicating that the kinetic current is lower than that obtained for Pt/C. However, Pt/rGO–N exhibits higher current at mixed kinetic-diffusion control region (between 0.8 and 0.9 V) than commercial Pt/C. Moreover, in alkaline media Pt/rGO–N catalyst shows superior performance in terms of all the kinetic parameters for O$_2$ reduction mentioned above. The half-wave potential ($E_{1/2}$) values were calculated from the RDE data and are presented in Tables 1 and 2. It was observed that in acidic media, all the electrodes showed comparable $E_{1/2}$ values to that of the commercial Pt/C (~0.85 V). In alkaline media, however, the highest $E_{1/2}$ value of 0.87 V was obtained for Pt/rGO–N catalyst.

Introducing N into the nanocarbon structure plays a critical role in determining the ORR performance. It has been reported previously, that pyridinic and/or graphitic N are actually responsible for the high ORR performance of N-doped carbon materials.[50–55]

Figure 10 represents Tafel plots constructed on the basis of the RDE data shown in Figure 9. Tafel slope values were determined from two characteristic Tafel regions and are presented in Tables 1 and 2. It can be seen that the Tafel slope values for all the electrodes are close to −60 and −120 mV at low and high current densities, respectively, indicating that the reduction reaction follows the same mechanistic pathway for all the electrodes in both media. The transfer of the first electron to the adsorbed O$_2$ molecule determines the ORR rate.[42,56]

According to previous reports, the change of the slope is not related to different reaction mechanism, but it has been attributed to the potential-dependent coverage of surface oxides on Pt catalyst that inhibit the adsorption of O$_2$ and reaction intermediates.[57–59] Tafel analysis results indicate that the reaction mechanism was the same for Pt/rGO, Pt/rGO–N and commercial Pt/C electrocatalysts.
Specific activities (SA) for O\textsubscript{2} reduction on the prepared catalysts were calculated using Eq. (2) and are summarized in Tables 1 and 2.

\[ SA = \frac{I}{A} \]  

(2)

In general, all the electrodes showed higher SA than that of the commercial Pt/C. The highest SA value of 0.22 and 0.38 mA cm\textsuperscript{-2} in acidic and alkaline media, respectively, was obtained for Pt/rGO–N catalyst. The values of SA obtained for commercial Pt/C catalyst were 2 and 3 fold lower than those obtained for Pt/rGO–N catalyst in acid and alkaline media, respectively. The superior SA values of plasma jet treated catalyst materials are obviously related to the unique morphology and uniform distribution of Pt nanoparticles, which is essential for enhancing the electrocatalytic ORR performance.\textsuperscript{(60)} In addition, the enhanced ORR activity may be ascribed to the superior electrical conductivities of Pt/rGO–N composites. RDE results clearly demonstrate that using one-step plasma-jet method in preparation of rGO-supported catalysts has a great effect on the activity of the supported metal nanoparticles.

3. Conclusions

Herein, we report a facile process to decorate reduced graphene oxide nanosheets with well-dispersed Pt nanoparticles by plasma jet treatment of aqueous solution of H\textsubscript{2}PtCl\textsubscript{6}. The plasma jet method allows efficient formation of Pt nanoparticles with variable loading, and the low cost of rGO could enhance the commercial viability of these supported Pt catalysts. Prepared catalyst materials showed remarkable electrocatalytic behavior toward ORR in both alkaline and acidic media. The main objective of the present work was to demonstrate the one-step plasma-assisted synthesis of Pt nanoparticles supported on rGO sheets and to establish their application in electrocatalysis.

Experimental Section

Preparation of Pt/rGO and Pt/rGO–N Materials by Plasma Jet Treatment

Deionized Milli-Q water (18.2 M\textsubscript{Ω} cm) was used throughout all experiments in this work. Stock 1 mM solution of Pt (IV) complexes was prepared by dissolving chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6} \textbullet 6H\textsubscript{2}O, 99.95%, Alfa Aesar) in water. Aqueous solutions of NaOH (0.1 M) and HCl (0.1 M) were prepared with analytical-grade reagents.
Graphene oxide (GO) was prepared by chemical oxidation of natural graphite powder by the modified Hummer's method. The powder of as-prepared GO was dispersed in water by sonication for 30 min, then centrifuged (2500 g, 15 min) to precipitate the non-exfoliated large GO flakes. The supernatant of this solution was a stable yellow colloidal suspension of predominantly single-layer GO flakes with the concentration of 2 mg mL$^{-1}$.

For comparison a powder of nitrogen-doped reduced graphene oxide (rGO/C$_0$N) (Graphitene Ltd., UK) was used. The rGO/C$_0$N material was poorly dispersible in water and therefore the suspension of rGO/C$_0$N was used immediately after the sonication procedure. He and H$_2$ gases with a purity of 6.0 and 5.0, respectively, were used in experiments with plasma-assisted processing.

rGO and rGO/C$_0$N supported PtNPs were synthesized by a method similar to that described in our previous work [63]. An atmospheric pressure bipolar pulsed discharge in He/H$_2$ (95/5) gas jet with a continuous gas flow of 100 standard cubic centimeters per minute (sccm) was used for the net transfer of the plasma active species into the aqueous solution of 0.1 mM of H$_2$PtCl$_6$ with small additives of rGO or rGO/C$_0$N. The current flow (peak value of about 2 mA) was arranged from a thin metal capillary through a plasma jet and over the electrolyte to a grounded Pt wire counter electrode immersed in the liquid. Pt nanocomposites were produced in plasma-liquid interface layer due to reduction of PtCl$_6^{2-}$ anions by solvated electrons e$_{aq}$ and H$^*$ radicals, which are the strongest and cleanest chemical reducing agents known. He/H$_2$ plasma in bipolar pulsed-current regime has several advantages for electrochemical reduction applications. First, is the negligible production of NO$_x$ (the absence of additional acidification of the solution) and OH$^{•-}$ (the absence of hydrogen peroxide H$_2$O$_2$ in the solution). These species could be harmful owing to the oxidative etching of metal NPs. Second, the directional drift of charged species, including the final products, in the electric field of the solution is absent. As a consequence, no deposition of these species to the grounded Pt electrode was observed. Third, O$_2$ or H$_2$ gas bubbles did not appear to evolve due to electrolysis of water. However, the short-lived active species (O$^•$ or H$^*$, e$_{aq}$) were generated in the plasma-liquid interface, just as in the case of a fixed polarity. Fourth advantage is that pulsed discharge is more stable against the glow-to-arc transition comparing the direct current regime.

The volume of the processing solution in a sealed silica cell was 4 mL. The overall temperature of the liquid did not exceed 40 $^\circ$C during the plasma treatment. In order to decrease the concentration of N$_2$ and O$_2$ the solution was deaerated by bubbling helium gas with a flow of 100 sccm during 10 min before plasma ignition. To minimize agglomeration and precipitation of nanocomposites during the plasma processing, vigorous stirring of the solution was arranged by a low-power (~1 W) ultrasonic (113 kHz) transducer contacted the bottom of the silica cell.

### Preparation of Pt/rGO and Pt/rGO-N Modified Electrodes

Glassy carbon (GC) electrodes of surface area of 0.126 cm$^2$, fixed in Teflon™ holders were polished on 1.0 and 0.3 µm alumina slurries (Buehler) to get a smooth shiny GC surface. The polished electrodes...
were then sonicated in Milli-Q water and 2-propanol for 3 min in each. Before the deposition of graphene-supported Pt catalysts onto the electrode, the concentration of the as-prepared colloidal solution was increased by about 20 times by simple centrifugal enrichment (10000 g, 10 min) and washing several times with water. Afterwards, 8 µL of the catalyst ink suspension was transferred to the GC electrode surface and dried in the oven at 60 °C for 30 min. The modified electrodes were then used for physical characterization and electrochemical measurements. We estimate the upper limit of Pt loading on the GC electrode as about 45 µg cm⁻². This calculation is based on the assumption of 100% efficiency of the plasma-assisted reduction of PtCl₄²⁻ anions and centrifugation enrichment, which is probably not realized in experiment. Apparently the real Pt loading is lower than 45 µg cm⁻².

**Instrumentation and Measurements**

The optical absorption spectra of solutions before and after plasma processing were recorded on a Jasco V-570 ultraviolet-visible UV/VIS/NIR spectrophotometer with 1 cm silica cell. The background spectrum from a cell filled with deionized water was subtracted from all measured spectra.

A homemade high-voltage bipolar pulsed generator with the repetition rate of 12 kHz was used for the discharge excitation in He/H₂ plasma jet. The voltage and current waveforms of the discharge were similar to that demonstrated in our previous works. The pH values of solutions were measured by a portable pH meter (pH-98103R, Analytical Instruments).

Surface morphology of the prepared nanocomposite catalysts was studied by a Helios NanoLab™ 600 (FEI) scanning electron microscope (SEM). For scanning transmission electron microscopy measurements, a Titan 200 (FEI) instrument was used. The samples for electron microscopy analysis were prepared by adding drops of colloidal catalyst suspensions onto a surface of polished GC substrate (for SEM) or a standard copper grid (for TEM) with subsequent air-drying for at least 2 h before imaging. The particle size distribution statistics were determined from the evaluation of the TEM images by measuring the diameter of at least 150 particles for each sample.

Surface chemical composition analyses were performed by X-ray photoelectron spectroscopy using a SCIENTA SES-100 electron spectrometer. The XPS analysis was carried out using monochromatized Mg Kα X-ray source (incident energy 1253.6 eV) with a take-off angle of 90° and a source power of 400 W. In the analysis chamber the pressure was less than 10⁻¹⁰ Torr. The following parameters were applied for collecting the survey spectra: energy range 600–0 eV, pass energy 200 eV and step size of 0.5 eV. High-resolution scans were performed in specific regions with the pass energy of 200 eV and the 0.1 eV steps.

Electrochemical measurements were conducted in a five-necked glass cell with a standard three-electrode configuration. For electrochemical decontamination and characterization of the electrodes surface, CO-stripping was performed. Cyclic voltammetry was performed at a scan rate (v) of 50 mV s⁻¹ in Ar-saturated 0.05 M H₂SO₄ and 0.1 M KOH solutions. The ORR measurements were performed at 10 mV s⁻¹ in O₂-saturated solutions at different rotation rates (ω), ranged from 360 to 4600 rpm, using rotating disk electrode system consisting of an EDI101 rotator and a CTV101 speed control unit (Radiometer Analytical). All the potential values are given with respect to the reversible hydrogen electrode (RHE).

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**: Electrocatalysis · graphene · nanoparticles · oxygen reduction · plasma jet treatment
