



# Evaluation of reduced-graphene-oxide-supported gold nanoparticles as catalytic system for electroreduction of oxygen in alkaline electrolyte



Sylwia Zoladek<sup>a</sup>, Iwona A. Rutkowska<sup>a</sup>, Magdalena Blicharska<sup>a</sup>,  
Krzysztof Miecznikowski<sup>a</sup>, Weronika Ozimek<sup>a</sup>, Justyna Orłowska<sup>a</sup>, Enrico Negro<sup>b</sup>,  
Vito Di Noto<sup>b</sup>, Paweł J. Kulesza<sup>a,\*</sup>

<sup>a</sup> Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland

<sup>b</sup> Department of Industrial Engineering, Università degli Studi di Padova in Department of Chemical Sciences, Via Marzolo 1, 35131 Padova (PD), Italy

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## ABSTRACT

Chemically-reduced graphene-oxide-supported gold nanoparticles with a diameter, of 40–60 nm are considered here as catalytic materials for the reduction of oxygen in alkaline medium in comparison to analogous systems based on conventional Vulcan carbon carriers. Gold nanoparticles are prepared by the chemical reduction method, in which the NaBH<sub>4</sub>-prereduced Keggin-type phosphomolybdate heteropolyblue acts as the reducing agent for the precursor (HAuCl<sub>4</sub>). Polyoxometallate (PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>) capping ligands stabilize gold nanoparticle deposits, facilitate their dispersion and attachment to carbon supports. Indeed, it is apparent from the independent diagnostic voltammetric experiments (in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>) that heteropolymolybdates form readily stable adsorbates on nanostructures of both gold and carbon (reduced graphene oxide and Vulcan). It is reasonable to expect that the polyoxometallate-assisted nucleation of gold has occurred in the proximity of oxygenated defects existing on carbon substrates. Under conditions of electrochemical diagnostic experiments (performed in 0.1 mol dm<sup>-3</sup> KOH): (i) the phosphomolybdate adsorbates are removed from the interface as they undergo dissolution in alkaline medium; and (ii) the Au nanoparticles (Au loading, 30 μg cm<sup>-2</sup>) remain well-dispersed on the carbon as evident from transmission electron microscopy. High electrocatalytic activity of the reduced-graphene oxide-supported Au nanoparticles toward reduction of oxygen in alkaline medium is demonstrated using cyclic and rotating ring-disk voltammetric experiments. The latter system could also act as the active support for Pt nanoparticles during the reduction of oxygen. Among important issues are possible activating interactions between gold and the support, as well as presence of structural defects existing on poorly organized graphitic structure of reduced graphene oxide (as evident from Raman spectroscopy).

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## 1. Introduction

A tremendous amount of research has been carried out in the field of oxygen electroreduction, particularly with respect to potential applications in the fuel cell research [1–11]. Obviously, many efforts have been made to develop suitable alternative electrocatalysts efficient enough to replace electrocatalysts based on scarce strategic elements such as platinum-group metals (PGMs) [5,6,8,9,12,13]. Despite intensive research in the area of

low-temperature fuel cells with proton-conducting electrolytes, the practical oxygen reduction catalysts still utilize systems based on PGMs.

More recently, the anion-exchange membrane low-temperature fuel cells [14,15], *i.e.* the systems mounting hydroxyl (OH<sup>-</sup>)-conducting polymer membranes, have been proposed. Because they operate in alkaline environment, other elements beyond PGMs can act as reasonable candidates for implementation as the oxygen reduction catalytic sites [16]. Representative examples include gold, silver and nickel-based catalytic materials that are obviously much cheaper and more abundant, and are promising for future commercialization. In this respect, the systems based on gold nanoparticles capable of oxygen reduction in alkaline medium

\* Corresponding author. Tel.: +48 22 5526344; Fax: +48 22 5526434.

E-mail address: [pkulesza@chem.uw.edu.pl](mailto:pkulesza@chem.uw.edu.pl) (P.J. Kulesza).

[17–20] should be mentioned. The enhanced catalytic activity of gold nanostructures is often attributed to existence of the high fraction of low-coordinated surface atoms at the corners and edges of Au nanoparticles, that play the roles of active sites [21,22]. The kinetics and mechanism of the oxygen electroreduction at Au(hkl) catalysts in alkaline medium is critically dependent on the interfacial gold structure as well as on the potential applied to the electrode [23]. It has been postulated that, in alkaline solutions, the four-electron reduction of oxygen on Au(100) involves the disproportionation mechanism [19] which seems to be enhanced on Au(100) in comparison to the performance of other two low-Miller index faces of Au. For example, on Au(111), the reduction of oxygen proceeds according to the 2-electron reaction mechanism with hydrogen peroxide as the final reduction product [24]. The role of the superoxide ( $\text{O}_2^-$ ) adsorptive intermediate has been postulated to be more significant during the  $\text{O}_2$ -electroreduction in alkaline media relative to that in acidic media [19,23]. When it comes to application of carbon-supported gold nanoparticles (with a diameter of 7–8 nm) for oxygen reduction, their electrocatalytic activity seems to vary inversely with the size of the particles [17]. In this respect, the decreased hydrophilicity and coordination of the smaller clusters of gold is believed to increase to the energy of binding of between O and Au and to decrease the activation energy during the dioxygen dissociative chemisorption.

The  $\text{O}_2$ -reduction electrocatalysts are typically nanocomposite materials utilizing metal nanoparticles bearing the active sites dispersed on suitable supports. While exhibiting long-term stability, a useful support should facilitate dispersion, provide easy access of reactants, and assure good electrical contact with active sites. In spite of limitations related to the durability, carbon nanoparticles of approximately 20–50 nm diameters (e.g. Vulcan XC-72R) are commonly utilized as supporting materials. Because of the high specific surface area and excellent thermal, mechanical and electrical properties, graphene and graphene-based materials [25–27] have recently been considered as supports for catalysts [28–32]. Under such conditions, the parasite effects related to agglomeration and thus degradation of catalytic nanoparticles are likely to be largely prevented.

In the present work, we consider the chemically reduced graphene-oxide-supported gold nanoparticles as catalytic systems for the electroreduction of oxygen in basic medium. The electrocatalytic diagnostic experiments involve comparative measurements utilizing commonly-used Vulcan (carbon) supports as carriers for the analogous gold nanoparticles. Here application of inorganic Keggin-type heteropolymolybdates ( $\text{PMo}_{12}\text{O}_{40}^{3-}$ ) as capping ligands (capable of chemisorbing on both gold and carbon substrates [33–40]) facilitates deposition, nucleation, stabilization and thus controlled growth of gold nanoparticles on surfaces of both Vulcan and graphene nanostructures. In the latter case, we have utilized the so-called reduced graphene oxide which, contrary to conventional graphene, still contains oxygen functional groups regardless of subjecting it to the chemical reduction step [25–27]. By analogy to graphene oxide, the existence of oxygen groups in the plane of carbon atoms of reduced graphene oxide not only tends to increase the interlayer distance but also makes the layers somewhat hydrophilic. Furthermore, during fabrication of the catalytic systems (in acid medium), the adsorbed polymolybdates [9,34] are likely to bind gold nanoparticles via the oxygen or hydroxyl groups on graphene and Vulcan surfaces. During operation in alkaline medium, polyoxometallates decompose and disappear; but the catalytically active gold centers remain stable on carbon surfaces. It is apparent from the diagnostic cyclic voltammetric and rotating ring-disk measurements in the oxygen-saturated  $0.1 \text{ mol dm}^{-3}$  KOH that the system utilizing Au catalyst deposited on the chemically reduced graphene oxide has exhibited higher electrocatalytic currents (and produced lower amounts of

the undesirable hydrogen peroxide intermediate) during oxygen reduction (relative to the performance of gold nanoparticles deposited on conventional Vulcan-carbon support or simple bare Au nanoparticles). The enhancement effect is particularly sound in the high potential range (0.8–1.0 V vs. RHE). On the whole, the combined effect of the high surface area and electrical conductivity of reduced graphene oxide should contribute to the overall enhancement effect and activity of Au nanoparticles toward the oxygen reduction. The reduced-graphene-oxide-supported Au-nanoparticles could also act as active matrices for Pt catalysts thus forming the potent  $\text{O}_2$ -reduction electrocatalytic systems.

## 2. Experimental

Chemicals were commercial materials of the highest available grade, and they were used as received. KOH, HCl,  $\text{HNO}_3$ ,  $\text{K}_2\text{SO}_4$ , ethanol and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  were obtained from POCh (Poland). The hydrogen tetrachloroaurate (III) trihydrate,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (>99.9%); sodium borohydride (powder, 98%),  $\text{NaBH}_4$ ; phosphomolybdic acid hydrate,  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  (ACS. reagent), 5 wt% Nafion solution were purchased from Sigma-Aldrich and were used without any further purification. Nitrogen and oxygen gases (purity 99.999%) were from Air Products (Poland). Platinum black was obtained from Alfa Aesar.

Graphene oxide sheets of 300–700 nm sizes (thickness,  $1.1 \pm 0.2 \text{ nm}$ ) were from Megantech. Reduced graphene oxide (rGO) was obtained using sodium borohydride as reducing agent at  $80^\circ\text{C}$  according to the procedure described earlier [41].

Vulcan XC-72R conductive carbon black was purchased from Cabot and purified by treatment in  $12 \text{ mol dm}^{-3}$  HCl solution for 1 h followed by washing out with distilled-deionized water several (3–4) times to remove any possible leftovers. The resulting carbon black particles were functionalized with interfacial oxygen-containing groups by subjecting them to  $3 \text{ mol dm}^{-3}$   $\text{HNO}_3$  for 8 h under reflux conditions, then washed thoroughly with water, (collected under high-speed centrifuging conditions) and, finally, dried completely at  $60^\circ\text{C}$ . Solutions (including  $0.1 \text{ mol dm}^{-3}$  KOH) were prepared by dissolving the respective chemical in the triply-distilled subsequently-deionized (with Milli-Q water purification system) water.

Fabrication of gold nanoparticles modified with heteropolymolybdates ( $\text{PMo}_{12}\text{O}_{40}^{3-}$ ) was achieved in a manner analogous to the approach described in our previous papers [34–38]. First, a stoichiometric volume of the freshly prepared aqueous  $0.016 \text{ mol dm}^{-3}$  sodium tetrahydroborate ( $\text{NaBH}_4$ ) was added to the  $30 \text{ cm}^3$  of  $0.256 \text{ mmol dm}^{-3}$  aqueous solution of phosphododecamolybdic heteropolyacid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) under vigorous stirring. In the next step, an equivalent volume (3 ml) of the aqueous  $7.5 \text{ mmol dm}^{-3}$   $\text{HAuCl}_4$  (precursor) was added. The resulting colloidal suspension was centrifuged, the supernatant solution was removed and, subsequently, replaced with water. A final solution of the water-dispersed gold nanoparticles (stabilized by  $\text{PMo}_{12}\text{O}_{40}^{3-}$ ) had a volume of  $0.5 \text{ cm}^3$ .

The syntheses of phosphomolybdate-modified gold nanoparticles supported onto Vulcan XC72R carbon and reduced graphene oxide matrices were performed in the analogous manner as described earlier [34–38] but in the presence of an appropriate carbon support. Among important features of both unsupported and carbon (Vulcan, graphene) supported phosphomolybdate-modified Au nanoparticles is their monodispersed character and low tendency to undergo agglomeration. To assure good dispersion of nanostructured carbon supports in water, they have been pre-modified with  $\text{PMo}_{12}\text{O}_{40}^{3-}$  adsorbates, namely, by exposing either 0.01 g of purified Vulcan XC72R carbon or chemically reduced graphene-oxide to  $30 \text{ cm}^3$  of the aqueous  $2.56 \text{ mmol dm}^{-3}$  phosphododecamolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) solution. The latter

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