Title:

Zero waste, single step methods of fabrication of reduced graphene oxide decorated with gold nanoparticles.

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Abstract:

This paper reports a novel approach to the use of carbon, in the form of reduced graphene oxide, as a reducing agent for Au(III) chloride complex ions. This approach allows fabrication of a composite material Au@GO in a single-step process. The reduction of Au(III) complex ions was performed using high pressure, 50 bar, and high temperature, 250°C, reactor. The average diameter of obtained gold nanoparticles was below 3 nm. The advantage of the reduced graphene oxide as the reducing agent is its high surface area. This accelerates the reaction rate significantly. The greenness and sustainability of the process are assessed by green chemistry metrics and circularity indicators recently applied for the first time to a nanomaterial synthesis. As a key green metrics, atom economy (AE) measures the degree of the incorporation of reactant atoms into the final product and in the case of the research presented scoring 99%.

Keywords: graphene oxide, gold nanoparticles, synthesis, deposition, adsorption, catalysis,
1. Introduction

During the last decade, graphene oxide (GO) was extensively studied as a potential host material for catalysts [1-6], sensors, etc. [7-9]. For many applications, the fluorescence quantum yield of GO is an important parameter. This can be enhanced by deposition of metallic nanoparticles [10]. Both the mass production and stability of aqueous suspensions of GO made its medical [11] and diagnostics[12] applications promising.

Graphene oxide-based catalysts can be fabricated using several different techniques [13-16]. In all those approaches, the reductant is required to deposit metallic nanoparticles at the surface of GO. Wide range of reductans can be applied starting from strong, such as NaBH₄ [17, 18] and dimethyl aminoborane [19, 20], through medium-strength e.g. hydrazine [21], to weak ones such as green plant extracts [22]. In all cases, the final reaction products are contaminated with impurities and, require further purification.

GO has been considered potential catalyst support for many years. Mastalir et al. [23], for instance, have shown that palladium nanoparticles (PdNPs) deposited on GO have a better catalytic property in the hydrogenation of 3-hexyne and 4-octyne. The GO-Pd catalyst indicated stereoselectivity exceeding 98%. Gold nanoparticles (AuNPs) also exhibit interesting catalytic properties [24], for example, in electro-oxidation of carbon monoxide [25-27], carbon dioxide [28, 29], ethylene glycol [30], cyclohexane [25], glycerol [25], methanol [31, 32], and benzyl alcohol [25].

AuNPs can be obtained via several different routes, e.g. chemical reduction [33, 34], thermal decomposition of precursor [35], laser ablation [36, 37], Gamma-ray irradiation [38, 39], and electrochemical reduction [40]. These methods yield particles differing in size and shape and, in turn, different properties such as light absorption, the intensity of localized surface plasmon resonance, red/blue–shift of the maximum wavelength of the plasmon peak, etc. [41].
Microwave (MW) radiation was used in inorganic chemistry for the first time in the early 70’s [42]. Nowadays, over 250 scientific papers published each year, describes the use of MW in chemical synthesis [43, 44]. It was noted that thanks to the high speed of temperature increase of reacting system, it is possible to significantly accelerate the chemical reaction compared to traditional techniques such as sand [45] or oil baths [46], heating jackets [47], etc. Also, by appropriate selection of reactor material, it is possible to avoid its heating during microwave irradiation. In effect, only the solvent and reagents are heated, and it is easier to achieve uniform temperature distribution in the reactor, avoiding the large temperature gradients observed when using traditional techniques[48].

Generally speaking, the effect of a chemical reaction acceleration can be explained using the Arrhenius eq. (1):

\[ k = A \cdot e^{-\frac{E_a}{RT}} \]  

Eq. (1)

where: \( A \) is the so-called pre-exponential factor, which is often described as the frequency of vibration of molecules on the surface on which the reaction occurs, \( E_a \) is the activation energy, \( R \) – is the universal gas constant and \( T \) – is the absolute temperature.

It is rather unlikely that the activation energy of the reaction will decrease under the influence of microwave radiation. Thus, two other effects are probably responsible for the acceleration of chemical reaction. The enthalpic one is associated with the storage of energy supplied by microwaves in the form of the vibrational energy of reacting particles. The entropic one, in turn, is related to the arrangement of particles [49]. They both are connected according to the Eyring-Polanyi equation. The Eyring-Polanyi equation is based on the transition state model and correlates the rate constant with thermodynamic characteristics of the process (eq. (2)):
\[
\ln \left( \frac{k}{T} \right) = -\frac{\Delta H^\dagger}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^\dagger}{R}
\] (2)

where: \(\Delta H^\dagger\) and \(\Delta S^\dagger\) stand for changes in the enthalpy and entropy of the activation stage, respectively, \(k_B\) is Boltzmann and \(h\) Plank constant.

Microwave radiation has already been used for the synthesis of nanoparticles and composites. Wang et al. [50] present microwave-assisted one-pot synthesis of metal/metal oxide nanoparticles on graphene with ethylene glycol as the reductant. Although its reducing strength is rather low, the reaction rate can be significantly increased at elevated temperatures. Xu et al. [51] have investigated the process of microwave-assisted synthesis of AuNPs on carbon nanotubes. In this case, sodium citrate acted as the reductant at elevated temperatures. Raghuveer et al. [52] also used a microwave-assisted method for the single-step functionalization of carbon nanotubes with AuNPs with ethylene glycol as the reductant.

In this work, we are going one step further and show the possibility of microwave-assisted fabrication of Au@GO composite material without using any additional reductant, besides GO. This is an important result indicating that the composite material, with potentially high catalytic activity, can be obtained in one step and does not require laborious and expensive purification.

The emergence of the so-called Green Chemistry (GC) concept by the end of the last century has promoted the higher concern in the development of environmentally friendly and less hazardous processes. On top of that, green metrics have been standardized to guide the research of new environmentally conscious green-by-design fundamental chemical synthesis pathways, by the use of renewable raw materials, eliminating waste, and avoiding hazardous reagents and solvents [53]. Semi-quantitative metrics, based on undesirable ecologic and hazardous penalties within 6 categories, have been further included as EcoScale, evaluating the overall greenness
of a chemical process with the highest green score of 100 points [54]. More recently, these concepts have been globalized in a wider vision, so-called Circular Economy (CE), which entails the waste design, the rational consumption of limited resources, and the longer lifetime of materials through their successive reuse. Accordingly, circular metrics have been recently developed by Ellen MacArthur Foundation (EMA) [55], to measure the degree of recycling, reusing, and resources consumption of a process. The main indicator is the Material Circularity Indicator (MCI), which quantifies the circularity degree of a process in a range between 0 (linear) and 1 (circular) [55]. In order to provide a comprehensive assessment of the process’ sustainability, green and circular metrics for Au@GO synthesis are also provided in this paper.

2. Experimental

Au@GO composite material was synthesized in the following way. Firstly, 19.7 g of metallic gold (99.999%) was dissolved in aqua regia (3:1 volumetric ratio of concentrated hydrochloric acid, 37 wt.%, and nitric acid, 65 wt.%, both of analytical purity), to obtain Au(III) chloride complex. To remove excess nitric acid, the obtained complex was alternatively distilled and dissolved with hydrochloric acid. Finally, obtained dry salt was dissolved in deionized water to obtain the stock solution with the initial concentration of 0.1 M. This was used in all experiments. Secondly, graphene oxide aqueous suspensions were prepared by diluting the stock solution, 5 g/L, obtained from Graphene Supermarket and used as a reducing and stabilizing agent. Magnum II (Ertec, Poland) 600 W microwave-heated digestion system was used for fabrication of the composite material 25 mL of the reaction mixtures, containing various amounts of Au(III) complex and GO were transferred to the 108 mL PTFE-made reaction vessel. Then they were heated for $t = 10$ min to $T = 523$ K using microwaves with a frequency 2.45 GHz. The pressure in the reaction vessel increased from atmospheric to ca. 40 bar. When the targeted value of $T$ was achieved, microwaves were switched off and the reaction mixture was cooled to room temperature using running water.
When the hydrothermal treatment was finished, the UV-Vis spectra of obtained Au@GO suspensions were recorded using a Shimadzu PC2501 PC spectrophotometer. Further characterization of these suspensions required the application of spectroscopic methods such as x-ray photoelectron (XPS), Fourier-transform infrared (FT-IR), and Raman spectroscopy. XPS analysis was performed using an ultrahigh vacuum system equipped with a hemispherical analyzer (SES R4000, Gammadata Scienta, Sweden). Mg Kα incident radiation with an energy of 1256.6 eV, was applied. The spectrometer was calibrated according to ISO 15472:2001 standard. The FT-IR spectra were registered on a Nicolet 380 spectrometer. Au@GO suspensions were mixed with potassium bromide powder of spectroscopic grade and dried for 24h at 353 K. The pellets were formed using a hydraulic press. Raman spectra were recorded using a triple-grating Raman Spectrometer (Horiba Jobin-Yvon T64000) with an argon laser excitation wavelength of 514.5 nm. The measurements were performed in a macro-chamber. Samples were placed in a spectrofluorometric QX (Hellma) quartz cuvette. The experiment was carried out in a classical configuration, where exciting and scattered beams were perpendicular to each other. The laser power measured directly on the samples was ~ 20 mW. The acquisition time for a single spectrum was experimentally adjusted to obtain a high signal-to-noise ratio. For all obtained data the baseline correction was done, the next spectra were normalized to the amplitude of the band assigned to water (located c.a. at 3400 cm^{-1}) and finally, the spectrum of deionized water was subtracted.

Apart from spectroscopic methods, Differential Thermal Analysis and Differential Scanning Calorimetry, DTA-DSC, were used for the characterization of GO and GOr, using TA Instruments SDT Q.600. Thermal analyses of the aforementioned materials were conducted in the Ar atmosphere, with the flow of the inert gas equal to 100 mL/min. The content of impurities in argon was the following: H2O<3 ppm/mol, O2<2 ppm/mol, CnHm<0.5 ppm/mol. The sample
of GO and GO, were droplet into measuring crucible and dried at 50°C (in air atmosphere) to avoid their thermal decomposition.

Microscopic characterization of Au@GO suspensions was conducted using transmission electron microscopy (TEM). They were homogenized with ultrasounds for ca. 5 minutes, transferred onto standard carbon-coated copper grids via drop-casting method, and dried at room temperature for 30 min. Then, they were observed on an FEI Tecnai TF20 X-TWIN (FEG) microscope working at an accelerating voltage of 200 kV.

The concentration of Au in the Au@GO suspensions was determined using an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES). For this purpose, 1 mL of Au@GO suspension was mixed with 1.5 mL of aqua regia. Gold was dissolved after 15 min and the specimens were diluted to 10 mL with deionized water.

The catalytic properties of Au@GO composite material were tested by using cyclic voltammetry (CV) in the three-electrode system. The working electrode was prepared by spreading and evaporation of different amounts of Au@GO colloidal suspensions on a freshly polished surface of glassy-like carbon (GC). The grain size of the polishing alumina was 0.05 μm. Saturated calomel electrode SCE was used as a reference whereas platinum wire was used as the counter electrode. All electro-catalytic studies were carried out in deoxygenated 0.1 M NaOH solution at pH = 13. using an Autolab PGST- AT12 potentiostat-galvanostat. In all experiments, 100 mVs⁻¹ scan rate and initial concentration of glucose of 10 mM were applied. Phase analysis was done using the XRD method (Rigaku MiniFlex II). A sample of the colloid was placed on a standard glass holder, then the solvent was evaporated. To obtain a satisfactory noise/signal ratio, the colloid application process was repeated several times.
3. Results and discussion

It is well known, that Au(III) chloride complexes can be reduced by activated carbon [56, 57]. In such a case, the following reaction scheme is proposed (eq. (3)):

\[
\frac{1}{3} \text{AuCl}_3 + C + 2\text{H}_2\text{O} \xrightleftharpoons{} \frac{1}{3} \text{Au} + \frac{5}{3} \text{Cl}^- + \text{CO}_2 + 4\text{H}^+
\] (3)

Thermodynamic calculations, conducted using the HSC software, clearly confirm that such reaction is spontaneous in a wide range of temperatures. Gibbs free energy change, \(\Delta G^0\), for \(T = 293\) and \(573\) K equals \(-1.0\) and \(-1.1\) MJ/mol, respectively. Thermodynamic calculations, however, cannot predict the kinetics of the process. In fact, this reaction is slow, therefore, high temperature is required to obtain metallic gold in a reasonable time. Moreover, in the case of graphene oxide, most of the carbon atoms are bound to oxygen, so the reaction (3) is limited by the presence of functional groups on the GO surface. When the reduction is conducted under atmospheric pressure, the boiling point of the reaction mixture defines the upper limit of temperature and, thus, the reaction rate. This is common to reduce noble metal complexes at a high temperature [58, 59]. Higher reduction rates can be achieved at temperatures above the boiling point of the reaction mixture, but the process must be conducted in a pressurized vessel. In this work, the microwave-heated reactor was applied. More details about microwave-heated reactor control can be found in the supplementary materials.

3.1 Interaction between graphene oxide, reduced graphene oxide, and Au(III) ions

The possibility of Au@GO\(_r\) composite formation during hydrothermal treatment in the pressurized reactor was studied using UV-Vis spectroscopy. This is a very useful method because it is possible to simultaneously observe changes in Au(III) complex concentration in the UV and the formation of solid particles. The latter effect manifests itself as the increasing background of the spectrum. When the reduction results in the formation of nanoparticles, the
absorption peak, related to localized surface plasmon resonance (SPR), appears in the visible part of the absorption spectrum. The maximum of this peak is strongly related to the nanoparticles’ size [60-62].

First of all, the absorption spectra of the reaction mixtures before hydrothermal treatment were recorded (Fig. 1a). Typically for Au(III) chloride complex, the maximum absorption peak is located at 314 nm [63]. In our case, it was shifted to 312 nm (Fig. 1a). This was related to the fact that the concentration of Cl\(^-\) ions in the reaction mixture was \(\sim 0\). GO, when dispersed in water, forms a colloidal suspension. Its particles scatter incident light and, thus, increase the absorbance. The shorter wavelength, the stronger scattering, and higher absorbance are observed. Thus, the absorption peak at 312 nm is hardly visible. GO also absorbs UV radiation with the absorption peak centered at 235 nm. This is attributed to \(\pi \rightarrow \pi^*\) transition. However, this is not a specific absorption band and its position depends on the method of GO synthesis [64, 65], defects in GO structure, as well as dispersant’s composition.

The UV-Vis absorption spectra of the reaction mixtures after hydrothermal treatment are presented in Fig. 1b. The hydrothermal treatment affected the absorption spectrum of the Au(III) complex itself. The absorbance at 312 nm decreased from 3.365 to 2.851 \(i.e\). for ca. 15%. The peak shape also changed slightly. A small increase of the absorbance level from 0 to 0.032 was observed in the Vis region of the spectrum, but no absorption peak that could be attributed to the surface plasmon resonance of AuNPs appeared. Therefore, changes in UV-Vis spectrum of the Au(III) complex, after hydrothermal treatment, can be related to its hydrolysis. This occurs in a weakly acidic environment if the content of the complexing ions is low. Redox reaction between water and gold(III) chloride complex ions can be excluded since the redox potential of gold(III) chloride complex ions is lower than water oxidation (see equations (4) [66, 67] and (5) [67])
\[ \text{AuCl}_4^- + 3e^- = \text{Au} + 4\text{Cl}^-; \quad E^0 = 1.002\, V \quad (4) \]

\[ \text{O}_2 + 4\text{H}^+ + 4e^- = \text{H}_2\text{O}; \quad E^0 = 1.230\, V \quad (5) \]

Thus, the electromotive force (EMF) of the galvanic cell, where reduction \( \text{AuCl}_4^- \) occurs together with oxidation of \( \text{H}_2\text{O} \) is negative, meaning that the process is not spontaneous at standard conditions.

What is more important, the absorbances of the reaction mixtures containing GO decreased significantly after hydrothermal treatment, and the absorption peak at 312 nm is no longer visible. Additional absorption peak appearing at 542 nm, clearly visible for \([\text{GO}] = 0.2 \) and \( 0.3 \) g/L, is related to the SPR of AuNPs. Absorbance changes are not proportional to the initial concentration of GO. This means that hydrothermal treatment affects also the GO itself; in fact the yellow-brown colloid turned black. Therefore, the influence of hydrothermal treatment on the UV-Vis spectrum of the GO colloid, without Au(III) complex, was also studied (Fig. 1c). The absorption peak at 235 nm slightly shifted to 234 nm after the hydrothermal treatment. What is more, a new peak, centered at 260 nm appeared. This was attributed to GO deoxygenation \( i.e. \) formation of the reduced graphene oxide, GO\(_r\). It was assumed that observed deoxygenation is related to the thermal dissociation of weak bonds between carbon atoms and functional groups. GO deoxygenation has already been achieved using various reductants such as rose extract, sodium borohydride, pyrogallol, vitamin C, and hydrazine [68]. Deoxygenation efficiency depended on the reductant applied. Annealing of GO is another, well-known, method of GO\(_r\) fabrication. This can be easily performed, but comes along with a tremendous weight-loss of material, about 30% up to 200 °C, which is accompanied by the formation of CO and CO\(_2\), and results in a highly disordered structure of GO\(_r\) [69]. The main disadvantage of the thermal treatment is the fact that all functional groups are removed simultaneously [70] and
there is no control over this process. This strongly deteriorates the ability of GO to form stable
water suspensions and thus limits somehow its possible applications.

Simultaneous reduction of Au(III) complex and GO deoxygenation complicates interpretation
of the UV-vis spectra. For instance, the position of the SPR peak, extracted from Fig. 1B
depends on the Au(III) complex/GO weight ratio (Fig. 2). The exact nature of this correlation,

Fig. 1 UV-Vis spectra of A) the Au(III) complex and GO reaction mixtures prior and B) after
hydrothermal treatment; C) GO colloid prior and after hydrothermal treatment; \( t =10 \) min.
however, remains unclear. Here, two possible explanations can be proposed. On the one hand, the SPR peak position for AuNPs may depend on the degree of GO’s deoxidation [71], since this phenomenon strongly depends on the properties of its surface. On the other hand, this correlation may be related to the dispersion of AuNPs’ size. It is well known that relatively small nanoparticles have the SPR peak shifted towards a shorter wavelength when compared to the bigger ones[60]. Thus, if we observe the superposition of SPR peaks from smaller and bigger nanoparticles, the peak position will depend on the fraction of small/big NPs in the composite material. It should also be noted that very small gold nanoparticles, below 2 nm, show no SPR peak at all [72]. In fact, the literature supports both explanations for the change in SPR position of AuNPs. Fakhri et al. [73] reported nonlinear optical responses of graphene oxide-Au nanoparticles dispersed in different solvents. The authors recorded the maximum absorption peak in the UV-Vis Au / GO spectrum at 527 nm. The position of the peak depended, e.g. on the composition of the dispersing phase as well as the size of the Au nanoparticles.

Au(III) complex reduction can be indirectly supported with the observation, that pH of the reaction mixture decreased after the hydrothermal treatment. The initial value was between 4.7 and 4.8 regardless of the GO concentration in the range between 0.1 and 0.8 g/L. The pH after hydrothermal treatment, however, was between 3.9 and 4.0. This change may be explained with eq. (3), where hydrogen ions are one of the reduction products.
The most important conclusion, drawn from this part of our work, is, that hydrothermal treatment caused reduction of Au(III) complex and deoxygenation of graphene oxide and the composite material, presumably Au@GO_r was formed. The evidences for Au NPs and GO_r formation are further provided, together with discussion of the reduction mechanism.

3.2 Evidences for Au reduction

Au NPs formation in the studied system was suggested on the basis of decreasing Au(III) complex concentration and rather a weak absorption peak attributed to the SPR of AuNPs. Thus, additional characterization of the obtained composite material was necessary. First, the x-ray diffraction method (XRD) was applied. Diffraction patterns of GO and Au@GO_r are compared in Fig. 4.
Diffraction lines corresponding to graphene oxide and metallic gold are clearly visible. Intensity of diffraction lines ascribed to GO (001) and graphite (002) crystal planes is much smaller when compared to the intensity of Au (111) line. At the same time, this diffraction line is relatively narrow suggesting rather good crystallinity of the gold deposit. These observations offered the possibility of estimation of Au NPs’ average size, \( d \), using Sherrer’s equation (see eq. (6)):

\[
d = \frac{K \cdot \lambda}{\beta \cdot \cos \Theta}
\]

where: \( \lambda \) is the wavelength of the incident x-rays, \( \beta \) is the width of the diffraction line at half of its height, \( \theta \) is the Bragg angle and \( K \) is a dimensionless shape factor. Its value was assumed as equal to 0.9. Calculated value of the average AuNPs’ diameter is 12 nm. This means that relatively large nanoparticles were obtained. Two obtain this value it was assumed that the gold particles were monocrystalline rather than polycrystalline, which is reasonable taking into account their nanometric size. The instrumental contribution to the diffraction line width was neglected.

Another analytical technique applied, much more sensitive than XRD, was X-ray photoelectron spectroscopy. At first, the XPS survey spectrum was registered (Fig. 4). The strong peaks...
ascribed to In and Mo come from the sample holder, whereas the peaks attributed to Au 4f, Cl 2p, C 1s, and O 1s correspond to Au@GO \(_r\) and adsorbed synthesis residues. Usually, one of the most important piece of information which can be obtained from the XPS spectrum is the electronic structure of the analyzed element. Detailed analysis of O 1s is usually of limited importance, because of the similar binding energy of many oxide-containing compounds. Analysis of Cl 2p XPS peak also does not bring about any important information of the composite material. Therefore, the analysis was focused on peaks attributed to C 1s and Au 4f.

![XPS spectrum](image)

**Fig. 4** XPS survey spectrum of the obtained composite material. Experimental conditions: \([\text{GO}]=0.1\text{g/L}, [\text{Au(III)}]=7.5\times10^{-5}\text{M}, \text{synthesis time 10 min.}\)**

XPS spectrum of graphene oxide is dominated by a signal coming from C-O and C-C bonds with sp\(^3\) hybridization, with a small admixture of ester and ketone groups as well as C=C sp\(^2\) bonds (Fig. 5 A). The binding energy for the latter can also be attributed to metal-C binding [74]. Because this peak was observed before Au(III) complex was reduced, its presence in the XPS spectrum of Au@GO \(_r\) cannot be used as proof for metallic Au formation and was deliberately not fitted for composite material. Apparently, GO’s deoxidation and Au(III) complex reduction changed the chemical state of carbon atoms. The proportion between
intensities of signals coming from C-O and C=C bonds changed towards C=C bonds, the content of ester groups increased, and carboxylic groups appeared (Fig. 5 B).

![Graph A)(B)](image)

**Fig. 5 C 1s XPS spectra for A) GO, and B) Au@GO, experimental conditions: [GO]=0.1g/L, [Au(III)]=7.5x10^{-5}M, synthesis time 10 min.**

The high-resolution Au spectrum confirmed the presence of metallic gold. XPS peaks were ascribed to Au 4f\(^{7/2}\) with binding energy 84 eV and spin-orbit energy shift 3.7 eV (see Fig. 6). This has already been confirmed using the much simpler XRD method, but XPS analysis of Au spectrum provided other valuable information. First is the difference in binding energy, when compared to the value typically reported for gold. This occurs due to the so-called initial state effect and indicates the presence of Au nanoparticles with a size < 3 nm [75]. Such small nanoparticles could not be responsible for the well defined diffraction line in the XRD pattern (see Fig. xxx). This suggests certain distribution of size of AuNPs and was further confirmed with high resolution transmission electron microscopy. However the most important observation is that there was no signal coming from gold in ionic form. Therefore, adsorption of Au(III) complex on the GO did not occur as a separate process, but only as the intermediate
one prior to reduction. In other words, XPS together with UV-Vis spectra confirms complete reduction of Au(III) complex i.e. 100% reaction yield.

**Fig. 6** Au 4f XPS spectrum for Au@GO.
Finally, high-resolution transmission electron microscopy was applied to ultimately determine the diameter of Au NPs (Fig. 7).

![HR-TEM analysis of Au-GO materials](image)

Fig. 7 HR-TEM analysis of Au-GO materials A) with Fast Fourier Transform (FFT), of selected areas A1-A4); B and C are a magnification of the selected area in A). Experimental conditions: [GO]= 0.1g/L, [Au(III)] = 7.5x10^{-5}M, synthesis time 10 min.

Large nanoparticles, with a diameter > 15nm, can be observed. This is in reasonably good agreement with the results of XRD analysis. Also, at higher magnification, ultra-small particles
were detected (see Fig. 7 B and C). Detailed analysis confirmed that these are AuNPs (see Fig. 7 A1-A4). The low observed contrast of AuNPs is related to their small diameter. Because the intensity of gray color on TEM images is proportional to the thickness of material exposed to radiation this was used for estimation of the NPs’ diameter assuming that they are spherical in shape. A 2-point calibration method was used. As a zero point, the gray intensity of graphene oxide was chosen. As the second calibration point, the center of the large particle with a known diameter was selected. Then, the thickness of the small AuNPs was estimated as equal to 2.5 nm. This result is in good agreement with the XPS data, and measurements shown in Fig. 7 B and C. This also confirms that the obtained AuNPs have a spherical shape.

The interplanar spacing of AuNPs crystal lattice were obtained from Fig. 7 A1-A4. These were compared to the values calculated according to equation (7):

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where: $d_{hkl}$ is the interplanar spacing for given Miller indices $h$, $k$, $l$ and $a$ is the Au lattice constant, 0.408 nm [76]. Good agreement between these two sets of data was found (Table 1). It further confirms formation of AuNPs.

<table>
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<tr>
<th>crystallographic plane</th>
<th>interplanar spacing, nm</th>
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<tr>
<td></td>
<td>calculated using eq. (6)</td>
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<tr>
<td>(111)</td>
<td>0.235</td>
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<tr>
<td>(110)</td>
<td>0.288</td>
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<tr>
<td>(300)</td>
<td>0.136</td>
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Table 1: Calculated and determined interplanar spacing for AuNPs
3.3 Evidences for GO reduction. Deoxygenation of GO during hydrothermal treatment was deduced from changes visible in the UV-Vis spectra of the GO suspensions and was also suggested by the results of XPS analysis. In this part, further evidences for GO reduction are provided. Starting with FT-IR analysis, it should reveal the differences between GO, GO\textsubscript{r} and Au@GO\textsubscript{r}, coming from adsorption of nanoparticles and/or involvement of the GO’s functional groups in the Au(III) complex reduction. GO\textsubscript{r} was obtained by hydrothermal treatment of pure graphene oxide at a concentration of 0.1 g/L. The sample labeled Au@GO\textsubscript{r} was obtained in the following way: GO dispersion was mixed with Au(III) chloride complex ions to finally reach the concentration of GO=0.1 g/L and [Au(III)]=7.5x10\textsuperscript{-5} M, the synthesis time was equal to 10 min.

Obtained results are shown in Fig. 8. The observed peak at 3452 cm\textsuperscript{-1} can be attributed to –OH groups [77]. The peak at 1384 cm\textsuperscript{-1} is due to the C-O stretching vibration of COOH groups [78].

![Fig. 8 FT-IR analysis of Au@GO\textsubscript{r} composite material. Experimental conditions: [GO]=0.1g/L, [Au(III)]=7.5x10\textsuperscript{-5}M, synthesis time 10min.](image)
The peak at 1720 cm\(^{-1}\), attributed to the C=O stretching in the carboxylic group of a carboxylic acid disappears after hydrothermal treatment [78]. This supports the observation that functional groups are removed during this process and suggests that the reduced graphene oxide is obtained. The peaks at 1627 and 1635 cm\(^{-1}\) correspond to C=C stretching. The hypsochromic shift from 1627 cm\(^{-1}\) to 1635 cm\(^{-1}\) stems from the disappearance of the overlapping peak at 1720 cm\(^{-1}\).

The most important results for this part of our work provided analysis of Raman spectra of GO, GO\(_r\) and Au@GO\(_r\) (see Fig. 9). Two peaks characteristic for graphitic materials, attributed to D and G bands of graphene, are well visible at 1364 cm\(^{-1}\) and 1602 cm\(^{-1}\), respectively [79-82]. The G band has E\(_{2g}\) symmetry and occurs for a carbon system with sp\(^2\) hybridization. This G mode arises from the in-plane stretching vibration of the C–C bonds [82, 83]. The D band is characterized by A\(_{1g}\) symmetry and signifies the in-plane breathing mode of the aromatic rings with sp\(^3\) hybridization in graphene structure. This band is registered only if some imperfections occur in the graphene sheets. At the same time, the intensity of the G band decreases with an increasing number of defects in the graphitic structure concerning the intensity of the D band [82]. The ratio of the intensities of D to G bands (\(I_D/I_G\)) read out from the Raman spectra of investigated samples, were found to be equal to 0.60 for GO, 0.63 for GO\(_r\), and 0.81 for Au@GO\(_r\), respectively. Obtained \(I_D/I_G\) values increase with the increasing number of more structural defects in the sample. The small difference between GO and GO\(_r\) is related to the partial deoxygenation of the former, during the hydrothermal treatment. For the Au@GO\(_r\) sample, intensities of the D and G bands decrease significantly. This can be related to structural changes, resulting from the decoration of the GO\(_r\) structure with Au nanoparticles [81].
Fig. 9 Raman spectra of GO\textsubscript{r} and Au@GO\textsubscript{r} composite material. Experimental conditions: [GO]=0.1g/L, [Au(III)]=7.5x10^{-5}M, synthesis time 10min (blue line) and [GO\textsubscript{r}]=0.1g/L hydrothermal treatment time 10min (black line).

The analysis of FT-IR and the Raman spectra confirm that graphene oxide was partially reduced during hydrothermal treatment. However, the hydroxide groups remained at the surface of GO\textsubscript{r}. This shows the significant difference between the applied hydrothermal method and annealing, wherein all functional groups are removed [70].

More information regarding to what extent GO was reduced during the microwave-assisted hydrothermal treatment was obtained with differential thermal analysis and differential scanning calorimetry. GO and GO\textsubscript{r} obtained via hydrothermal route, were annealed in the atmosphere of Ar. The mass loss, together with the DSC signal were recorded (see Fig. 10). Gradual mass loss of GO sample occurred up to 380 K. This may be related to evaporation of adsorbe moisture. Rapid deoxygenation of GO occurred at 380 K. It was related to significant mass loss of the specimen, ca. 50%. Strong thermal effect accompanied this process. The next one was observed at 474 K, but it was much weaker. The mass of the material at T > 380 K gradually decreased with increasing temperature. Different results were obtained for GO\textsubscript{r}. 

23
According to the literature [84], reduced graphene oxide should have a lower oxygen content than GO, because some functional groups were removed from the surface [85]. Therefore, neither significant mass loss, nor the prominent thermal effect were observed at 380 K. Interestingly, the thermal effect at 474 K was again detected. This is rather related to the carbon material, not to its functional groups. These studies quantitatively confirmed that graphene oxide was reduced during the hydrothermal treatment. Although FT-IR study revealed the presence of OH groups in GO, sample, their amount is rather insignificant, because there was no substantial mass loss related to its further deoxygenation.

These results provide also some insight to the mechanism of the studied process. Au(III) complex can be reduced with C atoms, as shown in equation (3). Surface functional groups may be useful in the case of adsorption, but they usually don’t act as electron donors in the reduction reaction. Therefore, GO reduction seems to be necessary prerequisite to reduction of Au(III) complex. This observation was confirmed in the subsequent part of our study.

Fig. 10 DSC-TGA analysis of A) GO and B) GO, under Ar flow
3.4 GO\textsubscript{r} as the reducing agent for Au(III) complex

Spectrophotometric analysis of the reaction mixture after hydrothermal treatment together with spectroscopic characterization of the obtained composite material unambiguously confirmed that it is composed of metallic gold and reduced graphene oxide, Au@GO\textsubscript{r}. The last remaining question concerned the identification of the reducing agent in the studied system. The results of thermal analysis of the GO and GO\textsubscript{r} suggest that the latter is responsible for Au(III) complex reduction. This assumption was confirmed with additional spectrophotometric studies. These were conducted using the tandem cuvettes. Such a cuvette contains two compartments. Thus, it is possible to measure the overall absorption spectrum which is the sum of the spectra of solutions from both compartments. The results for cuvettes containing GO in one compartment and Au(III) complex in another one, as well as GO\textsubscript{r} with Au(III) are presented in Fig. 11 A. The overall spectra slightly differ when compared to the spectra shown in Fig. 1 A. This is caused by the lower concentration of Au(III) ions in respect to GO/GO\textsubscript{r} in the mixture. To emphasize this, an exemplary spectrum of Au (III) complex is also included. When the solutions from both compartments were mixed, chemical reactions started. The UV-Vis spectra of both samples were then recorded, every 360 s. Two sets of spectra were obtained. The first one, describing the reaction between GO and Au(III) complex (Fig. 11 B), and the other one for the reaction between GO\textsubscript{r} and Au(III) complex (Fig. 11 C). In both cases, the absorption spectra changed over time. In the case of the GO+Au(III) system, the absorbances within the whole range of wavelengths, between 200 and 900 nm, gradually decrease. This means decreasing concentration of Au(III) complex. However, there was no absorption peak attributed to the SPR of AuNPs. In other words, the observed chemical process is not the reduction of Au(III). When Au(III) chloride complex was mixed with GO, the concentration of chloride ions in the solution decreased significantly. This, together with relatively high pH $\sim$ 4, caused gradual transformation of Au(III) chloride complex to hydroxyl complexes [20, 86] and aqua complexes [56, 87]. When Au(III) complex was mixed with GO\textsubscript{r}, in turn, the absorption peak at $\lambda \approx 500$
nm appeared. Its absorbance increased together with decreasing concentration of Au(III) complex. The location of this peak corresponds to SPR of AuNPs, and is comparable to Fig. 1B. The kinetic curves, showing how the absorbance at 550 nm changed with time, are presented in Fig. 1D. Thus, it can be concluded that GO\textsubscript{r} is able to reduce Au(III) complex, whereas GO is not. This is related to the presence of the functional group on the surface of GO. They probably hamper the electron transfer from carbon atoms to Au(III) ions. Hydrothermal reduction of graphene oxide removed this hindrance and reduction reaction became possible.
3.5 Catalytic properties of Au@GO$_r$

It is well known that gold both in the bulk and in the form of nanoparticles catalyzes the process of electrooxidation of glucose in alkaline media [88, 89]. The catalytic activity of Au@GO$_r$, obtained when [GO]=0.1 g/L and [Au(III)]=7.5x10$^{-5}$M, was studied with cyclic voltammetry. Voltammograms were recorded as a function of the amount of the composite material. This was droplet onto the glassy-like carbon electrode, 0.196 cm$^2$, and dried in air. Before catalytic tests, the electrode was activated electrochemically in 0.25 M H$_2$SO$_4$ solution.
This procedure was a repeated polarization between −0.4 and 1.2 V vs. SCE starting from the OCP (Open Circuit Potential), with the scanning rate of 100 mV/s. After 20 potential scans, the electrode was rinsed in deionized water. Electrode activation was necessary to observe glucose oxidation, otherwise, virtually no anodic current peaks were visible. Cyclic polarization removed CO$_2$ adsorbed on the surface of Au NPs (see analysis of FT-IR spectra) and the electrode became electrocatalytically active.

Subsequently, glassy-like carbon electrode covered with Au@GO$_r$ was immersed into 0.1 M NaOH solution containing 10 mM of glucose, and cyclic voltammograms were recorded in the potential range between −1.25 and 0.50 V vs. SCE; starting potential was −0.21 V. Electrooxidation of glucose was also studied at a polycrystalline gold electrode, $S = 0.196$ cm$^2$. Obtained cyclic voltammograms are typical for the aforementioned process. Three oxidation peaks centered at −0.5, 0, and 0.2 V vs. SCE correspond to oxidation of glucose. These oxidation peaks appear also when Au@GO$_r$ was used, but the peak positions are somewhat shifted. This is especially true for the peak centered at −0.5 V. Peak intensities are also much smaller when compared to the bulk gold electrode with current intensity depending on the volume of Au@GO$_r$ dropped onto the GC electrode (see below). There is also another important difference between Au and Au@GO$_r$ at potentials below ca. −0.5 V vs. SCE. On Au@GO$_r$ electrode certain reduction process occurs. This is not related to glucose, because it is neither visible on GC, nor Au electrodes. One possibility may be hydrogen evolution. This process should occur at potentials $< −1$ V vs. SCE; it is rather slow on the polycrystalline gold [90], but might be somewhat enhanced on GO$_r$ [91]. Alternatively, cathodic current may be related to further reduction of GO. It was also observed that anodic current density increased as the number of potential scans increased. This may support the hypothesis of ongoing GO reduction at potentials $< −0.5$ V vs. SCE. In such a case, two explanations can be provided. Either GO$_r$ itself catalyzes glucose oxidation to some extent, or the electrical conductivity of GO$_r$ increases.
Fig. 12 Cyclic voltammograms for glucose electrooxidation on glassy-like carbon, polycrystalline Au and Au@GO. Experimental conditions: 10mM glucose, 0.1 M NaOH, potential scanning rate 100mV/s., T = 20°C

The main objective of this part of the work was the evaluation of the catalytic performance of Au@GO composite material compared to polycrystalline Au. This required estimation of the surface area of Au@GO deposited onto the GC electrode. The first approach was based on simplified geometrical assumptions [14]: (i) the nanoparticles are spherical, (ii) they are deposited on both sides of GO’s plates, (iii) only half of AuNPs remains in contact with electrolyte.

The number of nanoparticles, \( N_i \), in the Au@GO composite material can be estimated using Eq. (8):

\[
N_i = \frac{C_{Au} \cdot V}{\frac{4}{3} \cdot \pi \cdot R_i^3} 
\]

where: \( C_{Au} \) is the concentration of gold in the Au@GO suspension, \( 1.043 \times 10^{-5} \) g/cm\(^3\) determined with MP-AES, \( V \) is the volume of Au@GO suspension droplet on the GC electrode,
and $\rho_{\text{Au}}$ stands for gold density 19.3 g/cm$^3$. The average nanoparticle radius, $R_i$, was assumed as 2.5 nm according to HR-TEM analysis (see chapter 3.2). Large particles were neglected since their number is significantly lower in comparison with the ultra-small ones. The total surface area of AuNPs that were in contact with the electrolyte $i.e.$ was assumed to be catalytically active was calculated using eq.(9):

$$S = \frac{1}{2} N_i \cdot 4 \cdot \pi \cdot R_i^2$$

(9)

The surface area of AuNPs increases linearly as the volume of Au@GO$_r$ suspension increases (Fig. 13 a). However, corresponding current densities, obtained for oxidation peak centered around 0.2 V vs. SCE do not increase and are over 4 times lower when compared to bulk Au electrode (Fig. 13 b). This means that obtained composite material does not have significant catalytic properties towards glucose oxidation. The presented methodology of evaluation of the active surface area of Au@GO$_r$ is very simplistic and, according to results of the Molecular Dynamic Simulations, gives overestimated values [92]. Therefore, the electrochemical method was also applied. It is commonly used for the determination of the active surface area of similar composite materials [93]. Cyclic voltammograms were recorded for Au@GO$_r$ deposited onto GC electrode in the potential range, where there were no electrochemical reactions, with different potential scanning rates. The current, measured in the middle of the potential window, was plotted against the potential scanning rate. The data points were fitted using the linear model with the slope indicating differential capacitance of the double layer $C_{\text{DL}}$. Results obtained are provided in supplementary materials. $C_{\text{DL}}$ is proportional to the surface area of the electrode which can be calculated when the specific capacitance of a given material $C_S$ is known (eq. (8))

$$ECSA = \frac{C_{\text{DL}}}{C_S}$$

(10)
McCready et al. reported $C_s$ values for different catalysts between 0.022 and 0.130 mF/cm$^2$ in alkaline solutions [93, 94]. In this work, the value of 40 µF/cm$^2$ was used. Obtained surface area is higher when compared to the geometric one. That is because the electrochemical method is not selective i.e. it takes into account the capacitance of the double layer of the whole composite material. This is especially true when the surface area of AuNPs is comparable to the surface area of the bulk electrode (Fig. 13a). There is also an additional factor complicating the electrochemical determination of the AuNPs’ surface area. GO$_r$ can behave as a semiconductor. Then, its space charge layer, rather than the electrical double layer contributes to the measured capacitance [95]. Accordingly, lower values of oxidation current densities were obtained (Fig. 13b).

![Graph A: Estimated surface area of AuNPs and current density corresponding to glucose oxidation peak centered around 0.1 V vs. SCE.](image1)

![Graph B: Current density as a function of volume of Au@GO$_r$ suspension.](image2)

Fig. 13 Estimated surface area of AuNPs A) and current density corresponding to glucose oxidation peak centered around 0.1 V vs. SCE B) as a function of the volume of Au@GO$_r$ suspension used for electrode’s fabrication

Provided results show that fabricated Au@GO$_r$ composite material has no significant catalytic effect on glucose oxidation in the alkaline solution when compared to bulk Au electrode. This
is probably because the size of AuNPs, 2.5 nm, is roughly comparable to a glucose molecule, 1 nm. This may hinder the charge transfer. Another limiting factor can be the electric resistivity of the composite material. This, however increases during hydrothermal treatment due to reduction of GO to GO$_r$.

3.6 Sustainable metrics.

The synthesis methodology presented herewith was assessed in terms of green and circular metrics. The first relates to the efficient utilization of materials and the second to the re-use and recycling capacity of a process. We follow our approach for the green metrics assessment of nanoparticles as recently described by Pho et al. [96] which is shown in Table 2. As a key green metrics, atom economy (AE) measures the degree of the incorporation of reactant atoms into the final product. In the case of the research presented in this paper, AE is favored by the absence of side reactions, scoring 99%. Nevertheless, the reaction mass efficiency (RME), defined as the product mass divided by the sum of the masses of reactants, results to below (8%) because of the large excess of hydrochloric acid, which it is used also as a solvent. The E-factor, defined as the mass of waste per mass of desired product, scores in the range of 5 kg·kg$^{-1}$ due to the consumption of HNO$_3$ in the reaction, which is considered as waste. For the same reason, the process mass intensity (PMI), defined as the total mass of resources used to produce the mass of product, scores around 6 kg·kg$^{-1}$. Both E-factor and PMI favorably score in the range which is considered to be a green process.

Other green metrics were calculated to assess the efficiency of the solvent used in the work-up operation. Here, the mass intensity (MI) scores higher value than the PMI because of the three loops of hydrochloric acid used in the workup for eliminating the traces of HNO$_3$, which increases the already high amount of hydrochloric acid used also as the reaction solvent. The MI-value obtained is average; neither good nor bad. The inverse of MI expressed in
percentage gives the effective mass yield (EMY). The use of water in the final solution is also considered in the process mass efficiency (PME), scoring double the value as compared to the mass productivity (MP) which does not consider water, because of the low concentration (0.1M) of the final solution. The solvent intensity (SI) was calculated according to the amount of water needed for the final dilution, scoring 33 kg of water per kg of dissolved product. All the latter values are considered good to average; yet certainly have room for optimization.

As a semi-quantitative sustainability assessment, the penalty-based EcoScale according to Van Aken et al. [54] methodology was performed, scoring 0 in terms of product yield (high reaction yield), 5 as the price of reaction components (due to Au’s price), 10 regarding safety (highly corrosive aqua regia), 3 as technical setup, 2 as temperature/time, and 0 for relatively simple workup/purification. Overall this sums up to 20 penalty points, which gives a notable EcoScale value of 80; meaning it scores less than average regarding the greenness, seeing from the viewpoint of assessment.

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Table 2 Green chemistry metrics calculated for the synthesis of Au@GO.
Regarding the circular assessment (see Fig. 14), the mass balance includes all solvents used in both the reaction path and in the work-up as inputs. Furthermore, different to treating HNO₃ considered as waste, where no-recycling is possible due to its consumption, the unreacted hydrochloric acid was considered as suitable for being collected and reused. As a result, the recycled fraction (FR) scores 0.46 since only hydrochloric acid is reused, which includes the recovered distilled fraction (CC) and the one collected by extraction (CR). The latter (CR) was also considered in the reaction efficiency (EF) together with the HNO₃ losses. The unrecoverable waste generated per kg of the final product resulted in 7.39 kg·kg⁻¹, mainly because of HNO₃. Overall, the linear flow index (LFI) scores 0.32, giving a mass circularity indicator (MCI) of 0.71. For a synthesis, not even designed with the full potential of circularity measures, the MCI is very good. The circularity indicator is favored by the absence of side compounds and the high reaction yield. Full conversion reduces the need of recycling, limiting this operation to the extraction and reuse of the solvents involved. Good points for circularity are the quantitative yield and the use of the solvent as an excess of reactant; thus, a high MCI might be achieved if solvent recycling is allowed and work-up operations are simplified. In addition, the MCI score could be improved by increasing the concentration of the final solution (water savings) by a factor of 4 keeping other conditions as these are. In this scenario, working with a final concentration of 0.4M in water instead of 0.1M would increase the MCI up to 0.81. Moreover, a reduction of the initial excess of aqua regia could also improve the MCI value, because of the nitric acid waste reduction.
One way to evaluate the relevance of these outcomes is by comparing them with two precedent procedures that use microwave-mediated synthesis paths related to the gold/graphene-containing nanoparticles production. For this purpose, the methodologies described by Xu et al. [51] and Wang et al. [50] were assessed respectively. In this context, Fig. 15 show a significant difference between all of them, being Au@GO the methodology which performs better. The methodology proposed by Xu et al. uses very low concentrations with a large amount of water giving a product: water ratio of 1000:1, which affects inevitably SI, MI and PMI metrics. One second issue is that the recycling chances are very low, which increases the waste, and consequently the E-factor. The procedure described by Wang et al. uses much less water, but it is still more than the half of the overall mass. In Au@GO, water is only used for dissolving acids, which are very concentrated, bringing these indexes towards lower and greener values.
Both the overuse of solvents and the scarce recycling chances in the precedent methodologies are also observed in Fig. 16. The productive metrics show (Fig. 16 left) the payment of using too much water, being Au@GO₉ process over the others in all polygonal vertex. The same is observed in circular metrics, where the recycling fraction ($F_R$) is more than double and more efficiently managed ($E_F$), as compared with the best precedent. This fact, together with a higher recycling capacity ($C_R$), gives Au@GO₉ methodology a prominent advantage in terms of circularity, reducing waste, and achieving an encouraging MCI, as compared with precedent methodologies.
4. Conclusions

The most important achievement described in this paper is the possibility of synthesis of the Au@GO$_r$ composite material without the use of an additional reductant/stabilizer, providing good scores in green chemistry metrics and achieving a high circularity degree with an MCI value of 0.71; which is remarkable seeing that even the full circularity measures such as recycling are not taken. The advantage of such a one-pot procedure is that the reaction product does not need a purification process, which reduces waste and expenses. In addition, virtually complete reduction of Au(III) complex to the metallic form was achieved. Thus, an efficient and environmentall friendly route of synthesis of the composite material with possible catalytic application was developed.

From a mechanistic point of view it can be concluded, that two following-up reactions occur. The first one is thermal decomposition i.e. deoxygenation of graphene oxide and formation of reduced graphene oxide. The other one is reduction of Au(III) complex with the
GO$_r$. As the overall result, gold nanoparticles are formed on the surface of GO$_r$ whereas the reduced graphene oxide is oxidized to some extent. In the second step, Au(III) ions are reduced with the products of the first step (reduced graphene oxide). As a result, the reduced graphene oxide is oxidized again. The degree of structure degradation of GO$_r$ increases with each successive stage. Two types of AuNPs were obtained. Relatively large ones, with average diameter $> 15$ nm and very small ones, with diameter $< 3$ nm.

The electrocatalytic properties of the obtained composite material are worse when compared to the polycrystalline gold. This was attributed to the very small size of AuNPs and possible low substrate conductivity due to reduction of GO to GO$_r$. This problem requires further studies. We believe that it is possible to fabricate the composite material, with controlled AuNPs size via the appropriate selection of synthetic conditions, and, thus improve its catalytic properties.

The results presented in this work open new possibility of fabrication of composite materials. For instance, other precious metals nanoparticles could be also deposited on the surface of reduced graphene oxide.

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1.13 - Noble Metal Nanoparticles: Synthesis and Optical Properties

From a Review of Noble Metal versus Enzyme Catalysts for Glucose Oxidation Under Conventional

Electrocatalytic hydrogen evolution reaction on reduced graphene oxide electrode decorated with

cobaltphthalocyanine.

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The Real Graphene Oxide Revealed: Stripping the Oxidative Debris from the Graphene-like

Reduced graphene oxide supported gold nanoparticles for electrocatalytic reduction of

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