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Microwave-Assisted Biogenic Synthesis of Metal-Decorated Reduced Graphene Oxide and their Electrochemical Properties

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Abstract

Herein we report a microwave assisted, fungal (*Ganoderma lucidum*) extract mediated synthesis of noble metal decorated reduced graphene oxide(r-GO). The carbon to oxygen ratio increased from 1.46 in GO to 2.72 in r-GO. The electron rate transfer capabilities of Pt, Pd, Ru, Pt—Pd and Pt—Ru decorated r- GO were tested in ferri-ferro coupling reaction. Excellent electrochemical behaviour were observed in their ability to oxidize hydrazine, reduce H₂O₂, as well as oxygen reduction in alkaline medium and hydrogen evolution in acidic medium. These reactions represent diverse applications in energy production, storage, electrochemical sensing and electro catalysis, thus the method presented here can be quite useful in diverse applications.

Keywords

Electrochemistry; fungal extract; *Ganoderma lucidum*; Metal doped graphene oxide; Microwave; r-GO

1. Introduction

Hybrid structures comprising of r-GO and metals or metal oxides^[1] are of great interest due to their unique properties where the former serves as a support for these moieties. Metal nanoparticles supported on graphene oxide (GO) or r-GO have been used in electro sensing,^[2] catalysis,^[3] electro catalysis^[4] and immobilization of bio-molecules.^[5] Several strategies

Conflict of Interest

The authors declare no conflict of interest.

Supporting information summary

The supporting information contains the experimental procedures for the synthesis of metal decorated r-GO using aqueous extract of the mushroom *Ganoderma lucidum* and also FTIR, raman and voltammograms.

Supporting information for this article is available on the WWW under<https://doi.org/10.1002/slct.201803420>

aimed at the synthesis of the metal r-Go hybrids have been reported.^[6] These include chemical reduction,^[7] microwave treatment,^[8] electrochemical reduction^[9] and electroless chemical vapour deposition.^[10] Of these, the microwave approach is a fast process for in situ reactions, and the microwave is also known to lower the activation energy needed for the reaction.

Biogenic reduction of GO to r-GO^[11] has an inherent advantage of being environmentally benign yet chemically active to reduce both the metals and the GO and lead to stable and well dispersible materials.^[12] The extract of the mushroom *Ganoderma lucidum* (GL) has been used as a reducing agent as it contains many polysaccharides and poly phenols which are known to be anti-oxidants and act as strong reducing agents.^[13] The effectiveness of biologically reduced r-GO nano metal hybrids in electrochemistry has not been studied to the best of our knowledge. The objective of this study was one step synthesis of noble metal decorated r-GO from GO and study their electrochemical behavior.

Results and Discussion

The extract from *Ganoderma lucidum*(GL) is known to contain biomolecules such as polysaccharides, triterpenoids, steroids, phenols, nucleotides and their derivatives.^[13a] The extract has strong antioxidant properties^[13b] which has the potential to reduce GO to r-GO and also reduces the metal salts to their respective nano particles.^[14] The process was expected to be speeded up in a microwave.

The one pot synthesis was effective in the synthesis of r-GO with nano particles (NP). SEM and TEM of all the materials are presented in Figure 1. The r-GO substrate had similar structures in all the samples and the presence of NP is evident from the SEM and TEM images. The NP particle sizes were found to be 25–30 nm from the TEM images. The NP loading was quantified using ICP-MS. The EDX spectra are shown in fig S1. Based on this, the carbon to oxygen ratio of the GO and r-GO were found to be 1.46 and 2.72 respectively. . A blank reaction in absence of the fungal extract did not show any reduction of GO. This clearly demonstrated the reduction of GO to r-GO by the fungal extract. The TGA curves clearly indicate that the hybrids have good thermal stability. (fig S2). The weight loss at 100° C was associated to the loss of adsorbed water from the samples. The gradual loss at 180°C to 320°C was associated with loss of oxygen functional groups.

The FTIR spectra of GO and r-GO (fig S3(a)) clearly depicts the loss of oxygen groups from GO suggesting the formation of r-GO. Hydrazine has been extensively used as a reducing agent for the synthesis of r-GO and is known to remove only some of the functional groups from GO.^[15] However in the current microwave induced biogenic reduction, the hydroxyls and acids functionalities were reduced to a large extent as evidenced by the lack of broad peak for $\nu_{\text{O-H}}$ stretch at 3400 cm^{-1} in the IR spectrum from GO to r-GO-NP. Also the carbonyl functional groups were reduced to a great extent as indicated by the reduction of the intensity of the $\nu_{\text{C=O}}$ peak at 1650 cm^{-1} in the IR spectra. However, the presence of $\nu_{\text{C-O}}$ at around 1100 cm^{-1} suggests that the epoxy functional groups were not completely reduced. This was also supported by the Raman spectral data (fig S4). The Raman shift also pointed at the formation of r-GO with a decrease in the intensities of G- band and an

increase in the intensity of the D-band. Further the Raman shifts indicated the formation of r-GO in the presence of metals also.^[5d] Also the strong D-peak suggested an arm chair conformation near the edges. Furthermore the lack of any changes in the spectra between r-GO and r-GO-NP indicate that there is no change in the inplane sp^2 domains. The crystallite sizes (L_a) of the sp^2 lattice of all the samples were calculated from the following equation where λ is the wavelength of the laser used and I_G and I_D are the intensities of the G- band and the D- band respectively from the spectra. The I_D/I_G ratios and L_a are given in Table 1. $L_a = 2.4 \times 10^{-10} \times \lambda_{\text{laser}}^4 \times I_G/I_D$

The above data specifically demonstrates that the adopted procedure results in materials with similar structural properties and equivalent defect densities and crystallite sizes. It also shows that the procedure holds good for a variety of metals, to produce even bimetallic catalysts at reflux temperatures when compared to high temperature annealing methods.^[16]

Cyclic Voltammetry (CV) was used to study the ability of these materials to catalyze select redox reactions relevant to both electrochemical sensing and energy storage and production. The electron transfer capability of the materials was tested on ferri-ferro couple. Also the capability of the material to oxidize hydrazine, reduce H_2O_2 , oxygen reduction in alkaline medium and hydrogen evolution in acidic medium were tested.

The CV of ferri-ferro redox couple was carried out in 50 mM PBS containing 10 mM of 1:1 molar ratio potassium hexacyano- ferrate(II) and potassium hexacyanoferrate(III) and the voltam- mograms are presented in Figure 2. Among all the materials the lowest peak to peak separation was found in the bimetallic r-GO-Pt-Ru and r-GO-Ru and all were found to be less than plain r-GO. The lower the peak to peak separation, the more facile was the electron transfer as seen by the K°_{obs} calculated using Nicholson method^[17] while the diffusion coefficient D was taken as $7.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for ferri-ferro redox couple. The results are presented in Table 2. Of all the materials r-GO-Ru and the bimetallic r-GO- Pt-Ru had the lowest E_p and hence the highest electron transfer rates followed by the bimetallic r- GO- Pt-Pd and r-GO-Pt which display similar electron transfer rates. The lowest rate is seen for the r-GO-pd.

The K°_{obs} values clearly point towards the superior electrochemical behaviour of the materials. Previous studies have reported similar K°_{obs} at a much higher metal loading.^[16] It is worth mentioning that the process used here was much simpler than the ones used before and did not require complex processing steps such as the high temperature annealing. Moreover, the biomolecules present in the fungal extract not only served as reducing agents but may have prevented the agglomeration of the nano particles thus forming highly electroactive species.^[11b,18]

The ability of these materials to catalyze electrochemical reactions were also studied on reduction of hydrogen peroxide (H_2O_2), oxidation of hydrazine (NH_2NH_2) and reduction of O_2 dissolved in KOH solution and H_2 production from H_2SO_4 , important processes in electrochemical energy production and storage.

The maximum reduction potential for H_2O_2 (fig S5) was around — 0.72 mV for all the materials. The earliest maximum peak potential was achieved at — 0.32 mV for r-GO—Pd.

The plain r-GO which was used as the reference material had the reduction material at — 0.89 mV. This clearly shows that the reduction of H_2O_2 was mainly due to the metal nano particles on the r-GO. Of all the hybrids r-GO—Pd showed early onset of the reduction, but good peak currents were observed for r- GO—Ru and r-GO—Pt. All the other hybrids show similar peak currents. Even though the reduction potential was earliest in r- GO—Pd the peak current was low owing to the low loading of the NP on r-GO.

The oxidation of NH_2NH_2 (fig S6) started in all the cases at 0.2 mV. The earliest oxidation peak potential was achieved by r- GO—Pt and r-GO—Ru at 0.69 mV and 0.67 mV. The materials r- GO—Pd and r-GO—Pt-Pd attained maximum oxidation peak at 0.82 mV and 0.8 mV. The bimetallic r-GO—Pt-Ru had the highest peak at 0.9 mV. The reference material attained maximum at 1.3 mV. This difference between plain r-GO and r-GO-NP hybrids clearly indicates that the oxidation reaction achieved is catalysed purely by the presence of nano metals on r-GO.

The reduction of oxygen is an important step in the energy converting processes of fuel cells. [19] The peak reduction potentials of dissolved oxygen in KOH (fig S7) were at — 0.32, — 0.35, — 0.3, — 0.32 and — 0.35 mV respectively for r-GO—Pt, Pd, Ru, Pt—Pd and Pt—Ru respectively. It is noted that the earliest peak potential was reached for r-GO—Ru followed by catalysts where Pt is involved. Traditionally Pt catalysts have been known to catalyze ORR. [20] Also the plain r-GO reached maximum at — 0.42 mV. Furthermore, the currents achieved in the case of r-GO-NP are much higher. This clearly proves that electro catalysis is due to the metal nanoparticles dispersed on graphene.

The voltammograms for the evolution of hydrogen from 0.1 M H_2SO_4 (fig S8) clearly indicate towards the catalysis of the HER by the materials with Pt—Ru giving maximum current and Pd and Pt—Pd giving the least. The hybrids r-GO—Pt and r- GO—Ru are in a similar range. The trend clearly demonstrated the suppression of the HER by Pd and enhancement by Ru in this case. However all the materials catalyzed the HER and it has been proved that the catalysis is due to the presence of metal nanoparticles on r-GO

4. Conclusion

The microwave assisted biogenic reduction of GO to synthesize metal decorated r-GO was successful. The carbon to oxygen ratio increased significantly from 1.46 in GO to 2.72 in r-GO. The electron transfer capability of the r-GO hybrids were tested in several well-known electrochemical reactions. Even at low metal loadings (0.6 to 1.85%) the r-GO hybrids were effective catalysts and showed activities that were similar to what has been reported earlier at much higher loadings. The advantage of the present approach is its simplicity, scalability, and the synthesis did not require high temperature annealing. It is postulated that the bio-molecules present in the fungal extract not only help in the reductions of GO and metals but also helped generate highly electroactive metal nano particles. Further optimizations would be needed to control the metal loading on the r-GO.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- [1]. Welch CM, Compton RG, Anal. Bioanal. Chem 2006, 384, 601–619. [PubMed: 16402180]
- [2]. Yang M, Yang Y, Liu Y, Shen G, Yu R, Biosens. & Bioelectron 2006, 21, 1125–1131.
- [3]. Zhao M, Crooks RM, Angew. Chem 1999, 38, 364–365. [PubMed: 29711654]
- [4]. Guo D-J, Li H-L, J. Electroanal. Chem 2004, 573, 197–202.
- [5]. a) Kamat PV, J. Phys. Chem. Lett 2009, 1, 520–527; b) Zhu C, Dong S, Nanoscale 2013, 5, 10765–10775; [PubMed: 24060985] c) Xie G, Xi P, Liu H, Chen F, Huang L, Shi Y, Hou F, Zeng Z, Shao C, Wang J, J. Mater. Chem 2012, 22, 1033–1039; d) Guo S, Dong S, Wang E, ACS nano 2009, 4, 547–555; e) Muthoosamy K, Bai RG, Manickam S, Curr. drug delivery 2014, 11, 701–718.
- [6]. Chua CK, Pumera M, Chem. Soc. Rev 2014, 43, 291–312. [PubMed: 24121318]
- [7]. Li Y, Fan X, Qi J, Ji J, Wang S, Zhang G, Zhang F, Nano Res. 2010, 3, 429–437.
- [8]. Vadahanambi S, Jung J-H, Oh I-K, Carbon 2011, 49, 4449–4457.
- [9]. Liu X-W, Mao J-J, Liu P-D, Wei X-W, Carbon 2011, 49, 477–483.
- [10]. Gutés A, Hsia B, Sussman A, Mickelson W, Zettl A, Carraro C, Maboudian R, Nanoscale 2012, 4, 438–440. [PubMed: 22147241]
- [11]. a) Park J. hyun, Kim J. hoi, Int. J. Nanomed 2014, 9, 1783–1797; b) Bai R. Geetha, Muthoosamy K, Shipton FN, Pandikumar A, Rameshkumar P, Huang NM, Manickam S, RSC Adv. 2016, 6, 36576–36587; c) Liu H, Li T, Liu Y, Qin G, Wang X, Chen T, Nanoscale Res. Lett 2016, 11, 211; [PubMed: 27094825] d) Abdullah MF, Zakaria R, Zein SHS, RSC Adv. 2014, 4, 3451034518; e) Wang Y, Wang C, Wang Y, Liu H, Huang Z, ACS Appl. Mater. Interfaces 2016, 8, 18860–18866; [PubMed: 27349132] f) Tran DN, Kabiri S, Losic D, Carbon 2014, 76, 193–202.
- [12]. a) Iravani S, Green Chem. 2011, 13, 2638–2650; b) Varma RS, Curr. Opin. Chem. Eng 2012, 1, 123–128; c) Muthoosamy K, Bai RG, Abubakar IB, Sudheer SM, Lim HN, Loh H-S, Huang NM, Chia CH, Manickam S, Int. J. Nanomed 2015, 10, 1505.
- [13]. a) Chang S-T, Buswell JA, Int. J. Med. Mushrooms 1999, 1; b) Mau J-L, Lin H-C, Chen C-C, J. Agric. Food Chem 2002, 50, 6072–6077. [PubMed: 12358482]
- [14]. John PA, Int. J. Nanomed 2013, 8, 4399–4413.
- [15]. Pei S, Cheng H-M, Carbon 2012, 50, 3210–3228.
- [16]. Giovanni M, Poh HL, Ambrosi A, Zhao G, Sofer Z, Sanék F, Khezri B, Webster RD, Pumera M, Nanoscale 2012, 4, 5002–5008. [PubMed: 22763466]
- [17]. a) Nicholson RS, Anal. Chem 1965, 37, 1351–1355; b) Brownson DA, Banks CE, The handbook of graphene electrochemistry, London, Springer, 2014.
- [18]. Mukherjee P, Ahmad A, Mandal D, Senapati S, Sainkar SR, Khan MI, Parishcha R, Ajaykumar P, Alam M, Kumar R, Nano Lett. 2001, 1, 515–519.
- [19]. Zhang L, Xia Z, J. Phys. Chem. C 2011, 115, 11170–11176.
- [20]. Morozan A, Jousset B, Palacin S, Energy Environ. Sci 2011, 4, 1238–1254.

Figure 1. Scanning Electron Microscope images of (a) Plain r-GO, (b) r-GO-Pt, (c) r-GO-Pd, (d) r-GO-Ru, (e) r-GO-Pt-Pd, (f) r-GO-Pt-Ru, (g, h, i) TEM images showing the presence of Pt nanoparticles.

Figure 2.
Cyclic Voltammograms of the r-GO-NP on GCE for ferri-ferro couple.

Table 1.

The ICP-MS data, D/G ratios and crystallite sizes of the hybrid materials.

Sample	ICP-MS (%)	I _D /I _G	L _a (nm)
r-GO	–	1.89	47.1
r-GO-Pt	0.67	1.83	48.6
r-GO-Pd	1.18	1.82	48.8
r-GO-Ru	1.85	2.01	44.3
r-GO-Pt-Pd	0.43, 0.85	1.78	49.8
r-GO- Pt-Ru	0.6, 1.59	1.88	47.3

Table 2.

Peak-to-peak separation (E_p) values and the corresponding heterogeneous electron transfer rates (k_{obs}°) of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple on all materials.

Sample	E_p (mV)	k_{obs}° (cm s^{-1})	k_{obs}° (cm s^{-1}) ¹³
Bare-GCE	359	2.54×10^{-4}	–
r-GO	290	6.94×10^{-4}	–
r-GO-Pt	155	2.8×10^{-3}	2.07×10^{-3}
r-GO-Pd	181	2.3×10^{-3}	2.68×10^{-3}
r-GO-Ru	130	4.1×10^{-3}	1.81×10^{-3}
r-GO-Pt-Pd	141	2.9×10^{-3}	–
r-GO- Pt-Ru	130	4.1×10^{-3}	–