2D Materials

PAPER

2D hematene, a bioresorbable electrocatalytic support for glucose oxidation

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Abstract

Towards the aim of developing implantable and fully biodegradable sensors and biofuel cells, 2D nanosheets of hematite have been exfoliated and processed into electrode materials for glucose sensing. Gold, (Au) nanoparticles were electrodeposited onto the 2D substrate to develop a sensitive non-enzymatic glucose sensor. Despite a low loading of a catalyst, the composite achieved a sensitivity of $10 \mu$A M$^{-1}$ cm$^{-2}$, good linearity (0–3.2 mM) with a detection limit of 0.4 mM, a response time of less than 10 s, and long-term performance stability. These results make Au/Fe$_2$O$_3$ hematene nanosheet, a promising catalytic material not only for glucose monitoring but also from which to construct biofuel cells using glucose as fuel.

1. Introduction

Glucose plays a pivotal role in several physiological processes and thus being able to measure its concentration is essential for monitoring specific medical conditions such as diabetes or use it as a fuel in biofuel cell applications. Whether to be converted in electrical energy or measured for diagnosis, glucose is electro-oxidized at the electrode surface. The importance of glucose oxidation has led to a steady increase in demand for more electroactive, stable and low-cost glucose catalysts. Implantable sensors or biofuel cells have been extensively studied over the past few decades with high sensitivity and low cost enzyme, used as electrocatalyst [1–3]. Enzymatic catalysts have been gradually replaced with non-enzymatic glucose electrocatalyst s to overcome drawbacks associated with the enzyme, i.e. complex immobilization processes, oxygen concentration dependence and poor thermal and chemical stability. Furthermore, while efforts have been focusing on performances (activity, durability and cost) and miniaturization to imply less tissue damage, further improvements of existing sensor and biofuel cell technologies with the use of biocompatible and resorbable materials for minimizing the need for a second surgery, reducing the risk for hemorrhage and infection is the next step for improving the quality of medical diagnosis and treatment.

Several metals such as Cu, Fe, Pt, and Au have been studied for glucose electrocatalytic activity resulting in different by-products depending on the pH and the metal used. Among them, Au has been particularly used for the electrochemical oxidation of glucose. Although bulk Au metal is poorly catalytically active, its properties can be enhanced when size reaches the nanometre scale because of the particle phase transitions. Although considerable efforts have been made on the synthesis of nanoporous Au [4–6] or nanoparticles [7, 8], films, nanowires [9], films [10], nanoclusters [11], nanoplates [12] etc research on the substrate has been neglected and is currently limited to the biocompatible carbon nanostructures such as graphene, carbon nanotubes. Among oxides, iron oxide is one of the most abundant materials readily available, and has been widely used for bio-applications [13–15]. Additionally, iron oxides possess intrinsic enzyme-like activity, and are now regarded as novel enzyme mimetics [16]. Hematite ($\alpha$-Fe$_2$O$_3$), the most thermodynamically stable iron oxide has shown to be biologically and electrochemically inert [17]. But by modifying its morphology, size, and crystallinity, its properties can be affected; for instance, hematite nanowire has been established

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to be an ideal electrode material for glucose oxidation due to the intrinsic peroxidase-like catalytic activity [18]. Additionally, hematite is biodegradable so using this electrode material enables development of sensors with the ability to entirely dissolve in the body after the implantation, which can prevent the need for transcutaneous removable sensors or retrieval surgery. In a recent work, we reported the mechanical exfoliation of 2D α-Fe₂O₃ sheet from core hematite [19]. 2D materials have excellent properties such as high mobility, high surface area and high Young’s modulus and strength, despite their low weight in comparisons to their bulk counterparts [19, 20]. The high mobility and electrical conductivity facilitate the electron transfer process during the glucose oxidation with reduced ohmic losses whereas its high surface area provides more accessible sites for gold nanoparticle deposition. The high mechanical strength ensures the stability of the electrodes during the use and the biodegradable properties can ensure the electrodes would be cleared from bodies after the designed time period. Furthermore, hematene can be prepared in a cost-effective and scalable method simply via sonication compared with other 2D materials. In the present work, we report the fabrication of a fully biodegradable glucose sensor made on 2D hematene for the electrocatalytic oxidation of glucose.

2. Experimental section

2.1. Au-hematene electrocatalyst preparation

Two-dimensional (2D) hematene was mechanically exfoliated mechanical in dimethylformamide (DMF) solution [19, 21]. Briefly, 15 mg of natural hematite (α-Fe₂O₃) was washed three times in water, acetone and then dispersed in 20 ml DMF solution. The solution was sonicated using an unmodified benchtop ultrasonic bath (Branson UltraSonic Model 1510 MT, 42 kHz, 70 W) for 24 h. The resulting reddish suspension (1 ml) was then transferred in a high-speed amalgamator (Ultramat 2, 4600 oscillations per min) and vigorously agitated for 10 min with a high-speed amalgamator (Ultramat 2, 4600 oscillations per min).

To prevent from potential overheating, the 10 min agitation is performed in two times. Finally, the solution was centrifuged with a mini-centrifuge for 1 min, and then the supernatant that contained the exfoliated hematene was pipetted for further tests.

Chronoamperometric electrodeposition technique was adopted for gold nanoparticle deposition in a nitrogen-purged electrolyte containing 1.5 mM HAuCl₄ 3H₂O and 0.5 M ethylene glycol (EG). Prior to the Au deposition, 40 μl of hematene suspension was drop-casted on well-polished glassy carbon electrodes (4.92 mm ø) followed by a constant applied potential at −0.2 V (vs. RHE) for 60, 120 and 180 s. The mass of deposited gold was obtained by integration of electrical charge consumed during the deposition process \( Q_{\text{Au}} \) (C cm⁻²), according to equation (1.1):

\[
m_{\text{Au}} = \frac{Q_{\text{Au}}}{3F}
\]

Where \( M \) and \( F \) are the atomic weight of Au (196.97 g mol⁻¹) and the Faraday constant (96 485.309 C mol⁻¹). The calculation is based on the assumption that the current efficiency was 100% for Au reduction (equation (1.2)).

\[
\text{AuCl}_4^- + 3e^- = \text{Au} + 4\text{Cl}^-
\]

2.2. Characterization of Au-hematene electrocatalyst

The morphology of the sample was investigated by transmission electron microscopy (TEM, FEI Tecnai F20, 200 kV) and scanning electron microscopy (SEM). The surface composition and atomic bonding information were studied by x-ray photoelectron spectroscopy (Thermo Scientific K-Alpha). X-ray diffraction (XRD) patterns were obtained on Bruker D8 Discovery instrument operating at 40 kV and 20 mA, using CuKα radiation.

Electrochemical measurements were tested in a cell with three electrode system; Au/hematene deposited on glassy carbon electrode as working electrode, Pt wire as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The cyclic voltammetry was carried out in 0.1 M KOH solution with and without 10 mM glucose at a scan rate of 10 mV s⁻¹. The chronoamperometric response of Au/hematene in 0.1 M KOH was tested in a constant potential of 0.9 V (vs. RHE) under stirring condition. The glucose concentrations in the solution was increased gradually from 0.4 mM to 3.2 mM.

3. Results and discussion

Here, we reported a mechanical exfoliation method involving two steps to isolate mono-layer hematene: sonication for 24 h followed by agitation with high-speed amalgamator for 10 mins in DMF. Bright-field TEM at low and higher magnifications confirm the exfoliation of single- and bi-layer hematene (figure 1). A high-resolution TEM image (figure S1) was showed bi-layer hematene with orientation in the [001] direction, corresponding to the hexagonal symmetry of hematene with lattice parameters \( \alpha = 0.50356 \text{ nm}, \beta = 1.37489 \text{ nm} \) [21]. After drop-casting hematene suspension in DMF on glassy carbon electrodes, gold nanoparticles were electrodeposited on hematene using chronoamperometry method at an applied potential of −0.2 V (vs. RHE) for 120 s [11]. A gold loading of 28.5, 76.5 and 81.2 μg cm⁻² was calculated based on
Figure 1. Schematic illustration of 2D hematene synthesis through liquid exfoliation process in DMF, and the optical image of hematene solution (a). TEM and high-resolution TEM images of exfoliated hematene (b), (c). The upper left figure in figure c is high-resolution TEM image with bilayer structure and the lower left figure in figure c is the atomic arrangements of hematene in [001] crystallographic plane, where the red spheres correspond to oxygen, yellow spheres correspond to iron atoms.

Figure 2. Characterization of Au/hematene electrode. SEM (a) and TEM (b), (c) images of deposited Au nanoparticles on hematene, and the corresponding EDS results (d). XPS spectrum of Au nanoparticles loaded on hematene (e)–(g).

the electrical charge consumed during a deposition process of 60 s, 120 s and 180 s respectively (figures S2 (stacks.iop.org/TDM/7/025044/mmedia), and S3). These electrodes were first screened electrochemically towards the electrooxidation of glucose to select the best candidate for further characterization. The results show that the electrode with 120 s deposition time exhibiting the best catalytic activity (figure S3). SEM and TEM results showed some Au clusters with the size of 30 ~ 50 nm deposited homogeneously on hematene supports (figures 2(a) and (b)). At higher magnification, TEM images showed that the Au clusters are made from distinct Au nanoparticles of ~5 nm (figure 2(c)), which was further confirmed with EDS (figure 2(d)). X-ray diffraction (XRD) was directly performed on GC and Au/hematene-GC samples, respectively (figure S4). The peaks associated with hematene have been detected and indexed to hematite crystal structure (JCPDS card 33–664, \(a = 5.035 \text{ Å} \) and \(c = 13.74 \text{ Å} \)), and the \(2\theta \) values of 38.1° and 64.5° were identified for the gold nanoparticles \([19, 22]\).

The chemical composition was investigated with x-ray photoelectron spectroscopy (XPS) (figures 2(e)–(g)). A higher resolution of Fe 2p spectrum reveals that the oxidation state of Fe was +3 with Fe 2p_1/2 and Fe 2p_3/2 peaks at 710.8 eV and 725.4 eV \([8]\). Au exhibits two main peaks at approximately 87.2 eV and 83.5 eV for Au 4f_5/2 and Au 4f_7/2 respectively; this result indicates that the majority
of Au is metallic. Previous reports have demonstrated the biocompatibility and biodegradability of Au without toxicity [23]. Above 50 nm, Au nanoparticles are considered not biodegradable, and even show some long term toxicity concerns [24] whereas nanoparticles with sizes less than ~6 nm have shown to achieve total clearance from the body [25, 26]. Given that we electrochemically deposited nanoclusters consisting of 5 nm Au nanoparticles adsorbed on 2D hematene, this composite catalyst is considered as nontoxic and biodegradable.

The performance of Au/hematene towards glucose oxidation was studied in 0.1 M KOH solution (figure 3). Cyclic voltammetry (CV) was performed with and without glucose (10 mM). The results clearly show that the oxidation of glucose peaked at ~0.6 V after glucose incorporation (10 mM) on Au/hematene electrode whereas no glucose oxidation occurred on the glassy carbon (GC) electrode. The mechanism upon which Au oxidizes glucose involves the creation of a thin layer of gold oxide (\( \text{Au}_n \text{O}_m \)) at high potentials followed by the reaction:

\[
\text{Au}_n \text{O}_{m-1} + 2\text{OH}^- = \text{Au}_n \text{O}_m + 2\text{H}_2\text{O}
\]  

Finally, it is thought that a rapid electrochemical regeneration of the surface oxide takes place followed by equation (1.3) [3, 4];

The electrocatalytic capacity of Au/hematene catalyst towards glucose oxidation was further studied at different scan rates (figure 3(a)). The cyclic voltammetry responses at different scan rates clearly shows that the oxidation current is proportional to the square root of the scan rate, which indicates that the electrooxidation reaction is not limited by the materials itself but by a diffusion process (figure 3(b)) [8]. The durability of the Au/hematene catalyst was investigated by multiple of oxidation cycle tests in 10 mM glucose solution (figure 3(c)). At 100 cycles, CV did not show any obvious decreased in current density compared to the first scan, confirming the excellent stability of this new electrocatalyst. Chronoamperometry was employed to evaluate the steady-state response of Au/hematene electrodes (figure 3(d)). The chronoamperometric response of Au/hematene in 0.1 M KOH was tested at a constant potential of 0.9 V (vs. RHE) under constant stirring to prevent mass diffusion limitation when adding glucose in the electrochemical cell.

The glucose concentrations in the electrochemical cell was steadily increased by 0.4 mM as soon as the current stabilised starting at 0 mM up to 3.2 mM. The response time of the electrode was less than 10 sec, indicating a fast response of the sensor towards glucose detection. The linear response of the glucose sensor to glucose concentration was linear with a detection limit (LOD) of 0.4 mM with the sensor sensitivity ca. 10 \( \mu \text{A mM}^{-1} \text{cm}^{-2} \). Some promising reports of glucose detection have been reported for Au NP decorated electrodes, such as Zeng et al reported a gold NPs/polyaniline/CNTs composite modified GC electrode with a high sensitivity of 29.17 \( \mu \text{A mM}^{-1} \text{cm}^{-2} \) [27], and Shan et al...
Table 1. Comparison of the non-enzymatic glucose oxidation reaction for different Au catalysts.

| Materials                        | Biodegradable | Electrolyte         | Glucose concentration (mM) | Current density (mA cm\(^{-2}\)) | Detection limitation (mM) | Ref. |
|----------------------------------|---------------|---------------------|---------------------------|-----------------------------------|---------------------------|------|
| Au/hematene                      | Yes           | 0.1 M KOH           | 10                        | 3.12                              | 0.4                       | This work |
| Au/glassy carbon (GC)            | No            | 0.3 M KOH           | 10                        | 2.0                               | NA                        | [34] |
| Au/C tip                         | No            | 0.1 M KOH           | 10                        | 1.7                               | NA                        | [35] |
| Au NPs/Au                        | No            | 0.3 M KOH           | 10                        | 2.1                               | NA                        | [36] |
| Au porphyrin/CNTs                | No            | 0.1 M KOH           | 250                       | 3                                 | NA                        | [37] |
| AuAg/GC                          | No            | 0.3 M KOH           | 10                        | 13                                | NA                        | [38] |
| Au/ordered mesoporous carbon     | No            | 0.1 M NaOH          | 18                        | NA                                | NA                        | [39] |
| AuPt/GC                          | No            | 0.1 M NaOH          | 5                         | ~0.6                              | NA                        | [40] |
| Au\(_{2}\) nanonanoparticle/C    | No            | 0.1 M NaOH          | 5                         | 0.2                               | NA                        | [41] |
| Au\(_{2}\) nanonanoparticle/C    | No            | Phosphate buffer (pH 7.0) | 5          | 0.15                              | NA                        | [41] |
| Laser-ablated gold nanoparticles/ carbon microelectrode | No | 0.1 M NaOH | 5 | ~3 nA | NA | [42] |
| Au\(_{77}\)/Cu\(_{23}\)         | No            | 0.1 M NaOH          | 5                         | ~1.5                              | NA                        | [43] |
| Au/ITO                           | No            | 0.1 M NaOH          | 14                        | 0.1                                | 2                         | [33] |
| Au@hydrogel/GC                   | No            | 0.1 M NaOH          | 10                        | ~0.2 mA                            | 0.067                     | [30] |
| AuNPs/CuONWs-MoS\(_{2}\)         | No            | 0.05 M NaOH         | 2                         | ~0.19 mA                           | 0.0005                    | [44] |
| Au nanotube                      | No            | PBS (pH 7.4)        | 10                        | 0.5 mA                             | 0.001                     | [45] |
| AuNP–ATP–MWCNTs                  | No            | PBS (pH 7.4)        | 8.1                       | 5 \(\mu\)A                        | 0.015                     | [32] |
| Au/3D graphene                   | No            | 0.1 M NaOH          | 2                         | 0.06                              | 0.0025                    | [31] |
| Plasmon-enhanced glucose sensor  | No            | 0.1 M NaOH          | 5                         | 0.002                             | 0.009                     | [46] |
| Polyimide-carbon-AuNP-GOx        | No            | PBS (pH 7.4)        | 0.1                       | ~100 nA                            | 0.026                     | [47] |

described graphene/Au NPs/chitosan composite film with a sensitivity of 0.55 \(\mu\)A mM\(^{-1}\) [28]. Instead of Au NPs, Wan et al employed gold electrode further modified by chitosan and CNTs, achieving a high sensitivity of 21 \(\mu\)A mM\(^{-1}\) cm\(^{-2}\) [29]. In addition to complex electrode fabrication process, they usually used enzymes (e.g. glucose oxidase), which in turns increase the costs of the system and require low-temperature storage conditions for long-term stability of these sensors. Compared to reported results, with a low gold loading of 76.5 \(\pm\) 10.2 \(\mu\)g cm\(^{-2}\), the Au-hematene electrode was able to achieve comparable sensitivity without the assistance of enzymes. With respect to non-enzymatic composite materials, such as Au deposited on carbon nanomaterials [30–32] (e.g. graphene or carbon nanotube) or Cu based substrate, the limit of detection of the Au-hematene electrocatalyst is fairly high (table 1). The low LOD of carbon- based substrate is probably due to its higher electrical conductivity compared to iron oxide. Indeed Au on ITO [33] exhibited an extremely poor LOD of 2 mM compared to Au-hematene (0.4 mM). In spite of being 10 and even 100 times higher than the biocompatible Au-carbon based support, Au-hematene must be appreciated as a fully resorbable electrocatalytic materials. This is the first time that an electrocatalytic materials can be implanted to electrooxidize glucose and dissolved over time without harming the body. The electrochemical results indicated that Au-hematene based electrode is a fairly sensitive, easy method made of biodegradable materials to quickly oxidise glucose for detection or energy supply purposes.

4. Conclusion

In summary, we successfully synthesized the first fully resorbable sensor for glucose oxidation prepared from hematene and gold nanoparticles, two biodegradable materials. The electrochemical investigation
of glucose oxidation in 0.1 M KOH solution was performed on Au nanoparticle-decorated hematene supported on glassy carbon electrodes. This innovative electrocatalyst exhibited excellent glucose oxidation in alkaline condition in contrast to the absence of any oxidative current on control unmodified glassy carbon electrodes. This Au-hematene electrode not only demonstrated a good sensitivity, linearity, short response time (less than 10 s), but also a high durability in KOH solution. In the future, we believe that the use of this new electrocatalyst can be extended to the development of entirely biodegradable fuel cells.

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References

[1] Lopes J H, Colson F X, Barralet J E and Merle G 2017 Mater. Sci. Eng. C 76 991
[2] Merle G, Habrioux A, Servat K, Rolland M, Innocent C, Kokoh K B and Tingry S 2009 Electrochim. Acta 54 2998
[3] Habrioux A, Merle G, Servat K, Kokoh K B, Innocent C, Cretin M and Tingry S 2008 J. Electroanal. Chem. 622 97
[4] Liu Z, Huang L, Zhang L, Ma H and Ding Y 2009 Electrochim. Acta 54 7286
[5] Li Y, Song -Y Y, Yang C and Xia X-H 2007 Electrochem. Commun. 9 1981
[6] Chen L Y, Lang X Y, Fujita T and Chen M W 2011 Scr. Mater. 65 17
[7] Jena B K and Raj C R 2006 Chem. A Eur. J. 12 2702
[8] Saha K, Agasti S S, Kim C, Li X and Rotello V M 2012 Chem. Rev. 112 2739
[9] Cherkevko S and Chung C-H 2009 Sens. Actuators B 142 216
[10] Bai Y, Yang W, Sun Y and Sun C 2008 Sens. Actuators B 134 471
[11] Hussain A M P, Sarangi S N, Kesarwani J A and Sahu S N 2011 Biosens. Bioelectron. 29 60
[12] Zhang Y, Chang G, Liu S, Lu W, Tian W and Sun X 2011 Biosens. Bioelectron. 28 344
[13] Berry C C and Curtis A S G 2003 J. Phys. D: Appl. Phys. 36 R198
[14] Hasanzadeh M, Shadlou N and de la Guardia M 2015 TrAC, Trends Anal. Chem. 72 1
[15] Zhang X-Q, Gong S-W, Zhang Y, Yang T, Wang C-Y and Gu N 2010 J. Mater. Chem. 20 5110
[16] Wei H and Wang E 2013 Chem. Soc. Rev. 42 6060
[17] Tsang S C, Caps V, Paraskevass L, Chadwick D and Thompsett D 2004 Angew. Chem. Int. Ed. 43 5645
[18] Cao X and Wang N 2011 Analyst 136 4241
[19] Zhang Z, Ye M, Harvey E J and Merle G 2019 J. Electrochem. Soc. 166 H1135
[20] Kim J H, Jeong J H, Kim N, Joshi R and Lee G-H 2018 J. Phys. D: Appl. Phys. 52 083001
[21] Puthirath Balan A et al 2018 Nat. Nanotechnol. 13 602
[22] Krishnamurthy S, Esterle A, Sharma N C and Sahai S V 2014 Nanoscale Res. Lett. 9 627
[23] Huang P et al 2013 Angew. Chem. Int. Ed. Engl. 52 13958
[24] Anker J N, Hall W P, Lyandres O, Shah N C, Zhao J and Van Duyne R P 2008 Nat. Mater. 7 442
[25] Tam J M, Tam J O, Murthy A, Ingram D R, Ma L L, Travis K, Johnston K P and Sokolov K V 2010 ACS Nano 4 2178
[26] Choi H S, Liu W, Misra P, Tanaka E, Zimmer J P, Itty Ipe B, Bawendi M G and Frangioni J V 2007 Nat. Biotechnol. 25 1165
[27] Zeng X, Zhang Y, Du X, Li Y and Tang W 2018 New J. Chem. 42 11944
[28] Shan C, Yang H, Han D, Zhang Q, Ivaska A and Niu L 2010 Biosens. Bioelectrochem. 25 1070
[29] Van D, Yuan S, Li G L, Neoh K G and Kang E T 2010 ACS Appl. Mater. Interfaces 2 3083
[30] Zhao J, Hu X, Huang X, Jin X, Koh K and Chen H 2019 Colloids Surf. B 183 110404
[31] Bui Q B, Nguyen D M, Nguyen T M L, Kwac L K, Kim H G, Ko S C and Jeong H 2018 J. Electrochem. Soc. Sci. Technol. 9 229
[32] Bas S Z 2014 Anal. Methods 6 7752
[33] Rong Y, Malpass-Evans R, Carta M, McKeown N B, Attard G A and Marken F 2014 Electroanalysis 26 904
[34] Arjona N, Guerra-Balcázar M, Trejo G, Ledesma-Garcia J and Arriaga I G 2012 New J. Chem. 36 2555
[35] Pasta M, Ruffo R, Falletta E, Mari C M and Pina C D J B G 2010 Gold Bulletin 43 37
[36] Jin C-C and Taniguchi I 2007 Chem. Eng. Technol. 30 1298
[37] Elouarzaki K, Le Goff A, Holzinger M, Agnès C, Duclain P, Putaux J-L and Cosnier S 2014 Nanoscale 6 8556
[38] García-Morales N G, García-Cerda L A, Puente-Urbina B A, Blanco-Jerez I M, Antaño-López R and Castañeda-Zaldivar F 2015 J. Nanomater. 2015 295314
[39] Qi P, Chen S, Chen J, Zheng J, Zheng X and Yuan Y 2015 ACS Catal. 5 2659
[40] Tominaga M, Shimaizoe T, Nagashima M and Taniguchi I 2005 Chem. Lett. 34 202
[41] Tominaga M, Shimaizoe T, Nagashima M and Taniguchi I 2005 Electrochem. Commun. 7 189
[42] Liu Y, Austen B J J, Cornelis C, Tilbury R D, Buntine M A, O’Mullane A P and Arrigan D W M 2017 Electrochem. Commun. 77 24
[43] Tominaga M, Taerna Y and Taniguchi I 2008 J. Electroanal. Chem. 624 1
[44] Bao J, Qi Y, Hao D, Hou J, Geng X, Samalo M, Liu Z, Luo H, Yang M and Hou C 2019 J. Electrochem. Soc. 166 81179
[45] Zhou Y-G, Yang S, Qian Q-Y and Xia X-H 2009 Electrochem. Commun. 11 216
[46] Wang C, Nie X-G, Shi Y, Zhou Y, Xu J-J, Xia X-H and Chen H-Y 2017 ACS Nano 11 5897
[47] Benson J, Fung C M, Lloyd I S, Deganello D, Smith N A and Teng K S 2015 Nanoscale Res. Lett. 10 127