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Sensitive electrochemical sensing of acetaminophen and hydroquinone over single-pot synthesized stabilizer free Ag/Ag-oxide-graphene nanocomposites

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ABSTRACT

A single-step, one-pot synthetic approach for decorating graphene with nanodimensional silver under mild, stabilizer free and eco-green reducing conditions is presented. The synthesized nanocomposites were adequately characterized for their chemical state through UV–vis spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and electrochemical technique. The synthesized nanocomposite depicts excellent electrochemical stability and promising electrocatalytic and electroanalytic activity as demonstrated by the estimated sensitivity parameter ($\bar{i}_p$), of 18.48 and 12.35 ($As^{1/2}\ V^{-1/2}\ M^{-1}\ cm^{-2}$) for acetaminophen and hydroquinone respectively. Very low detection limits of 0.022 μM and 0.004 μM with very high sensitivities of 20,153 $\mu AM^{-1}\ cm^{-2}$ and 13,942.31 $\mu AM^{-1}\ cm^{-2}$ for acetaminophen and H_2Q respectively were estimated.

1. Introduction

Unique two-dimensional (2D) structure, large surface area per unit mass, desired electronic, mechanical and electrical properties of graphene and the novel synergism offered by the constituents of graphene-metal/metal oxide nanocomposites has triggered a gold-rush in the design and application of these nanohybrid materials for catalysis, sensing, energy storage and production etc. [1–3]. In fact the metal-graphene nanohybrid materials offer promising solutions for enhancing the life time, selectivity and efficiency of the core functioning materials in the electrosensing and electrocatalysis setups [4–6]. It is in this context that design of graphene-metal/metal oxide nanocomposites has been attracting a considerable research interest since last two decades. Many synthetic protocols have been reported for the synthesis of appropriately constituted and chemically functionalized graphene-metal/metal oxide nanocomposites [6,7–12]. Most of these synthetic procedures are multistep and involve use of harsh and sometimes toxic to environment reducing agents like formaldehyde, sodium borohydride, strong alkaline solution (NaOH and KOH) etc. [8–12]. These reducing agents are enough harsh to cleave the hexagonal framework of graphene and hence result in structural damage and some undesired and impossible to restore chemical changes in the graphene sheets. Additionally, the desired action of few of these reducing agents requires an extra stabilizing agent that significantly adds up to the complexity and cost of overall synthesis. For example, R. Chen et al. demonstrated one pot synthesis of Ag/AgCl nanocubes on reduced graphene oxide but the method involves use of polymeric chitosan as stabilizing agent [13]. Very recently J. Park et al. communicated a multistep procedure for the synthesis of graphene-nanometal composites that involves prefunctionalization of nanoparticles with perfluorophenyl azide followed by their conjugation with graphene [14]. However the presence of additional functionality on to the nanoparticle surface does alter their properties and hence decreases the efficiency of such nanoconjugates. All these concerns like use of stabilizing agent (polymer/surfactant) and pre-functionalization in the reported procedures warrant the design of these nanocomposites through environmentally safe and simple synthetic protocols based on the use of mild reducing agents with selective and desired reducing ability of eco-green reagents for the synthesis of graphene based metal nanohybrids. X. Zhou et al. have reported a simple, efficient and cost effective approach for the synthesis of single layer graphene sheets through reduction of graphene oxide (GO) by hydroxylamine (NH_2OH) [15]. It is pertinent to mention that NH_2OH as such or in the form of salts viz. chloride or sulphate, possess low capability to react with water that in turn limits its poisonous and explosive properties. Interestingly NH_2OH has been found to have sufficient and efficient reducing ability to reduce metal ions like Ag^{+}, Au^{3+}, Pd^{2+} and Cu^{2+} [16–18]. It is well documented in the literature that under basic conditions the presence of oxy-functionalities viz. hydroxyl, carboxyl, epoxy, aldehydic and ketonic groups on its basal and

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edge planes make graphene oxide a modest reducing agent. This reducing ability of graphene oxide under alkaline conditions is well suited for the reduction of Ag^{+} to plasmonic silver Ag(0) and the self reduction of GO to reduced graphene oxide [12]. This combination of Ag (0) or any other metal in the form of nanoparticles with graphene and different forms of graphene has been proved to achieve desired sensitivity and selectivity which otherwise cannot be achieved alone [1–3]. In view of these reports it seems logical to expect that hydroxylamine can be used as a versatile reductant for decoration of graphene with transition metal nanoparticles through simultaneous reduction of GO and metal ions in a single-step one-pot reaction; the same is demonstrated through results of present study. The synthetic scheme presented here makes no use of polymeric or surfactant stabilizer during the reduction process which could be advantageous for the practical use of resulting silver/silver-oxide-graphene nanocomposite (Ag/Ag-oxide-Gr). Redox probes like ferricyanide, acetaminophen (AC) and hydroquinone (H_2Q) were selected to test the electrochemical performance of the synthesized Ag/Ag-oxide-Gr nanocomposite. These probes were chosen in view of the vast literature related to their electrochemical, biochemical and sensing aspects. While acetaminophen used as a drug whose bioaccumulation can result in serious liver and kidney damage, H_2Q is an undesirable contaminant in medicine, food and environment and possess high toxicity and low degradability and can lead to myeloid leukaemia and kidney damage [19–20]. A range of analytical methods like spectrophotometry [21], liquid chromatography [22], and titrimetry methods [23] have been applied for the determination of acetaminophen and hydroquinone. However, such methods are time consuming and involve hectic extraction procedures before their sensing. In comparison to these procedures it has been proved that electrochemical techniques are advantageous in many respects like quick response, low cost, high sensitivity and specificity. A wide variety of electrode materials have been applied to improve the detection performances towards acetaminophen and hydroquinone as shown in Table 1. Still there is need of an electrochemical sensor which shows excellent electrochemical performance towards the detection of these analytes. In this study, stabilizer free Ag/Ag-oxide nanoparticles homogenously dispersed on graphene sheets were fabricated and tested for their catalytic and sensing ability towards acetaminophen and hydroquinone. The results obtained from the present study indicate that the high performance sensor with low detection limit, high sensitivity and wide linear range based on Ag/Ag-oxide-Gr modified electrode was obtained.

Table 1
Comparison of efficiency of some modified electrodes towards electroanalysis of acetaminophen and hydroquinone.

Modified electrode	Linear range (μM)	Detection limit (μM)	Ref.
Acetaminophen			
C-Ni/GCE	2.0–230	0.6	[34]
CNT/SPCE	2.5–2000	0.1	[35]
GR/GCE	2.0–230	0.6	[36]
Nafion/TiO_2-GR/GCE	1–100	0.21	[37]
nPt-MWCNTPE	0.5–100	0.17	[38]
AuNP-PGA/SWCNE	8.3–145.6	1.18	[39]
LNT-CFO/GCE	0.5–901	0.19	[40]
CNT/TCPE	0.1–100	0.05	[41]
SWCNT-GNS/GCE	0.05–64.5	0.038	[42]
Fe_3O_4/PDDA/GR/GCE	0.1–100	0.037	[43]
MWCNT-polyhis	0.25–10	0.032	[44]
L-Cysteine/GCE	–	0.05	[45]
Ag/Ag-oxide-Gr/GCE	9.9–64.9	0.022	Present work
Hydroquinone			
Fe_2O_3/CNTs/FTO	1–260	0.5	[46]
ECF-CPE	1.0–200	0.4	[47]
GMC/GCE	2.0–100	0.37	[48]
PIL-MWCNTs/GCE	1–500	0.4	[49]
Pt-graphene/GCE	20–145	6	[50]
Pt/ZrO_2-RGO/GCE	1–1000	0.4	[51]
Paraffin/graphite/SP	75–1600	8.1	[52]
Cu(II) complex/CPE	60–2500	0.3	[53]
AuNPs/CNF/Au	9.0–500	0.86	[54]
CdS/rGO/GCE	0.2–2300	0.054	[55]
Ag/AgCl/rGO	0.08–1000	0.0094	[13]
Cu-MWCNTs@Chi/GCE	0.1–100	0.04	[56]
PANI-Fe_2O_3-rGO/GCE	0.1–550	0.06	[57]
PANI/MnO_2/GCE	0.2–100	0.13	[58]
CNT-PEDOT/CPE	1.1–125	0.3	[59]
TiO_2/Au/CNTs	1–100	0.01	[60]
Ag/Ag-oxide-Gr/GCE	4.99–49.95	0.004	Present work

CNT/SPCE: carbon-nanotubes modified screen printed carbon electrode. GR/GCE: graphene-modified glassy carbon electrode. nPt-MWCNTPE: multi-walled carbon nanotube and Pt-nanoparticles modified carbon paste electrode. AuNP-PGA/SWCNE: co-deposit in glutamic acid and gold nanoparticles on single-walled carbon nanotube film electrode. LNT-CFO/GCE: $LaNi_{0.5}$-$Ti_{0.5}O_3$/$CoFe_2O_4$ nanoparticle modified electrode. CNT/TCPE: multi-walled carbon nanotube/thionine modified carbon paste electrode. SWCNT–GNS/GCE: single-walled carbon nanotube–graphene nanosheet hybrid film modified electrode. Fe_3O_4/PDDA/GR/GCE: Fe_3O_4 nanoparticles-coated poly(diallyldimethylammonium chloride)-functionalized graphene nanocomposite film. MWCNT-polyhis: multiwalled carbon nanotubes dispersed in polyhistidine. L-Cysteine/GCE: covalently modified GCE by L-cysteine. D50wx2/GNP/GCPE: a cation exchanger resin, Dowex 50wx2 and gold nanoparticles modified glassy carbon paste electrode. Fe_2O_3/CNTs/FTO: Fe_2O_3 nanoparticle single-walled carbon nanotube composite electrode. ECF-CPE: electrospun-carbon nanofiber modified carbon paste electrode. GMC/GCE: graphite-mesoporous carbon modified GCE. Paraffin/graphite SP: paraffin/graphite modified sweet potato electrode. CdS/rGO/GCE: cadmium-sulphide quantum dots on reduced graphene oxide. Ag/AgCl/rGO/p-ATT/CFME: Ag/AgCl nanocrystals on reduced graphene oxide modified p-ATT/CFME. Cu-MWCNTs@Chi/GCE: copper nanoparticles on multi walled carbon nanotubes and chitosan nanocomposite modified GCE.

2. Experimental

2.1. Reagents and materials

Graphite powder with particle size < 50 μm, CAS# 7782-42-5 and hydrogen peroxide (30%) were obtained from E-Merck. Sulphuric acid (98%), potassium permanganate, sodium hydroxide pellets, potassium nitrate and potassium ferricyanide were procured from Merck India. Silver nitrate ($AgNO_3$) of AR grade was obtained from SRL chemicals. AR grade hydroquinone from SD Fine chemicals, Acetaminophen from Sigma Aldrich chemicals, Hydroxylamine hydrochloride ($NH_2OH.HCl$) and glutaraldehyde (25%) procured from Himedia and triple distilled water as solvent, were used for the presented study.

2.2. Synthetic procedure

Improved Hummers method was followed for synthesis of GO [24]. Briefly, the graphite powder was subjected to oxidation under oxidizing conditions of $KMnO_4/H_2SO_4$. The GO sheets were obtained by exfoliating 125 mg of graphite oxide in 100 mL of triple distilled water in a round bottom flask under ultrasonication. The reduction of GO and its decoration with nanosized silver using hydroxylamine hydrochloride was carried in water at temperature of 60 °C. In a typical experiment, 250 mg of $NH_2OH{\cdot}HCl$ and 2 mL of 30% ammonia were added to exfoliated GO kept under constant stirring conditions. The addition of ammonia helps in in situ formation of hydroxylamine from its salt. On addition of 0.11 g of $AgNO_3$, the reaction mixture changed its colour from yellow to dark brown in a time span of an hour. Reduced graphene oxide (rGO) as a control was also synthesized following same procedure except the addition of $AgNO_3$.

2.3. Instruments

UV–visible spectra were recorded on Shimadzu UV–vis spectrophotometer (UV-1650PC) equipped with a thermostat for temperature control with accuracy of ±0.1 °C. Powder X-ray diffraction (PXRD) measurements were done using a Bruker D8 Advance Diffractometer with Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). The data was collected in the 2θ range of 20°–80° with a step size of 0.02° and step time of 1 s. The surface morphology and size of graphene oxide and its composite with Ag i.e. Ag/Ag-oxide-graphene was analyzed from TEM images.