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Graphene Interface for Detection of Resorcinol an Endocrine Disruptor in Solubilized Ionic Liquid System: Electrochemical and COSMO-RS Quantum Studies

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We report synthesis, characterization and covalent fabrication of graphene nanosheets (GR) on Au electrode. The GR nanosheets were characterized by XRD, Raman spectroscopy, FESEM and TEM techniques. The GR nanosheets were functionalized by reduction of aryl diazonium salt ($\text{Cl}^- \text{N}_2^+ \text{Ph-COOH}$) to produce GR-Ph-COOH. In another step, Au electrode was modified by cysteamine (Cyst) to form Au-S-CH₂-CH₂-NH₂ surface. Finally, GR-Ph-COOH was covalently attached to Au-S-CH₂-CH₂-NH₂ by carbodiimide chemistry. The GR-Cyst-Au interface was used for electrochemical determination of resorcinol (RS) in ionic liquid [C₄mim][Cl] system over a concentration range from 0.3 to 45.2 μM with a detection limit (LOD) of 0.02 μM . The faster electron transfers kinetics of RS in [C₄mim][Cl] system was attributed to synergetic effects of GR nanosheets and [C₄mim][Cl] medium. The GR-Cyst-Au interface was successfully applied for determination of RS in Garnier hair-color cream as a real sample analysis. Computational quantum approach i.e. COSMO-RS model was also used to study trend of interactions in a ternary mixture of water, RS and [C₄mim][Cl] system for proposed RS sensor.

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Graphene (GR) is honeycomb lattice of sp^2 -bonded carbon atoms which has received increasing attention due to its unique physicochemical properties such as high surface area, excellent conductivity, high mechanical strength, ease of functionalization and mass production.^{1,2} GR sheets have extraordinary electronic transport properties for electro-catalysis,^{3,4} super-capacitors,⁵ chemical sensors⁶ and biosensors.⁷ In comparison with carbon nanotubes, GR exhibits numerous potential advantages including low cost, high surface area, high signal to noise ratio that promotes fast-heterogeneous electron transfer. Recently, significant efforts have focused on covalently functionalizing GR to achieve bandgap tuning and modulation of its doping level for various electronic and sensing applications.^{8,9} It has been known that, covalent functionalization of GR is simple and robust method, which alters the electronic properties of GR due to disruption of crystallographic lattice.¹⁰ The reduction of aryl diazonium salts is one possible alternative, and frequently been used as a method for the covalent derivatization of organic surfaces.^{11,12} The reduction reaction involves liberating nitrogen gas for formation of aryl radical that instantaneously reacts with the surface of carbon, semiconductor, and metals.¹³ Furthermore, gold (Au) electrodes are useful to construct electrochemical sensors due to large potential interval and their chemically inert nature. The well-established strategy of a self-assembled monolayer formation on Au electrode surfaces via attachment of thiol (-SH) or disulfide (-S-S-) functional groups.^{14,15}

Ionic liquids (ILs) are considered as novel class of chemical compounds, existing as salts in liquid state with interesting properties, such as high conductivity and stability.^{16,17} ILs have fascinated much interest for potential applications in the field of green chemical processes as an ionic conductive matrix and benign reaction solvents in electrochemical systems (actuators, electro-catalysis, batteries, super-capacitors and electrochromic windows) and photovoltaic cells.¹⁸⁻²¹ For any electrochemical process, the conductivity is the main property of primary importance and hence ILs are considered to be best electrolytes with maximum charge carriers per unit volume.²² Imidazolium-based ILs are actively investigated for their applications in electrochemical devices, gas capture and anionic membranes.^{23,24} COSMO-RS (Conductor-like Screening Model for Real Solvents) is a novel program for calculating thermodynamic properties of pure and mixed fluids based on quantum mechanical data.^{23,24} COSMO-RS procedure calculations consists of following two steps: (i) quantum

chemical COSMO calculations for the molecular species involved which gives information about solvents and solutes; (ii) COSMO-RS statistical calculations performed with the COSMOtherm program.^{23,24} In this article, COSMO-RS at thermodynamic level is used to generate data that explains the fundamental properties of IL-hydrate and surfactant-hydrate solubilized systems in presence of resorcinol (RS).

Resorcinol (RS) is one of the endocrine disrupting chemical (EDC) used in many industrial processes including adhesives, dyes, tanneries, food processing, agricultural research, pharmaceuticals and cosmetics.²⁵ Due to its high toxicity and low degradability in the ecological environment,²⁶ it was included in the list of priority EDC pollutants to be monitored by international agencies such as the US Environmental Protection Agency (EPA) and the European commission.²⁷ The evidences from in-vivo tests of rats and epidemiological studies of humans have demonstrated that RS can interfere with triiodothyronine (T₃) and thyroxine (T₄) metabolism, causing disruptions in thyroid activity.²⁸ Consequently, several analytical methods have been developed for quantification of RS based on chromatography,²⁹ fluorescence,³⁰ and capillary electrophoresis.³¹ Among them, electrochemical methods have fascinated great attentions due to their advantages of fast response, low cost, simple operation, time-saving, high sensitivity, high stability, and excellent selectivity.

The aim of present work is to synthesize, characterize and covalently fabricate GR-Cyst-Au interface. This procedure involves the functionalization of GR nanosheets by chemical reduction of aryl diazonium salt ($\text{Cl}^- \text{N}_2^+ \text{Ph-COOH}$) to form modified GR-Ph-COOH nanosheets. On the other side, Au electrode was modified with cysteamine (cyst) through Au-S linkage to give obtain an amine terminated Au electrode (Au-S-CH₂-CH₂-NH₂). Then carboxylic groups of GR-Ph-COOH were covalently linked to amine groups of Au-S-CH₂-CH₂-NH₂ using carbodiimide chemistry to form GR-Cyst-Au interface. The constructed GR-Cyst-Au interface was used for electrochemical detection of RS in a solubilized IL [C₄mim][Cl]. Computational quantum approach i.e. COSMO-RS model was used to study trend of interactions in a ternary mixture of water, RS and [C₄mim][Cl] system for proposed GR-Cyst-Au interface for detection of RS.

Experimental

Chemicals and instrumentation.—All the chemicals used in this work were of analytical grade and used without further purification.

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Pristine graphite powder with purity $\geq 99.99\%$, sodium nitrite (NaNO_2), sodium nitrate (NaNO_3), sodium borohydride (NaBH_4), *p*-aminobenzoic acid (*p*-ABA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), surfactants like cetyltrimethylammonium bromide (CTAB), Sodium dodecyl sulfate (SDS) and tritonix-100 (TX-100), and standard resorcinol (RS) were obtained from Sigma-Aldrich Chemie, Germany. 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}][\text{Cl}]$) was purchased from IoLiTec (Germany). A stock solution of 0.1M RS was prepared in different solubilized systems for comparison analysis. Phosphate buffer solution (PBS) of pH 7.0 was prepared by mixing appropriate amounts of potassium orthophosphate (KH_2PO_4) and dipotassium phosphate (K_2HPO_4).

Electrochemical measurements were performed by potentiostat (Gamry Instruments, USA) connected to a conventional three electrode cell system consists of Au electrode, platinum wire (Pt) and Ag/AgCl (saturated KCl) used as working, counter and reference electrodes, respectively. The Fourier transform infrared (FTIR) spectroscopic analysis was recorded at Carry FTIR-660 instrument (Agilent) using potassium bromide (KBr) pellets as reference for the samples. Ultraviolet-visible (UV-vis) spectra of as-prepared samples were recorded on UV-1800 (Shimadzu) fitted with 1.0 cm diameter of quartz cell. The X-ray diffraction (XRD) characterization was carried by Shimadzu XRD 6100 Cu K α 0.15419 nm. The morphological characterization of GR nanosheets was performed by Field emission scanning electron microscopy (FESEM, Tescan Lyra-3) and Transmission electron microscopy (TEM, JEOL JEM-3010). The Raman spectrum of GR was recorded on a Nicolet Nexus FT-Raman spectrometer with a Ge detector and a 1064 nm Nd: YAG laser. COSMOlogic GmbH & Co KG, Leverkusen, Germany, provided the COSMOtherm software with parameter file BP_TZVP_C30_1301.

Synthesis of GR nanosheets.—Graphene oxide (GO) was prepared from graphite powder by a modified Hummers method.³² In detail, graphite (1.0 g), NaNO_3 (1.0 g) and 46 mL of H_2SO_4 (98%) were added into a flask under stirring in an ice bath. After the addition of KMnO_4 (6 g), the reaction vessel was transferred into a water bath (35°C) and stirred for 1 h to complete the deep oxidation process. Next, 70 mL of deionized water was slowly added and temperature was adjusted to 95°C stirred for another 2h until suspension turned brown. Finally, brown suspension was further treated with 30 mL of H_2O_2 (30%) to reduce the residual oxidants and intermediates to soluble sulfate. This prepared suspension was centrifuged at 10000 rpm for 20 min to remove residual graphite, and subsequently washed with 1.0 molL⁻¹ HCl and deionized water repeatedly. The washed suspension was dried under vacuum to obtain GO powder. The aqueous solution of GO (0.1 mg mL⁻¹) was prepared by ultra-sonication for 30 min which exfoliates GO into nanosheets. The chemical reduction of GO was carried out in presence of 10 mM sodium borohydride (NaBH_4) at pH 10 under constant stirring for 20 minutes to yield GR nanosheets settled at bottom as insoluble product. GR nanosheets were separated by centrifugation step and used for further grafting on Au electrodes.

Construction of GR-Cyst-Au interface.—Prior to surface modification, Au electrodes (3-mm-diameter) were mechanically polished with 1.0 and 0.05 μm alumina slurry until a mirror finish was achieved. The cleaned Au electrodes were sonicated for 10 min followed by rinsing with double distilled water and dried at room temperature. The Au electrodes were further cleaned electrochemically in 0.05M H_2SO_4 solution by cycling over a potential between -300 mV to +1500 mV ($v = 50 \text{ mVs}^{-1}$) until reproducible cyclic voltammograms were achieved. Then pretreated Au electrodes were immersed in an aqueous solution of 100 mM Cyst for 2 h followed by rinsing with distilled water and dried under a stream of nitrogen to fabricate Au-S-CH₂-CH₂-NH₂ modified electrodes. The diazonium salt ($\text{Cl}^- \text{N}_2^+ \text{-Ph-COOH}$) is prepared from an aqueous solution of 1.0 mM NaNO_2 and 1.0 mM *p*-ABA (0.5M HCl) followed by degassed with N_2 flow and left to react for 10 min at 0°C. The GR is functionalized by chemical reduction (N_2H_4) of $\text{Cl}^- \text{N}_2^+ \text{-Ph-COOH}$ to form GR-Ph-COOH. The GR-Ph-

COOH surface was covalently bonded with Au-S-CH₂-CH₂-NH₂ modified electrode in presence of 2 mM EDC and 5 mM NHS by amide linkage to form GR-Cyst-Au interface. For comparison analysis, we have also prepared another GR/Au electrode by casting 10 μL of 1.0 mg/mL GR suspension dissolved in DMF and dried under N_2 gas for 10 min to obtain GR/Au electrode. The construction strategy of GR-Cyst-Au interface is summarized in Scheme 1.

COSMO-RS modeling studies.—COSMO-RS method is a continuum solvation model COSMO to simulate a virtual conductor environment for the molecule of interest, followed by a screening charge density σ_i obtained through standard quantum chemical calculations. The COSMO file is used to estimate σ_i profile and chemical potential for a particular molecule to evaluate their possible molecular interactions and thermodynamic properties.³³ The statistical thermodynamics treatment of molecular interactions is performed using COSMOtherm software with parameter file BP_TZVP_C30_1301 (COSMOlogic GmbH & Co KG, Leverkusen, Germany).³⁴

Results and Discussion

Characterization of GR nanosheets and GR-Cyst-Au interface.—The synthesized GR nanosheets were characterized by various spectroscopic and microscopic techniques. The presence of functional groups in GO was identified by FTIR spectroscopy. FTIR spectra of GO shows peaks at 1023 cm⁻¹ (C-O-C), 1330 cm⁻¹ (C-OH stretching), 1710 cm⁻¹ (O=C) and 3345 cm⁻¹ (OH), respectively. In addition a peak observed at 1613 cm⁻¹ relates to skeletal vibrations of un-oxidized graphitic domains (Figure 1A).³⁵ UV-vis spectra of GO shows characteristic absorption bands at 229 nm corresponds to $\pi \rightarrow \pi^*$ (C=C) of original graphite and a band 300 nm attributed to $\pi \rightarrow \pi^*$ (C=O) of Go (Figure 1B).³⁶

The GR nanosheets were further characterized by X-ray diffraction technique (XRD). The XRD pattern of pristine graphite flakes shows characteristic sharp and intensive peak at $2\theta = 26.37^\circ$ corresponding to (002) plane indicates highly organized layered structure with interlayer spacing of 0.375 nm (JCPDS 75-2078, 0.375 nm) (Figure 1C).³⁷ In contrast, the characteristic peak (002) of GR nanosheets becomes very weak in intensity, broader in shape and shifted to $2\theta = 25.12^\circ$. This result indicate smaller crystalline size of GR nanosheets compared to graphite flakes which is attributed to the presence of thin GR layers due to high degree of exfoliation.³⁸ The calculated *d*-spacing between layers of GR nanosheets is 0.399 nm, suggesting distance between layers of GR is close to the theoretical value.³⁹

The typical Raman spectrum of GR nanosheets (Figure 1D) shows D, G and 2D bands due to in-plane vibrations (Figure 1D). The D peak corresponds to breathing modes of six-atom rings and requires a defect for its activation. The D band at 1340 cm⁻¹ was assigned to local defects and disorders particularly at edges of GR nanosheets owing to Brillouin zone (1270 and 1450 cm⁻¹).⁴⁰ The G band at 1590 cm⁻¹ is consigned to E_{2g} phonon mode of sp² hybridized carbon atoms is main spectral feature of GR. This band is very sensitive to strain effects and indicates the number of GR layers.⁴¹ It has been know that G band position moves to lower frequencies due to the increase in GR layers. However, in the present studies, there is no major change in G band position (1590 cm⁻¹) confirms single layer of synthesized GR nanosheets. The third 2D band is a second order overtone of the D band process dependent on excitation laser and occurs usually at 2700 cm⁻¹. For single layer GR, the 2D band shows sharp peak, this peak becomes much broader and blue shifted when thickness increases from single to multilayer GR.⁴²

The morphological characterization of synthesized GR nanosheets was examined by FESEM and TEM techniques (Figure 1E). The surface morphology of GR reveals single layer nanosheets in the form of wrinkled, crumpled and rippled structures.⁴³ TEM analysis confirmed GR nanosheets shows highly transparent regions indicates the possible existence of monolayer GR nanosheets (Figure 1F).

Scheme 1. Construction of GR-Cyst-Au interface.

The GR-Cyst-Au interface was characterized by FTIR spectroscopy to verify successful immobilization of GR nanosheets on Au electrode. Figure 1G shows FTIR spectrum of GR-Cyst-Au interface displays well distinguished peaks at 3565 cm^{-1} (N-H) and 1650 cm^{-1} ($\text{C}=\text{O}$) corresponds to the presence of amide linkage ($-\text{CONH}_2$) between GR-Ph-COOH and Au-S- $\text{CH}_2\text{-CH}_2\text{-NH}_2$ functionalities. In addition, peaks at 3030 cm^{-1} (C-H stretching), 1576 cm^{-1} ($\text{C}=\text{C}$) and 850 cm^{-1} (C-H bending) attributes to aromatic ring of GR-Ph-COOH nanosheets. The absence of thiol (S-H) vibrations (2500 to 2900 cm^{-1}) in FTIR spectrum of GR-Cyst-Au interface (Figure 1G) endorses Au-S bond. Moreover, the presence of band between 500 to 750 cm^{-1} further confirms presence of Au-S bond.⁴⁴ The electrochemical appraising of GR-Cyst-Au interface was studied by electrochemical impedance spectroscopy (EIS) and CV using

$10.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{3-/4-}$ redox (Supporting information, S1 and Figure S1). It was observed that GR-Cyst-Au interface shows significant amplification in redox peak currents due to decrease of resistance at GR-Cyst-Au interface to catalyze the electrochemical reactions.

Electrochemical behavior of RS in different solubilized systems.—The study of depolarizer in solubilized systems (surfactants and ILs) adds a beneficial and new dimension to improve the sensitivity and selectivity.^{45,46} In present work, the electrochemical behavior of 0.02 mM RS at GR-Cyst-Au interface in different solubilized surfactant systems viz., cationic (CTAB), anionic (SDS), non-ionic (Tween-20) was studied using CV (pH 7.0). The CV response of RS at GR-Cyst-Au interface in different surfactants and water shows an increasing electron transfer rate (diffusion current) due to formation

Figure 1. (A) FTIR spectrum of GO; (B) UV-vis spectra of GO; (C) XRD analysis of GR and graphite; (D) Raman spectrum of GR nanosheets; (E) FESEM image of GR; (F) TEM image of GR nanosheets; (G) FTIR analysis of GR-Cyst-Au interface.

Figure 2. (A) Electrochemical behavior of 0.02 mM RS in different solubilized systems; (B) effect of [C₄ mim][Cl] concentration on oxidation of RS at GR–Cyst–Au interface.

of aggregates as bilayers, cylinders, surface micelles on electrode surface that promotes electron transfer kinetics.

Studying electrochemical behavior of various electroactive species at solid electrodes in IL electrolytes is a very active research area for understanding the reaction mechanisms and comparing behavior to conventional electrolyte systems.^{47,48} In present work, the CV response of depolarizer (RS) at GR–Cyst–Au interface shows well-defined peak and significant increase in catalytic currents observed in presence of [C₄ mim][Cl] in comparison to surfactants (Figure 2A). These results were attributed to high intrinsic conductivity, high polarity and good solvating ability of [C₄ mim][Cl]. The electrochemical oxidation of RS at GR–Cyst–Au interface in [C₄ mim][Cl] involves two-electrons to form doubly protonated o-benzoquinone at a potential of 0.59 V. This protonated o-benzoquinone species undergoes deprotonation reaction with Cl[−] of [C₄ mim][Cl] to form HCl results in increases in acidic nature of medium as reported for oxidation of catechol in IL.⁴⁹ The presence of acidic medium (antifouling capacity) averts the polymerization of RS, which prevents further passivation of GR–Cyst–Au interface. This RS oxidation mechanism in [C₄ mim][Cl] significantly enhanced the diffusion current of RS compared to surfactants. The obtained results were verified by calculating diffusion coefficient of 0.02 mM RS in different solubilized systems (surfactants and [C₄ mim][Cl]) using Randles-Sevcik equation.⁵⁰

$$I_{pa} = (2.99 \times 10^5) n \alpha^{1/2} A C_0^* D_0^{1/2} \nu^{1/2}$$

Where, I_{pa} (μA) is anodic peak current, D_0 (cm² s^{−1}) is diffusion coefficient of RS and ν is scan rate (mVs^{−1}), n is number of electrons involved in oxidation, α is transfer coefficient, A is apparent surface area of Au electrode (cm²), C_0^* is concentration of RS in different mediums. The D_0 of 0.02 mM RS ($\nu = 25$ mVs^{−1}, $n = 2$, $A = 0.3$ cm² and $\alpha = 0.5$) in presence of different surfactants, [C₄ mim][Cl] system

and in water is summarized in Table S2 (supporting information). The D_0 can be considered as an average value of diffusion process in different mediums at GR–Cyst–Au interface. The calculated D_0 (7.9×10^{-2} cm² s^{−1}) of RS in solubilized [C₄ mim][Cl] was higher in contrast to surfactants indicates faster electron transfer kinetics in [C₄ mim][Cl] system.

The enhancement in anodic peak current of RS was further investigated by varying the concentration of [C₄ mim][Cl]. Figure 2B shows anodic peak current of RS increases steadily with increase in [C₄ mim][Cl] concentration which reaches a maximum at 0.001% (5.72×10^{-5} M [C₄ mim][Cl]). The anodic peak current of RS decreases due to increase in [C₄ mim][Cl] concentration, which results an inhibition of electron transfer by aggregates of [C₄ mim][Cl] micelles which entraps RS molecules leads to drop in anodic peak current. Therefore, 0.001% (5.72×10^{-5} M) [C₄ mim][Cl] concentration was an ideal for electrochemical detection of RS.

COSMO-RS modeling studies.—The COSMO-RS method was used to synchronize the interaction behavior of RS in solubilized [C₄ mim][Cl] and surfactant system. COSMO-RS an adaptive and proven method for deriving thermodynamic and chemical properties of fluids in their pure or mixed state based on uni-molecular quantum chemical calculations.⁵¹ In the literature, it has already been established that reliability of COSMO-RS to calculate excess enthalpies of binary mixtures.^{52,53} The effect of [C₄ mim][Cl] concentration and surfactants with an excess enthalpy was studied and found significant changes in system. The excess enthalpy and free Gibbs energy was found to be negative for all studied systems at various concentration of [C₄ mim][Cl] in binary mixture of RS with [C₄ mim][Cl] system as presented in Figure 3 (for surfactant see supporting information Figure S2 and S3).

Similarly, the comparative excess enthalpy and Gibbs free energy as depicted in Figure 4 speculates that RS interacts more with [C₄ mim][Cl] system compared to studied surfactants. The ranking of interaction of RS with studied solubilized system based on G_m^E and H_m^E follows order IL > CTAB > SDS > TX100 that is comparable to the experimental trend. Interaction energy provides an information about the ion-pair and contact probability speculates an idea of compactness of the ion-pair. Usually, interaction energy and distance within the ions are inversely proportional, showing dominance of charge-charge interaction in ILs.⁵⁴ Therefore, Figure 5 shows the contact probability of entities present in system with each other.

After visualizing the Figure 5, it is clear that contact probability mainly based on lowest energy contact with [C₄ mim][Cl] system and RS i.e. the percentage of closeness is lowest compared to studied surfactants. The interaction strength of RS with [C₄ mim][Cl] system is higher which increases electron transfer rate compared to other solubilized surfactants. In addition, Figure 6 shows contact probability, which signifies anion of [C₄ mim][Cl] system played a significant role to enhance the sensitivity of GR–Cyst–Au interface. Therefore, to check the sensitivity of GR–Cyst–Au interface an effect of various anions would also be an interesting study in the future aspects to improve the sensitivity and selectivity in the various solubilized IL systems. Direct comparison of contact probability of TX 100 with other solubilized systems was not possible since there were three components in TX100 (water, RS and TX100) and in other four (water, resorcinol, cation and anion) components.

Electroanalytical performance of GR–Cyst–Au interface toward detection of RS.

The electrochemical behavior of 0.02 mM RS was investigated by CV in 5.72×10^{-5} M [C₄ mim][Cl] system at bare Au electrode, GR/Au and GR–Cyst–Au interface (pH 7.0). Figure 6 shows appearance of a cathodic peak at bare Au electrode, GR/Au and GR–Cyst–Au interface over 0.30 – 0.65 V corresponds to reduction of gold oxide.⁵⁵ In addition Au electrode, GR/Au and GR–Cyst–Au interface exhibits a single well-defined irreversible anodic peak at + 0.64V in 5.72×10^{-5} M [C₄ mim][Cl] attributed to oxidation of phenolic groups of RS to benzoquinone derivatives. The GR–Cyst–Au interface shows 9-fold times higher peak current for oxidation of RS

Figure 3. (a) Estimated total excess enthalpies; (b) Estimated excess Gibbs Free energy of mixture of [C₄ mim][Cl] + RS at various [C₄ mim][Cl] concentrations (298.2 K) predicted by COSMO-RS.

compared to bare Au electrode. The enhancement in peak intensity could be associated with synergetic effects of (i) large surface area of GR (ii) high conductivity and charge transporting abilities of GR and (iii) highly conductive medium of [C₄ mim][Cl] system suggesting faster electron transfer kinetics. It is worth mentioning, that increase in peak intensity of RS oxidation at GR-Cyst-Au interface is also accompanied by a net anodic shift ($\Delta E_p = -40$ mV) indicating less polarization (decrease in overvoltage) compared to Au electrode. By combining the specific properties of [C₄ mim][Cl] and GR-Cyst-Au interface promotes facile electron transfer kinetics and hence this system is more suitable from the practical point of view for detection of RS. The performance of GR-Cyst-Au interface was also compared with GR/Au modified electrode prepared by drop-casting method. The GR-Cyst-Au interface shows much higher response compared to GR/Au modified electrode due to covalent immobilization of GR nanosheets, which enhances its stability and sensitivity for detection of RS.

Effect of scan rate.—The influence of scan rate plays an important role for studying electrochemical reactions. The electrochemical behavior of 0.02 mM RS at GR-Cyst-Au interface was studied by CV in 5.72×10^{-5} M [C₄ mim][Cl] system (pH 7.0) at different scan rates (Figure 7A). It was observed that I_p of RS increases linearly with

$v^{1/2}$ from 10–125 mV s⁻¹, indicating oxidation of RS is controlled by electron transfer reactions (Figure 7B). The diffusion-controlled behavior of RS at GR-Cyst-Au interface was confirmed by plotting $\log I_p$ vs. $\log v$ corresponding to equation: $\log I_p/\mu A = 0.6881 \log v$ (mV s⁻¹) + 0.0866; $R^2 = 0.996$. The obtained slope of 0.68 is close to 0.5 confirms diffusion controlled nature of electrode process (Figure 7C). The effect of scan rate on E_p of RS shows linear relationship with $\ln v$ expressed by Laviron Equation:⁵⁰

$$E_p = E^{\circ'} + \left(\frac{RT}{\alpha n F} \right) \ln \left(\frac{RT K^{\circ}}{\alpha n F} \right) - \left(\frac{RT}{\alpha n F} \right) \ln v$$

where $E^{\circ'}$ is formal potential, k_0 is standard heterogeneous rate constant, n is number of electrons transfer, v is scan rate, A is electrode area, and α is electron transfer coefficient of oxidation of RS ($R = 8.314$ J mol⁻¹ K⁻¹, $T = 298$ K, and $F = 96,487$ C mol⁻¹). The $E^{\circ'}$ can be deduced from intercept of E_p versus v plot corresponding to equation: E_p (V) = 0.0299 $\ln v$ + 0.423 ($R^2 = 0.985$) on ordinate by extrapolating line $v = 0$ ($E^{\circ'} = 0.42$) (Figure 7D). The slope $RT/\alpha n F = 0.0299$ gives value of $\alpha n = 1.12$ and for irreversible electrode process $\alpha = 0.5$, hence oxidation of RS at GR-Cyst-Au interface involves two electrons ($n = 2.24$). The value of k_0 was calculated and found to be 1.24 s⁻¹ suggests GR-Cyst-Au interface effectively promotes the electron transfer kinetics for oxidation of RS.

Figure 4. Comparison of (a) Estimated total excess enthalpies; (b) Estimated excess Gibbs Free energy for mixture of solubilized studied system [C₄ mim] [Cl], SDS, CTAB) at fixed concentration of 0.5 with RS predicted by COSMO-RS.

Figure 5. Contact probability of binary mixture of [C₄ mim] [Cl] and RS using COSMO-RS at equimolar concentration of each species i.e. water (1); RS (2); [C₄mim] or SDS or CTAB (3); [Cl] or Na⁺ or Br⁻ (4).

Figure 6. Comparison of CV studies ($v = 25 \text{ mVs}^{-1}$) of 0.02 mM RS in 0.001% ($5.72 \times 10^{-5} \text{ M}$ [C₄ mim] [Cl] at Au, GR/Au and GR-Cyst-Au interface (pH 7.0).

Linearity and related figures of merit of developed GR-Cyst-Au interface.—Square-wave voltammetry (SWV) was used to evaluate the performance of GR-Cyst-Au interface to study the linearity range, calculate limit of detection (LOD) of RS under optimized conditions. The calibration curve was obtained at GR-Cyst-Au interface by measuring SW peak current at different concentrations of RS from 0.3 to 45.2 μM corresponds to linear regression equation: $I_p (\mu\text{A}) = 1.37 [\text{RS}/\mu\text{A}] + 14.03$ ($R^2 = 0.997$) (Figure 8 and inset). The detection limit (LOD) was calculated from linear regression equation and found to be 0.02 μM ($S/N = 3$). The analytical performance of GR-Cyst-Au interface was compared with reported electrochemical sensors, which reflects present work shows lower LOD values (0.02 μM) than reported modified electrodes for detection of RS (Table I).^{56–62} To the best of our knowledge, no reports are available on electrochemical determination of RS in solubilized IL [C₄ mim] [Cl] system. Therefore, present method is novel and highly suitable for the determination of RS.

The long-term stability of GR-Cyst-Au interface was studied to detect same concentration of RS (0.02 mM) by CV after a period of one week and found that 86% response of RS at GR-Cyst-Au interface was retained indicates good stability of developed interface (Figure 9A). The reproducibility of three fabricated interfaces was tested by comparing CV peak currents of 0.02 mM RS which shows a relative standard deviation (RSD) of 2.4% reveals good reproducibility of GR-Cyst-Au interface (Figure 9B).

Application of GR-Cyst-Au interface for real sample analysis.—The GR-Cyst-Au interface was applied for detection of RS in commercial cosmetic product (Garnier color naturals cream) (supporting information: Figure S4). The sample preparation consists of

Figure 7. (A) Effect of scan rate on 0.02 mM M RS; (B) Plot $v^{1/2}$ vs. I_p ; (C) Plot of $\log v$ vs. $\log I_p$; (D) Plot of $\log v$ vs. E_p of RS.

Figure 8. SW peak currents obtained at GR-Cyst-Au interface for different RS concentrations (0.3, 3.8, 7.5, 13.3, 19.3, 24.3, 28.3, 32.6 and 45.2 μM) in [C₄ mim] [Cl]. (Inset) Linear calibration plot of [RS] vs. I_p . The error bars represent standard deviation from three separate experiments.

dissolving 0.1 g of cosmetic sample in 25 mL of $5.72 \times 10^{-5} M$ [C₄ mim] [Cl] by ultra-sonication for 15 min followed by centrifugation to remove excipients. An aliquot of 300 μL of this solution was added to 15 mL of phosphate buffer (pH 7.0). The amount of RS present in Garnier cream was determined by measuring SWV peak current and compared to linear calibration curve of standard RS solutions. The obtained results indicates Garnier color naturals cream contains 0.5 μM RS (2.5% wt/wt) which is within permissible limit (5% wt/wt) according to the EU Cosmetics Directive permits.⁶³ The reliability of proposed method was confirmed by calculating recoveries of RS in Garnier color naturals cream by standard addition method. The obtained recoveries of RS range from 97.14% to 100.6% with RSD value less than 5% (supporting information: Table S3) designates high accuracy and precision at GR-Cyst-Au interface.

Conclusions

We have proposed a simple and reliable technique to covalently immobilize GR nanosheets at the surface of Au electrode to form GR-Cyst-Au interface. This developed GR-Cyst-Au interface was effectively applied for electrochemical detection of RS in [C₄ mim] [Cl] system. The GR-Cyst-Au interface displayed enhanced electrochemical responses of RS in [C₄ mim] [Cl] medium corresponds

Figure 9. (A) Stability and (B) reproducibility of GR-Cyst-Au interface for detection of 0.02 mM RS in solubilized 0.001% ($5.72 \times 10^{-5} M$) [C₄ mim] [Cl] system.

Table I. Comparison studies for electrochemical performance of GR-Cyst-Au interface with reported electrochemical sensors for determination of RS.

Modified electrodes	Linearity range/ μM	LOD/ μM	Reference
MWCNT/GCE	1.2 – 190	1.10	56
Nafion/MWCNTs/CDs/MWCNTs	3.0 – 400	0.15	57
CTAB-GO/MWNT/GCE	0.1 – 20	0.30	58
MWNTs-CHT/GCE	5.0 – 192	5.20	59
Graphene-chitosan/GCE	1.0 – 55	0.75	60
WS2-Gr composite	1.0 – 10	0.70	61
Graphene screen-printed	1.0 – 50	2.40	62
GR-Cyst-Au	0.3 – 40	0.02	This work

Au: Gold electrode, MWCNT: Multi-walled carbon nanotubes, NAF: Nafion, CDs: Carbon dots, GO: Graphene oxide, GR: Graphene, Cyst: Cysteamine, WS2-Gr: tungsten sulfide-graphene.

to synergetic effects of high charge transporting abilities of GR nanosheets and presence of highly conductive solubilized [C₄ mim][Cl] electrolytic system that promotes faster electron transfer kinetics compared to surfactants. In addition, the advantages of using [C₄ mim][Cl] do not require addition of supporting electrolyte. The COSMO-RS model was successfully applied to study the trend of interaction in ternary mixture of water, RS and solubilized components at GR–Cyst–Au interface. Finally, the GR–Cyst–Au interface demonstrated as potential candidate for detection of RS in cosmetics real sample (Garnier color naturals cream).

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