Graphene are the layers having two-dimension structures with high surface area where sp2-hybridized carbon atoms are covalently bonded, arranged in a hexagonal network. Graphene serves as the basic structural unit for other allotropic forms of carbon i.e. zero dimension fullerences shaped by wrapping up graphene layer to make sphere (Bucky ball) similarly, Carbon nanotubes (CNTs) having one dimension are shaped by rolling the graphene sheets to form cylindrical structure and three-dimensional graphite are formed by piling many sheets of individual graphene layer bonded together by van der Waals bonds. Graphene exhibits extraordinary properties containing, such as high exterior capacity, extraordinary inherent flexibility of electron and admirable thermal conductivity. Graphene and its composite had attracted vast courtesy over the chemical activities in the body. Ef chemical sensors desirable for inspecting the concentration and the electrochemical sensors that deliver continuous evidence about the changes in the ecosystem. Experimental simplicity, detectability and low price are certain of the important points of the electrochemical sensors enabling them to be essentially applied in different zones. Due to its high sensitivity graphene can be applied as an electrochemical sensor for advancement of the sensing capacity. The Graphene sheets have been seemed on the life science and health platform due to their fascinating material performance like, outstanding conductivity, biocompatibility, and tremendous Para magnetism, chemical, thermal, metallurgical and mechanical properties to use as a sensor constituent. Determination of daphnetin, synthesis of hydrophilic surface of graphene is some of the accomplishments when using graphene as an electrochemical sensing element. Hence, it is pre-requisite to explore graphene composite as a photometric sensor. In addition, due to excellent adsorbent ability of graphene can be applied in photometric sensors. Modern improvements in sensor of chemical based have been targeted for the sensing of local magnetic field, chemical bonding, and viscosity. Graphene is considered to be the upcoming material for the physio-chemical sensing as it has excellent thermal, electrical and chemical stability.

Thiourea (CH4N2S) as shown in Figure 1, is very life-threatening chemical and hazardous for humans as well as for animals when thiourea is heated upon decomposition, it releases poisonous gases of nitrogen oxide and sulphur oxides. Long term contact of humans who had been in contact with the chemical for 5 years. Thiourea as catalyst toward Uric acid and Dopamine was done by Ag-rGO pasted on glassy carbon electrode. Furthermore, the Ag-rGO
improved electrode gave nearly four times greater anodic current as compared to bare GCE. In current study, Ag-rGO composite has been applied as an electrochemical thiourea sensor in aqueous samples of different concentration of TU. Different electrodes have different limit of detection (LOD) toward TU. The present electrode has shown 10 µM LOD for TU as shown in Table I. Table II shows the approach of electrode toward real water samples in which some amount of TU has added. The results have shown better sensitivity and selectivity toward TU.

Experimental

Materials and instrumentation.—All the chemicals used in this work like graphite concentrate (GC) Sodium borohydride (NaBH₄ 98 wt%), Potassium permanganate (KMnO₄ 98 wt%) Sodium nitrate (NaNO₃ 98 wt%) Silver nitrate (AgNO₃ 98 wt%) Sulphuric acid (H₂SO₄ 98 wt%), and Hydrogen peroxide (H₂O₂ 98 wt%) were bought from Sigma Aldrich (Germany) and used as such without further purification unless specified. Redox reactions were accomplished in an electrochemical cell applying an Autolab device cyclic voltammetry of EZ stat-pro NuVant system Inc. model (Netherland). There are three electrodes, working, reference and auxiliary electrode in electrochemical cell. Modified glassy carbon electrode with rGO, Ag–rGO nanocomposites were applied as working electrode, glass electrode was applied as a reference electrode and platinum electrode was applied as the auxiliary electrode. Scanning electronic microscopy was used to check the attachment of Ag-nanoparticles on the layers of rGO. Intensive electrons beam were produced at the uppermost of the column, faster down by applying high voltage and moved through an arrangement of aperture and lens to make a focus shaft of light of electron by striking the sample’s surface and tested the specimens. The collaboration of electronics with sample generates various signals which were taken by indicators for image processing of sample presented at monitor reader. Penetration of electrons beams deep into the specimen depends upon specimen density and useful voltage. XRD is a fast expressive technique and mostly use for the compositional study of crystal. In (XRD) the sample was prepared excellently normal mass and inspected its homogeneity. The X-ray diffraction technique was used to see the changing of composition of rGO due to decomposition of Ag-NP’s. Crystal arrangement and functional group of organic compounds were studied by FTIR spectroscopy. Usually, molecules showed absorption in IR region of the electromagnetic spectrum. The absorption exhibited the existence of several types of interactions in the molecules in the range of 4000 to 400 cm⁻¹. It is usually working for the identification of unidentified samples. The information’s are extremely precise and distinguishes like material. The fastness of FTIR makes it extraordinary in screening application, while the sensitivity endows several progressive research applications. The study of changing GO to rGO was performed by FTIR.

Synthesis of graphene oxide (GO) (G₀).—While making of Graphene Oxide, we arranged 12 M H₂SO₄ solution and 23 ml of deionized water. Some of the negative charge functional group on electrode has shown 10 µM LOD for TU as shown in Table I. Table II shows the approach of electrode toward real water samples in which some amount of TU has added. The results have shown better sensitivity and selectivity toward TU.

Preparation of reduced Graphene Oxide (rGO) designated as (G₁).—For the reduction of GO further it was sonicated the dried graphene oxides in 50 ml ethanol for 24 h. at 400 °C, when sample reduced then we heated the r-GO and got it in dried form.

Adsorption of Ag-nanoparticles on surface of rGO designated as Ag–rGO (G₂).—At this stage 20 mg rGO was collected and added 25 ml (1 mM AgNO₃) solution followed by 3 ml (10 mM NaBH₄) solution for the reduction of AgNO₃. The mixture was stirred up to 2 h. Now on reduced graphene oxide surface the Ag-nanoparticles become adsorbed. The product was then separated by method of vaporization and washed with distilled water for many time and heated at 50 °C until it dried. The preparation of Ag–rGO initiated with mixing highly dispersed rGO sheets with silver nitrate in deionized water. Some of the negative charge functional group on the layers of rGO performed a role of adsorption positions for the silver ions of positive charge. The negative charges on the sheets of rGO were fashioned by the growing of hydroxyl, carbonyl, epoxide functional group and electron density of pi bonds on the surface of rGO by the process of oxidation followed by reduction. These three steps have shown in Fig. 2 respectively. To produce silver NPs on little cost we can follow the green synthesis as stated preparation silver nanoparticles by using Clitoria ternatea and Solanum nigrum.

Results and Discussion

Powder X-ray diffraction analysis was accomplished for the phase and structural study of the GO, rGO, Ag–rGO and Ag–rGO nanocomposite. These are synthesized by modified Hummer’s method and chemically reduction method. XRD shape of rGO exhibited in Fig. 3. In previous study it is stated that GO show a characteristic peak at the angle of 10.1° that is related to (001) reflection plane shown in Fig. 3. The (001) reflection plane fully vanished when the GO is converted to rGO, and fresh broad peak grown at 23.6° that related to the reflection plane (002).

In Fig. 3, the graph of r-GO demonstrated a growth in the graphite nature of rGO due to the contraction of area in between sheets upon subsequently reduction. The extensive peak in the graph indicated the destruction of crystallinity of graphite oxide. The graph of Ag–rGO due to the addition of Ag-NPs to the r-GO sheets, the recombining form of r-GO sheets is missed which is seemed from disappearing of the (002) diffraction peak can compare with graph of pure Ag nanoparticles. As we compare pure XRD graph of Ag with Ag–rGO, there is one broad peak in Ag–rGO due to rGO. This shows that it is not pure Ag but impregnated Ag on rGO sheets.

The graph of Ag–rGO due to the addition of Ag-NPs to the r-GO sheets, the recombining form of r-GO sheets is missed which is seemed from disappearing of the (002) diffraction peak can compare with graph of pure Ag nanoparticles. In the graph there are four sharp and discrete diffraction peaks at angles 39.1°, 43.6°, 65.3° and 76.8° which are concerned to Ag–NPs decorated on r-GO as (111), (200), (311) respectively.

Figure 4, clarify the spectra of FTIR of GO exhibited and absorption peak at 1067 cm⁻¹ was due to the stretching manner of (C–O of alkyl group), the peak at 1709 cm⁻¹ was due to C=O, the peak at 1560 cm⁻¹ was due to C=C stretching, the peak at 1244 cm⁻¹ was due to (C–O epoxy group) and 1430 cm⁻¹ was due to O–H group.

In this Fig. 4, the spectra of rGO which have been showed the absorption peak at 1067 cm⁻¹, 1244 cm⁻¹, 1430 cm⁻¹, 1560 cm⁻¹, 1709 cm⁻¹ region disappeared, which reveals the absence of OH, C–O (epoxy group), C–O (alkoxy group) and C=O group after reduction. And the peak at 1560 cm⁻¹ gone to C=C. One additional
peak was appeared at 1000 cm$^{-1}$ which indicated the Carbon-Nitrogen bond stretching. This additional peak was due to ammonia because during experiment we have used pipette mistakenly having ammonia. Due to this result has not disturbed. These results specified that during hydrothermal method the GO was reduced to r-GO. The combined graph in this figure showed that after reduction of graphene oxide to reduce graphene oxide the absorption peaks of different oxygen containing group is reduced and some disappeared. It confirmed that GO changed into reduced graphene oxide effectively.

Scanning electronic microscopy was performed to confirm the structural morphology of the composite material. The below graph of SEM expressed various arrangements of the sample. In figure no. 5 the sample (A,B) (rGO) displayed stacked sheets which made logic that these are the rGO layers having superior surface space as compare to graphene oxide. The nanomaterial surface study was checked by SEM where silver nanoparticles appeared on the sheets of rGO exposed in Fig. 5 (C,D) (Ag-rGO). On the surface and in between these sheets the Ag nanoparticles arranged and exfoliated the sheets. The white spots that are on the surface of rGO are actually Ag N-Particles.

**Cyclic voltammetry (CV).**—The as prepared Ag-rGO nanomaterial was developed as a sensor for chemical to measure the property such as finding limit and association number for sensing of thiourea in water sample. In present work the deposition of silver nanoparticles onto the rGO surface was done and normally the contact between them is naturally covalent. More chemical contact between Ag NPs and rGO had therefore enhanced the electrocatalytic activity of the electrode due to the greater electric conductivity of Ag NPs on the GO which offered superior surface area. Cyclic voltammogram of rGO electrode was taken at different concentration of electrolyte. These concentrations are 10 μM, 20 μM, 30 μM, 40 μM and 50 μM of thiourea (TU) over a voltage window in the range of −0.5 V to 1.2 V at the different scan rate. The Ag/AgCl was used as reference electrode shown in Fig. 6A. The cathodic and anodic current peaks were appeared at −24 μA and 7 μA respectively at concentration of 10 μM of thiourea. The cathodic and anodic current peaks were appeared at −20 μA and 10 μA respectively at concentration of 20 μM of thiourea. While at 30 μM concentration of thiourea the cathodic and anodic current peaks were appeared at −20 μA and 30 μA respectively. At 40 μM conc. of TU the cathodic and anodic current appeared at −7 μA and 62 μA. However, at 50 μM concentration of thiourea the cathodic and anodic current peaks were appeared at −10 μA and 70 μA. Hence, it is noticed that by increasing the concentration thiourea the rGO/GCE electrode show better oxidation peaks.

On the other hand, the fabricated Ag-rGO/GCE showed a significant oxidation peak in graph of Ag-rGO (A). As the concentration of thiourea increased, so did the anodic current,
ensuring that adsorbing Ag nanoparticles on reduce graphene oxide layers improved the composite material’s electrolytic property. This is because the AgNPs were firmly attached to the rGO allowing for quick oxidation-reduction reaction.

It is exhibited that by using Ag-rGO, the cathodic and anodic current were appeared at $-8 \mu$A and $15 \mu$A respectively at $10 \mu$M concentration of thiourea (TU). While by increasing the concentration of thiourea from $10 \mu$M to $20 \mu$M the cathodic and anodic current changed to $-15 \mu$A and $22 \mu$A respectively. Increasing the concentration of thiourea further to $30 \mu$M, the cathodic and anodic current increased by $-11 \mu$A and $26 \mu$A respectively. Now at $40 \mu$M the cathodic and anodic current changed to $-26 \mu$A and $71 \mu$A, while at $50 \mu$M conc. of thiourea the cathodic and anodic current changed to $-30 \mu$A and $88 \mu$A respectively.

Both rGO/GCE and Ag-rGO/GCE electrodes are analysed at various scan rates. By using rGO/GCE electrode at scan rate $20 \text{ mV s}^{-1}$, $40 \text{ mV s}^{-1}$, $60 \text{ mV s}^{-1}$, $80 \text{ mV s}^{-1}$, and $100 \text{ mV s}^{-1}$ the current at anode appeared as $10.62 \mu$A, $30.32 \mu$A, $60.73 \mu$A, $101.43 \mu$A and $110 \mu$A respectively at potential of 0.25 V which exhibited that by increasing the scan rate the anodic current enhanced. Whereby using Ag-rGO/GCE electrode scan rate of $20 \text{ mV s}^{-1}$, $40 \text{ mV s}^{-1}$, $60 \text{ mV s}^{-1}$, $80 \text{ mV s}^{-1}$, and $100 \text{ mV s}^{-1}$ the current at anode appeared as $20.48 \mu$A, $90.23 \mu$A, $126.35 \mu$A, $141.42 \mu$A and $151 \mu$A respectively at potential of 0.25 V exhibited in Fig. 6B. Hence confirmed from the results that by using Ag-Nanoparticles on the surface of GO, it enhanced the sensing ability toward thiourea (TU).

These findings confirmed that the as prepared nanoparticles play an important role in TU sensing. If stored safely at a suitable temperature and in an airtight container, the synthesised chemical sensor based on Ag-rGO exhibited good reproducibility and was effective for 4 to 5 weeks with no shift of potential and peak current. The graph showed in Fig. 6A, the current and concentration of TU relation. And in Fig. 6B, the graph exhibits the current and scan rate relation. These different electrodes in different concentration of thiourea and upon variable voltage show variable results. As rGO show less current as compare to Ag-rGO, because Ag increase the active sites for coming electrons of thiourea.

Relationship of current with concentration and scan rate.—In Fig. 7 the graph exhibited that the oxidation is more prominent as compared to reduction that came out from cyclic voltammetry technique.
Figure 4. FTIR graph of sample GO, r-GO, and combined form.

Figure 5. SEM image of sample rGO (G1) and Ag-rGO (G2).
Interface effect of some impurities (Selectivity).—For checking the selectivity of the Ag-rGO/GCE, the impact of certain ions was analysed in stream water of dhodial Mansehra containing 250 μM Thiourea. The results showed that NO₃⁻, SO₄²⁻, F⁻, CN⁻, Cl⁻, Br⁻, I⁻ ions did not affect the sensing of thiourea concentration.

Repeatability and stability.—The recurrence of comeback current of the Ag-rGO/GCE electrode was examined in the concentration of thiourea of 550 μM. The variant coefficient was 2.2% for three consecutive analyses. The stability and lifespan of the sensor was inspected by computing the comeback current of the sensor after three and four weeks. The falls observed in the electrode response were 3 and 11.7% of the initial current after three and four weeks correspondingly. Hence, it was confirmed that Ag-rGO has excellent stability, good reproducibility and reusable.

Conclusions

It concluded from the results that GO changed to reduced graphene oxide and then Ag nanoparticles are successfully attached.
on rGO sheets. From the morphology it approved that Ag NPs adorned on rGO sheets with the help of SEM. The nanocomposite pasted on GCE to make Ag-rGO/GCE. Different electrodes displayed various approaches towards analyte. During detection of Thiourea (TU), by altered the concentration, altered the current at anode. As concluded that at low concentration showed low current and vice versa. The current at anode increased by increasing the scan rate and the construction of higher signals of thiourea oxidation by facilitating the electrons handover between the analyte and the electrode. The outcomes of this work showed the competence of the design sensor to sense and determined the small concentration of thiourea in ecological samples of water. Ag NPs enhanced the conductivity of r-GO observed by CV.

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