This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Development of ZnO@rGO Nanocomposites for the Enzyme Free Electrochemical Detection of Urea and Glucose

K. B. Babitha¹, P. S. Soorya¹, A. Peer Mohamed¹, R. B. Rakhi¹,²,*, and S. Ananthakumar¹,*

¹Functional Materials Section, Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Industrial estate P.O., Thiruvananthapuram-695019, Kerala, INDIA

²Department of Physics, University of Kerala, Kariavattom P.O., Thiruvananthapuram-695581, Kerala, INDIA

* Corresponding Author. Tel.: +91 471 2515289; fax: +91 471 2491712
¹E-mail addresses: ananthakumar70@gmail.com; ananthakumars@niist.res.in
¹,²E-mail addresses: rakhisarath@gmail.com; rakhiraghavanbaby@niist.res.in

Graphical Abstract
Abstract

Herein, we report a green synthetic strategy for the preparation of ZnO@rGO nanocomposites. Bioinspired synthesis of ZnO nanoarchitectures has been done using a series of biotemplates such as dextrose, sucrose, soluble starch, and carboxy methyl cellulose. The as-prepared morphologically tuned ZnO nanoarchitectures are homogeneously distributed over the surface of rGO sheets, resulting in the formation of ZnO@rGO nanocomposites. For the first time, zinc (Zn) dust, a waste byproduct from an industry (Binani Zinc Limited, Kerala, India), is employed for the chemical reduction of GO. ZnO@rGO nanocomposites based nonenzymatic urea and glucose sensor have been developed over glassy carbon electrode, and the electrochemical performance of the nanocomposite for the detection of urea and glucose are investigated. The biosensor electrode is sensitive to urea in the concentration range of 0.02x10^{-3} mM to 7.2x10^{-3} mM with a detection limit of 0.012 μM. When used for glucose detection, the linear range is 0.02x10^{-3} mM to 18x10^{-3} mM, with a detection limit of 0.008 μM. The developed sensor exhibits ultra-high sensitivity of 682.8 μA mM^{-1} cm^{-2} towards urea and 481 μA mM^{-1} cm^{-2} towards glucose.

Keywords: ZnO@rGO nanocomposites, nonenzymatic sensor, urea, glucose, sensitivity, detection limit

1. Introduction

Urea is the most widely used fertilizer, and its production and consumption in India are about 23 and 31 million tonnes. Due to higher solubility in water, a large amount of the applied urea may get dissolved in groundwater and leads to water pollution [1]. In the biological aspect, urea is the final product of protein degradation and nitrogen metabolism. The normal concentration of urea in the blood serum is 2.5-7.5 mM [2]. The higher or lower amount of urea in the body leads to several diseases such as renal failure, urinary tract obstruction,
dehydration, shock burns, gastrointestinal bleeding, hepatic failure, nephritic syndrome, and cachexia [3, 4]. So the monitoring of the urea level has great significance in both the environmental and clinical samples.

Glucose is the primary source of energy in the human body [5]. The acceptable range of blood glucose level in the human body is ~ 3.9-6.2 (empty stomach) or ~ 3.9-7.8 (2h after food) mM [6]. If the human body is unable to control the amount of glucose due to the decreased insulin secretion, the condition results in Diabetics Mellitus [7]. Further, it leads to different health problems like cardiovascular, nervous, ocular, cerebral and peripheral vascular diseases, kidney failure, tissue damage, blindness, etc. [5, 8]. Hence, quantitative monitoring of blood glucose level is essential, to avoid the adverse effects of Diabetics [5].

A quantum of research studies has been conducted to develop an efficient and reliable method for urea and glucose sensing. Electrochemical sensing strategy has been considered as the most promising tool for urea and glucose detection [9, 10]. Metal oxides such as ZnO, Fe₂O₃, CeO₂, SnO₂, Ag₂O, ZrO₂, TiO₂, Co₃O₄, NiO, Cu₂O, MnO₂, MgO, RuO₂, Mn₃O₄ have been extensively studied for electrochemical sensors. Among these, ZnO nanoparticles were most widely studied for electrochemical biosensing applications. In electrochemical sensors, nonenzymatic sensors are most popular because they can overcome the disadvantages of enzymatic sensors [11].

Graphene-based nanomaterials are widely used in electrocatalytic sensing applications. rGO is found to be the most preferred sensor platform due to the following reasons: (1) rGO is electrically conductive compared to the non-conductive GO (2) a large number of edges and defects facilitate electron transfer (3) conductivity and surface functional groups could be turned for detection of specific chemical species. Different methods are reported for the preparation of rGO from GO. In 2010, X. Gao et al., investigated that deoxygenation of GO with hydrazine or heat treatment results in rGO [12].
In 2011, P. Cui et al. report a new reducing system i.e., hydriodic acid with trifluoroacetic acid, which can chemically convert GO into rGO at subzero temperature (below 0 °C) with a mass production [13]. In 2012, V. H. Pham et al. reported a simple and effective method to reduce the aqueous suspension of GO using nascent hydrogen generated in-situ by the reaction between Al foil and HCl, Al foil and NaOH, and Zn powder and NaOH [14]. In 2012, O. Akhavan et al. reported a single-step green method for the reduction and functionalization of GO by glucose was developed [15]. In 2012, R. S. Dey et al., demonstrated a facile route for the synthesis of rGO sheets by chemical reduction of GO using Zn/acid solution at room temperature [16]. To best of our knowledge, no attempts were made to conduct the reduction of GO using waste materials.

The use of biomaterials as templates has become significant in the green synthesis of nanomaterials with controllable morphology. Biomaterials are cheap, economical, environmentally benign, and renewable. In the present work, ZnO nanoarchitectures with varied morphology were prepared via the biotemplate assisted microwave method. Here dextrose, sucrose, soluble starch, and carboxy methyl cellulose were used as biotemplates. At the same time, rGO was prepared by the chemical reduction of GO using nascent hydrogen. Zn dust, a waste material obtained from an industry, was used for the generation of nascent hydrogen. It acts as a strong reducing agent. ZnO nanoarchitectures prepared with different biotemplates are attached on rGO via microwave assisted ex-situ technique, which results in ZnO@rGO nanocomposites. Structural and morphological studies were carried out, which shows the formation of homogeneous distribution of ZnO nanoarchitectures on rGO sheets. The as-prepared ZnO@rGO has been used for the nonenzymatic sensing of urea and glucose. Since the studies on nonenzymatic ZnO based glucose and urea sensors are rarely explored area, the fabrication and performance of ZnO@rGO based sensors has got much importance.
Similarly, the synergic effect of both ZnO and rGO provides excellent sensing characteristics in the as-prepared nonenzymatic sensor.

2. Experimental Section

2.1 Materials

Graphite (99.9%), Nafion solution (5 wt % in lower aliphatic alcohols and water, contains 15-20% water) and Potassium ferri cyanide (C₆N₆FeK₃, 99.9%) were procured from Sigma Aldrich, Germany. Sodium nitrate (NaNO₃, 99.5%), Potassium permanganate (KMnO₄, 99%), Hydrogen peroxide (H₂O₂, 99%), Dextrose anhydrous (D-glucose anhydrous, C₆H₁₂O₆, 99%), Sucrose (Saccharose, C₁₂H₂₂O₁₁, 99%), and Carboxy methyl cellulose sodium salt were obtained from S. D. Fine Chemicals limited, India. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%), conc. Sulphuric acid (H₂SO₄, 99%) and Soluble starch ((C₆H₁₀O₅)ₙ, 99%) were supplied by Merck, India. Lithium hydroxide (LiOH, 99%) was purchased from SRL, India. Zn dust obtained from Binani Zinc Limited was used for the reduction of GO. All the reagents were used as received without any further purification.

2.2 Preparation of GO

GO has been prepared via Hummers method. In a typical procedure 1g graphite and 1g NaNO₃ were dispersed in 50 mL conc. H₂SO₄ while keeping in an ice bath. 3g of KMnO₄ was added slowly to the reacting mixture and not allowed to increase the temperature to 20 °C. The reaction mixture was then transferred to a water bath kept at a temperature of 35 °C. 50 mL of distilled water was added to the system and the temperature raised to 98 °C. It was followed with the addition of 150 mL of distilled water and 10 mL of 30 % H₂O₂. The oxidized graphite was then centrifuged and washed with double distilled water until the pH becomes 7. Finally, on freeze drying graphene oxide with a fluffy nature was obtained [17, 18].
2.3 Preparation of rGO via Nascent Hydrogen Chemical Reduction

In a typical procedure, 20mg of GO was dispersed in a 200 mL double distilled water using a probe sonicator. It was further treated with conc. HCl (1M) followed by the slow addition of Zn dust (2 g). The whole mixture was stirred overnight using a magnetic stirrer. The gradual change in the colour from orange-brown to black indicates the reduction of GO to rGO. The obtained rGO was then collected by centrifugation. Further, it was washed three times with 0.1 M HCl, followed by washing with double distilled water. After removing all impurities, the rGO nanosheets were freeze-dried. Illustration for the nascent hydrogen chemical reduction is shown in Fig. 1.

![Illustration of the Zn mediated nascent hydrogen chemical reduction of GO in presence of conc. HCl.](image)

**Fig. 1** Illustration of the Zn mediated nascent hydrogen chemical reduction of GO in presence of conc. HCl.

2.4 Synthesis of ZnO Nanoarchitectures via Biotemplate Method

ZnO nanoarchitectures were prepared via biotemplate assisted microwave technique (Fig. 2, step 1). In a typical procedure, 0.3 M Zn(NO₃)₂·9H₂O was dissolved in 500 mL double-distilled water, and an appropriate amount of carbohydrate/cellulose was dispersed eventually by keeping the wt ratio of Zn(NO₃)₂·9H₂O and carbohydrate/cellulose as 1:1. Dextrose,
sucrose, soluble starch, and carboxy methyl cellulose were used as structure-directing agents. The pH of the solution was adjusted with 10 wt % LiOH solution. The obtained solution was kept in the microwave synthesis work station (Sineo MAS II) at 80 °C for 30 min (P=300 W). The obtained powder was washed repeatedly with double distilled water to remove the impurities. The final product was dried in the oven at 50 °C. The obtained ZnO samples were denoted as ZD, ZS, ZSs, and ZC, respectively.

2.5 Preparation of ZnO@1rGO Nanocomposites

In a typical synthesis of the nanocomposites, 0.0025 g of rGO (1 wt %) was uniformly dispersed in 30 mL of DMF with the aid of ultrasonication for 1h to obtain a uniform suspension of rGO. Then 0.2475 g of ZnO (ZD, ZSs, ZS, and ZC) was added. It was followed by magnetic stirring for 1 h to attain uniform dispersion. The product obtained was collected by centrifugation and repeatedly washed with ethanol to remove the impurities and dried at 85 °C. The illustration is provided in Fig. 2, step II.

![Fig. 2 Schematic illustration showing the synthetic procedure of ZnO and ZnO@1rGO.](image-url)
2.6 Characterization

The X-ray diffraction patterns of the samples were collected on a X-ray powder diffractometer X’ Pert Pro Philips using Cu Kα radiation (λ=1.5406 Å) in the diffraction angle (2θ) ranging between 10° and 60°. The crystallite size was calculated using the Debye-Scherrer formula \( D_{\text{XRD}} = \frac{k \lambda}{\beta \cos \theta} \), where \( D_{\text{XRD}} \) is the average crystallite size in nm, \( k \) is the shape factor (0.9), \( \lambda \) is the X-ray wavelength in nm, \( \beta \) is the full width at half maximum of (101) peak in radian and \( \theta \) is the Bragg angle (degree) [19]. The lattice parameters of the samples were calculated using the equation \( \frac{1}{d^2} = \frac{4}{3(1/a^2)} + \frac{1}{c^2} \), where \( d \) is the interplanar distance, \( a \) and \( c \) are the lattice parameters in nm (being hexagonal \( c/a = (8/3)^{1/2} \) ) [20]. The optical absorption spectra of the samples were recorded over a wavelength range of 200-800 nm using a UV-Vis spectrophotometer UV 2401-PC, Shimadzu. Fourier transforms infrared spectra (FTIR) of the samples were carried out using IR Prestige 21 (Shimadzu) spectrophotometer using the KBr method at a scanning range of 500 to 4000 cm\(^{-1}\). The morphology of the samples was determined by using a scanning electron microscopy (SEM, ZEISS EVO 18) applying an acceleration voltage of 20 kV. The elemental analysis of the samples was obtained by the energy dispersive X-ray (EDX) technique equipped with the SEM instrument. Elemental mapping was determined by using EDX spectroscopic technique associated with ZEISS EVO 18 instrument. The transmission electron microscopic (TEM) images were collected by using Tecnai G2 model FEI microscope operating with an accelerating voltage of 300 kV. The Brunner-Emmet-teller (BET) surface area of the samples was evaluated on the basis of N\(_2\) adsorption-desorption isotherm with a Micromeritics Gemini 2375 Surface Area Analyzer. Prior to the surface area analysis, the samples were degassed for 2 h at 150 °C.
2.7 Fabrication of the Nonenzymatic Electrochemical sensor Electrodes

The nonenzymatic electrochemical sensor electrodes (glassy carbon electrode (GCE) with ZnO or ZnO@1rGO) have been prepared by the following procedure. GCE was first cleaned by polishing with 0.3 µm alumina powder. The polished GCE was further processed by ultrasonication for 5 min each in acetone and double-distilled water, respectively, and dried in ambient air. 1 mg mL\(^{-1}\) of ZnO or ZnO@1rGO was sonicated in nafion for 10 min to get a uniform dispersion. The cleaned GCE was drop cast with 2 µL of ZnO or ZnO@1rGO dispersed in nafion. This thin film of the materials deposited on the surface of the electrodes was left overnight at room temperature for drying the deposited material, and the same was used as a working electrode (nonenzymatic electrochemical sensor electrode) for the detection of urea or glucose.

2.8 Electrochemical Studies

The electrochemical behavior of ZnO (ZD, ZS, ZSs, and ZC) and ZnO@1rGO nanocomposites (ZD@1rGO, ZS@1rGO, ZSs@1rGO, and ZC@1rGO) based electrochemical sensor electrode has been performed with urea or glucose. The electrochemical experiments, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis, were conducted in a conventional three-electrode cell using an electrochemical work station (VMP3-Biologic). The modified glassy carbon electrode (GCE) was used as the working electrode (with a GC disc diameter of 3 mm) in combination with a platinum (Pt) wire and Ag/AgCl (in saturated KCl) as the counter electrode and reference electrode, respectively. 0.1 M potassium ferricyanide solution was used as the electrolyte. All measurements were conducted at ambient conditions. The EIS analysis was performed in 0.1 M potassium ferricyanide solution at a potential of 0.32 V in a frequency range of 10–10\(^6\) Hz at a signal amplitude of 10 mV.
3. Results and Discussion

3.1 Characterization of rGO Prepared via Zn Mediated Nascent Hydrogen Reduction

Zn dust obtained as a waste by-product from industry was used for the generation of nascent hydrogen for the chemical reduction of GO. The detailed characterization studies of freeze-dried GO prepared via the Hummers method had been reported in our earlier work [18]. The XRD pattern of the Zn dust is given in Fig. S1. The characteristic diffraction peaks at the 2θ positions of 36.5°, 39.2°, 43.4°, 54.36°, 70.54°, and 70.7° are corresponding to the (002), (100), (101), (102), (103), and (110) lattice planes of pure Zn metal, respectively (JCPDS file no. 00-004-0831) [21] confirms the presence of pure Zn metal in the waste by-product.

![XRD pattern of rGO prepared using Zn dust](image1)

![UV-vis spectra of rGO dispersed in DMF](image2)

![FTIR spectra of GO and rGO](image3)

**Fig. 3** (A) XRD pattern of rGO prepared using Zn dust rGO (B) UV-vis spectra of rGO dispersed in DMF (C) FTIR spectra of (a) GO and (b) rGO. Inset of (A) is the XRD pattern of GO and inset of (B) is the UV-vis spectra of GO.
The XRD analysis of rGO sheets prepared using nascent hydrogen reduction with Zn dust is given in Fig. 3A. The XRD pattern of GO is given in the inset of Fig. 3A. The main intensity peak of GO is at 10.8° corresponding to the (001) reflection plane. After reduction with Zn dust, this peak was completely disappeared, and a new broad diffraction peak centred at ~ 24.5° was appeared indicating the complete conversion of GO to rGO. This peak corresponds to the (002) plane of rGO nanosheets [22]. The appearance of a low-intensity peak exhibited by rGO nanosheets at ~ 44° corresponds to the (100) reflection plane of rGO [23].

The UV-vis absorption spectrum of rGO, studied by dispersing rGO nanosheets in DMF is given in Fig. 3B. The optical property of GO is also given in the inset of Fig. 3B. The maximum absorption peak of rGO is found to be at 267 nm. During the reduction of GO to rGO, the absorption band corresponding to the aromatic C-C bond (\(\pi-\pi^*\) transition) is red-shifted from 230 to 267 nm. Hence, the restoration of electronic conjugation and structural ordering in the carbon framework after Zn mediated hydrogen reduction provides clear evidence for the complete reduction of GO to rGO [16].

The FTIR spectra obtained for GO and rGO are given in Fig. 3C. In the FTIR spectra of GO we could see a broad absorption band in between 3000-3400 cm\(^{-1}\), which corresponds to the \(-\text{OH}\) stretching. This peak completely vanishes in the FTIR spectra of rGO. Similarly, a remarkable decrease in the band intensity was observed in the bands corresponding to the stretching of oxygen-containing functionalities such as C=O carbonyl (1720 cm\(^{-1}\)), epoxy C-O (1231 cm\(^{-1}\)), -OH deformation vibrations (1389 cm\(^{-1}\)), alkoxy C-O (1043 cm\(^{-1}\)) after the nascent hydrogen reduction of GO [16].

Typical low and high magnification SEM images of rGO are presented in Fig. 4A and 4B, respectively. The fluffy and thin layered nature of rGO nanosheets was confirmed from
the SEM images. The microstructure of the rGO nanosheets was again confirmed with the TEM image of rGO, as shown in Fig. 4C.

The probable mechanism for the nascent hydrogen chemical reduction of GO with Zn dust can be explained as follows: Epoxy, carbonyl, and hydroxyl groups are the main oxygen-containing functional groups presented on the GO surface. The homogeneous dispersion of GO in water facilitates the intimate contact between Zn dust and conc. HCl thus leads to the in-situ generation of nascent hydrogen. This highly reactive nascent hydrogen acts as a reducing agent for the chemical reduction of GO.

\[
\text{Zn dust} + 2 \text{conc. HCl} \rightarrow \text{ZnCl}_2 + 2[H]
\]

![Fig. 4](A and B) Typical low and high magnification SEM images of rGO prepared via Zn dust mediated nascent hydrogen reduction of GO. (C) TEM image of rGO prepared via chemical reduction with Zn dust.
The chemical reduction of GO involves the removal of the above mentioned functional groups. It involves the deoxygenation of epoxide groups through ring-opening mechanism and decarboxylation of carboxylic acid groups [16]. Both reactions led to the restoration of π conjugation [14] and resulted in olefins. Similarly, carbonyl groups are reduced to the corresponding alcohols, which further give olefins. The conversion of GO to rGO is again clear from the colour change of the reactant mixture from dark brown to black [24].

The BET surface area of GO and rGO were measured using N₂ adsorption desorption isotherm and is presented in the supporting information Fig. S2. The BET surface areas of GO and rGO are 161 m² g⁻¹ and 153 m² g⁻¹. During reduction process there is a chance of agglomeration of the nanosheets and it will result in the decreased surface area of the rGO compared to GO.

The electrochemical impedance spectroscopy is a powerful tool for identifying the electrical conductivity of the sensor electrode material. The Nyquist plot of the electrochemical impedance spectra (EIS) of rGO modified GCE in 0.1M K₃[Fe(CN)₆] electrolyte solution is in Fig. S3. Extremely low value of the charge transfer resistance (250 mΩ) of rGO clearly indicates that the material is having high electrical conductivity.

3.2 Characterization of ZnO Nanoparticles Prepared via Biotemplate Assisted Method

Fig. 5A shows the XRD patterns of pure ZnO synthesized with carbohydrates/cellulose. The XRD pattern indicates that all samples are highly crystalline. All of the diffraction peaks of the as-prepared ZnO nanoarchitectures match well with those of the standard XRD file of ZnO (JCPDS standard card no. 79-0205) and can be indexed as the wurtzite phase of ZnO. The diffraction peaks at 31.7 °, 34.57 °, 36.09 °, 47.53 °, 56.67 °, 62.78 °, and 67.86 ° are corresponding to (100), (002) (101), (110), (103), and (112) lattice planes of wurtzite ZnO.
No other impurity peaks arising due to carbohydrate/cellulose as well as no remarkable shift in all diffraction peaks were detected in the XRD patterns of as-prepared samples, which confirm the phase purity of the products. The lattice parameters of the as-prepared samples

![XRD patterns and UV-vis absorption spectra](image)

**Fig. 5** (A) XRD patterns and (B) UV-vis absorption spectra of (a) ZD (b) ZS (c) ZSs, and (d) ZC.

![SEM images](image)

**Fig. 6** SEM images of (A) ZD (B) ZS (C) ZSs, and (D) ZC.
calculated and were given in Table 1. The calculated values of lattice parameters $a=b=0.32379-0.32406$ nm and $c=0.52865-0.5291$ nm are consistent with the reported values of ZnO [25]. The crystallite size was evaluated using the Scherrer formula is presented in Table 1. From the Scherrer formula, the crystallite size was estimated to be ~43.99, 27.77, 26.62, and 33.75 nm, respectively, for ZD, ZS, ZSs, and ZC.

![TEM images](image)

**Fig. 7** TEM images of (A) ZD (B) ZS (C) ZSs, and (D) ZC.

The optical property of ZnO nanoarchitectures synthesized with different carbohydrates/cellulose is studied using UV-vis absorption spectroscopy and is given in Fig. 5B. The maximum absorption peak of ZD is at 372.95 nm. A blueshift in the UV-vis absorption spectra was observed from ZD to ZSs (372.95-344.99 nm), which is mainly due to the crystallite size reduction from 43.99 to 26.62 nm. From ZSs to ZC a redshift was
observed from 344.9 to 370.4 nm and is mainly attributed to the increase in the crystallite size from 26.62 to 33.75 nm.

Table 1. Crystallite size ($D_{XRD}$), lattice parameters (a and c), absorption maxima ($\lambda_{max}$), morphology of ZnO nanoarchitectures prepared using different carbohydrate/cellulose.

| Samples | $D_{XRD}$ (nm) | Lattice parameter (nm) | $\lambda_{max}$ | Morphology | $D_{TEM}$ |
|---------|----------------|------------------------|-----------------|------------|-----------|
|         |                | a  | c  | c/a  |              |           |
| ZD      | 43.99          | 0.32406 | 0.5291 | 1.6327 | 372.95 | Rods | $L=800.8$, $W=140.5$ |
| ZS      | 27.77          | 0.32385 | 0.52875 | 1.6327 | 367.84 | spheres | 109.72 |
| ZSS     | 26.62          | 0.32379 | 0.52865 | 1.6326 | 344.9  | aggregates | 50 |
| ZC      | 33.75          | 0.32386 | 0.52877 | 1.6327 | 370.4  | Square | 188.19 |

Fig. 6 displays SEM images of ZnO nanoarchitectures prepared with different carbohydrates/cellulose. ZnO nanoarchitectures (ZD) synthesized with dextrose as a structure-directing agent found to be in a rod shape with ~800 nm length and ~140 nm width (Fig. 6A). From Fig. 6B, it can be seen that sucrose leads to the formation of ZnO nanoarchitectures with a diameter of ~91.5 nm. Synthesized ZnO nanoarchitectures (ZSS) using soluble starch as a structure-directing agent were found to be spherical in shape with smaller particle size. But some agglomeration was also observed in this case. Carboxy methyl cellulose leads to the formation of ZnO nanoarchitectures (ZC) with agglomerates of spherical particles of relatively larger size compared to ZS and ZSS nanoarchitectures. Similar observations are obtained in the TEM imaging also. The synthesized ZD nanoarchitectures having a rod shape with ~800.8 nm length and ~140.5 nm diameter (Fig. 7A). The spherical shape of the ZS nanoarchitectures is more clearly seen in the TEM image.
(Fig. 7B) with a diameter of ~109.72 nm. Soluble starch leads to the formation of ZnO nanoarchitectures (ZSs) with a relatively small size of ~ 50 nm. As seen in the SEM image, Fig. 7C also shows uniform-sized agglomerated particles of ZSs nanoarchitectures. Relatively square-shaped particles are observed in the TEM image of ZC with a particle size of 188.19 nm (Fig. 7D).

3.3 Characterizations of ZnO@1rGO Nanocomposites

The XRD patterns of ZnO@1rGO prepared with different carbohydrate/cellulose are presented in Fig. 8A. All samples show the diffraction patterns of wurtzite ZnO even in the presence of rGO. The XRD results of all samples show diffraction peaks at 31.77°, 34.31°, 36.09°, 47.53°, 56.67°, 62.78°, and 67.6° corresponding to the lattice planes of (100), (101), (102), (110), (103), and (112). No remarkable shift in the diffraction peaks was observed in the presence of rGO in the nanocomposite. Since the amount of rGO in the nanocomposite is very small, no peaks of rGO were observed in the XRD patterns of nanocomposites. The lattice parameter calculated was listed in Table 2. The lattice parameter values (a=0.3232-0.3236 nm, and c=0.52765-0.52834 nm) are consistent with the reported lattice parameter.
values of ZnO. The crystallite size evaluated using the Scherrer equation is given in Table 2. The results indicate that the presence of rGO in the nanocomposite did not remarkably affected the crystallite size and lattice parameter of ZnO nanoarchitectures.

**Fig. 9** SEM images of (A) ZD@1rGO (B) ZS@1rGO (C) ZSs@1rGO, and (D) ZC@1rGO.

The optical properties of the as-prepared ZnO@1rGO nanocomposites are given in Fig. 8B. We could see a redshift in the absorption spectra of all nanocomposites compared to the spectra of ZnO nanoarchitectures. The redshift in the $\lambda_{\text{max}}$ values is attributed to the incorporation of rGO in the nanocomposites, and the $\lambda_{\text{max}}$ values were presented in Table 2.

Fig. 9 shows the SEM images of ZnO@1rGO nanocomposites synthesized with different carbohydrate/cellulose. Insets of Fig. 9B and 9D show the SEM images at high resolution. The presence of both rGO nanosheets and ZnO are clearly seen in the SEM
Fig. 10 TEM images of (A) ZD@1rGO (B) ZS@1rGO (C) ZSs@1rGO, and (D) ZC@1rGO.

Table 2. Crystallite size ($D_{\text{XRD}}$), lattice parameters (a and c), absorption maxima ($\lambda_{\text{max}}$), morphology of ZnO@1rGO samples.

| Samples    | $D_{\text{XRD}}$ (nm) | Lattice parameter (nm) | $\lambda_{\text{max}}$ | Morphology | $D_{\text{TEM}}$ |
|------------|------------------------|------------------------|------------------------|------------|------------------|
| ZD@1rGO    | 38.17                  | 0.3236 0.52834 1.6326  | 375.77                 | Rods       | L=780, W=140     |
| ZS@1rGO    | 25.32                  | 0.3236 0.52829 1.6325  | 373.71                 | spheres    | 102.5            |
| ZSs@1rGO   | 23.61                  | 0.3232 0.52765 1.6325  | 362.75                 | aggregates | 50               |
| ZC@1rGO    | 30.12                  | 0.3236 0.52833 1.6326  | 373.71                 | Square     | 187.8            |
images of all samples. It is clear that ZnO nanoarchitectures are deposited on the surface of rGO sheets. The same observations were again found in the TEM images of ZnO@1rGO (Fig. 10). The SEM and TEM images confirm that the morphology of pure ZnO is not altered after the preparation of composite with rGO.

The N$_2$ adsorption-desorption isotherms of ZnO@1rGO nanocomposites are shown in Fig. 11. All samples show type IV isotherms. The BET surface areas of ZD@1rGO, ZS@1rGO, ZSs@1rGO, ZC@1rGO are 6.47, 18.33, 20.03, and 13.21 m$^2$g$^{-1}$. Based on the BET surface area analysis, it is clear that a higher surface area is obtained for ZSs@1rGO nanocomposite, which is in agreement with the XRD and TEM/SEM results. It is due to the low crystallite size or low particle size shown by the ZSs@1rGO nanocomposite.

The elemental analysis (EDS) spectra of rGO and ZSs@1rGO are presented in Fig. S4. The EDS of rGO (Figure S4A) shows the peaks of carbon and oxygen. However, the intensity of oxygen is less compared to carbon in rGO. The presence of Zn in the
nanocomposite is confirmed by the EDS spectrum of ZSs@1rGO. Additional peaks of C and O are also seen in the composite. The elemental mapping of ZSs@1rGO is shown in Fig. S5. The presents of elements such as C, O, and Zn are well mapped in the images.

3.4 Electrochemical Studies

3.4.1 Electrochemical Detection of Urea

![CV curves of ZD GCE with various additions of urea from 0 to 14 μM.](image)

**Fig. 12** CV curves of ZD GCE with various additions of urea from 0 to 14 μM.

The electrochemical behavior of the ZD modified GCE towards urea detection was studied with cyclic voltammetry (CV). The CV curve at a scan rate of 50 mVs⁻¹ and potential ranges of -0.8 to 0.8 V at different urea concentrations from 0 to 14 μM is given in Fig. 12. The improvement in the oxidation/reduction peak current after the addition of urea into the electrolyte is very evident from the figure. After the addition of 14 μM urea, the oxidation current peak increases from 0.1 mA to 0.15 mA. The cyclic voltammograms of different nanocomposites (ZD@1rGO, ZS@1rGO, ZSs@1rGO, and ZC@1rGO) modified GCEs are shown in Fig. 13A-D. In all these cases, oxidation/reduction peak currents increase with the
addition of urea into the electrolyte. In the case of ZSs@1rGO modified GCE, the oxidation current increases from 0.1 mA to 0.36 mA (Fig. 13C). The enhancement in the oxidation current was more than double with ZSs@1rGO nanocomposite modified GCE compared to ZD modified GCE. The presence of both ZnO nanoarchitectures and rGO nanosheets in the nanocomposite results in different architectures on the electrode surface. This will provide greater active surface, improved immobilization of the target molecules, and a more efficient electron transfer. A comparative study of the CV measurements has been carried out using different nanocomposites modified GC electrodes (ZD@1rGO, ZS@1rGO, ZSs@1rGO, and ZC@1rGO) after the addition of 14 μM urea into the electrolyte solution and the results are shown in Fig. 14. The best performance was exhibited by ZSs@1rGO. The higher

**Fig. 13** CV curves of (A) ZD@1rGO (B) ZS@1rGO (C) ZSs@1rGO, and (D) ZC@1rGO modified GCEs with various concentrations of urea addition from 0 to 14 μM.
The electrochemical activity of ZSs@1rGO is due to the smaller crystallite size or particle size, as well as, the higher BET surface area of ZSs@1rGO compared to other nanocomposites.

**Fig. 14** CV measurements of ZnO (ZD) and ZnO@1rGO nanocomposites (ZD@1rGO,

**Fig. 15** (A and B) Nyquist diagram of electrochemical impedance spectra of ZD and ZSs@1rGO modified GCEs in 0.1M K₃[Fe(CN)₆] electrolyte solution (C) Randles equivalent circuit.
Fig. 16 (A) Calibration study of ZSs@1rGO modified electrode towards 4mM urea using CV
(B) Plot of $I_P$ versus concentration (C) Scan rate study using ZSs@1rGO modified electrode
with different scan rates (D) Plot of $I_P$ versus square root of scan rate.

EIS is a commonly used characterization technique to study the impedance changes of
the electrode surface, mainly due to the electron transfer between electrolyte and electrode
surface. The Nyquist plot contains a semicircle region and a linear region. The semicircle
portion corresponds to the electron transfer limited process, and the linear part corresponds to
the diffusion process. The diameter of the semicircle arc is equivalent to the electron transfer
resistance ($R_{ct}$), which reflects the conductivity and the electron transfer process [26]. A large
semicircle arc with high $R_{ct}$ indicates that the system has a higher resistance to the flow of
electrons. In Fig. 15A and B the ZnO modified GCE showed a higher $R_{ct}$ with a larger
semicircle diameter ($R_{ct}=169 \ \Omega$), indicating that ZnO nanoarchitectures were successfully
immobilized on the GCE surface, which hindered the electron transfer of the electrochemical
probe. This hindrance was decreased ($R_{ct}=74 \ \Omega$) after the incorporation of rGO in
nanocomposites. The small semicircular diameter of the ZSs@1rGO modified GCE implies it has low resistance towards the electron transfer process. These results showed the efficiency of ZSs@1rGO modified GCE compared to ZnO modified GCE [27, 9].

The calibration study was conducted using CV by the addition of 0.02 μM to 32 μM urea to the electrolyte solution (Fig. 16A). From the plot of $I_p$ versus concentration of urea given in the Fig. 16B, the linear range was calculated and is between $0.02 \times 10^{-3}$ to $7.2 \times 10^{-3}$ mM. The effect of scan rate for 50, 100, 150, 200, 300, 400, and 500 mVs$^{-1}$ towards the electrochemical oxidation of urea using cyclic voltammetry as determining mode is shown in the Fig. 16C. The oxidation/reduction peak current increases with increasing scan rate. It is evident that the oxidation peak current has a linear dependence upon the square root of scan rate (Fig. 16D) compared to $I_p$ versus scan rate. It means that the electrochemical oxidation process is purely diffusion-controlled on the surface of ZSs@1rGO modified GCE surface. The lowest detection limit calculated was 0.012 μM, and the sensitivity was found to be 682.8 μA mM$^{-1}$ cm$^{-2}$. The proposed sensing mechanism for the fabricated urea sensor is described as

\[
\text{CO(NH}_2\text{)}_2 + 8\text{OH}^- \rightarrow 6 \text{H}_2\text{O} + \text{CO}_3^{2-} + \text{N}_2 + e^- 
\]

3.4.2 Electrochemical Detection of Glucose

The calibration study was conducted using CV by the addition of 0.02 μM to 160 μM glucose (Fig. 17A). The $I_p$ was plotted against concentration (Fig. 17B), and the linear range was calculated ($0.02 \times 10^{-3}$ to $18 \times 10^{-3}$ mM). The effect of scan rate on the electrochemical behavior of ZSs@1rGO modified electrode towards the oxidation of glucose has been conducted using cyclic voltammetry and is shown in Fig. 17C. From the graph it is clear that the oxidation/reduction peak current increases with an increase in the scan rate from 50-500 mV s$^{-1}$. The linearity of oxidation peak current ($I_p$) with the square root of scan rates was
observed within the scan rate of 50-500 mV s\(^{-1}\) (Fig. 17D). This indicates that the electrochemical oxidation process is purely diffusion controlled. The lowest detection limit calculated was 0.008 μM, and the sensitivity was found to be 481 μA mM\(^{-1}\) cm\(^{-2}\).

**Fig. 17**

(A) Calibration study of ZSs@1rGO modified electrode towards 4 mM glucose
(B) Plot of I\(_P\) versus concentration
(C) Scan rate study using ZSs@1rGO modified electrode with different scan rates
(D) Plot of I\(_P\) versus square root of scan rate.

The proposed sensing mechanism for the fabricated glucose sensor is described as

\[
\begin{align*}
\text{O}_2 \text{ g (air/liquid interface)} & \rightarrow \text{O}_2\text{ads (ZnO@rGO)} \\
\text{O}_2\text{ads (ZnO)} + 2\text{e}^- \text{ (ZnO@rGO)} & \rightarrow 2\text{O}^- \text{ads (O}^\text{-}/\text{O}_2^-) \\
\text{Glucose + O}^\text{-}\text{glucono-} & \rightarrow \delta\text{-lactone} + 2\text{e}^- \\
\text{glucono-δ-lactone} & \rightarrow \text{gluconic acid}
\end{align*}
\]

The present study confirms that the ZnO nanoarchitectures act as an efficient electron mediator for the fabrication of efficient nonenzymatic sensor.
The results obtained in the present study are compared with the literature data on similar types of nonenzymatic sensors for detecting urea or glucose. The comparison shown in Table 3 reveals that the fabricated urea and glucose sensor based on ZSs@1rGO modified GCE is highly effective in the accurate detection of urea and glucose. The developed ZSs@1rGO modified GCE has showed lowest detection (0.008 µM for glucose and 0.012 µM for urea), excellent sensitivity (481 mA mM⁻¹ cm⁻² for glucose and 682.8 mA mM⁻¹ cm⁻² for urea) in the concentration range of 0.02x10⁻³-18x10⁻³ µM for glucose and of 0.02x10⁻³-7.2x10⁻³ µM for urea.

Table 3. Comparison of the sensing characteristics of the developed urea and glucose sensors using ZSs@1rGO with the other nonenzymatic sensors.

| Electrode material | Analyte | Linear range (mM) | Lowest detection limit (µM) | Sensitivity (mA mM⁻¹ cm⁻²) | Reference |
|--------------------|---------|-------------------|-----------------------------|-----------------------------|-----------|
| ZnO NRs            | glucose | -                 | 0.5                         | 5.601                       | [5]       |
| Cu/CuO/ZnO        | glucose | 0.1-1             | 18                          | 408                         | [28]      |
| Ni_{0.31}Co_{0.69}S_2/rGO | glucose | 0.001-5, 5-16 | 0.078                       | 1753, 954.7                | [29]      |
| Ni(OH)₂-rGO       | glucose | 15-30             | 15                          | 11.4                        | [30]      |
| Cu@Cu₂O/rGO       | glucose | 0.005-7           | 0.5                         | 0.1452                      | [31]      |
| ZnO/rGO           | glucose | 0-33.5 x10⁻³     | 0.0002                      | 39.78                       | [32]      |
| ZSs@1rGO          | glucose | 0.02x10⁻³-18x10⁻³ | 0.008                      | 481                         | Present work |
| nanoZnO           | urea    | 0.6-4.4           | 0.1527                      | 0.0259                      | [33]      |
| NiO                | urea    | 0.1-1.1           | 10                          | -                           | [4]       |
| ZSs@1rGO          | urea    | 0.02x10⁻³-7.2x10⁻³ | 0.012                      | 682.8                       | Present work |

Interference study of rGO based metal oxides is well established. From the literatures it was observed that in the case of CeO₂/rGO or AgFe₂O₃/rGO modified GCEs, the presence
of biological interfering species show no significant effect on the peak current [34, 35]. The reported studies say that similar observation will be obtained with AA, UA, H₂O₂ and DA.

4. Conclusions

In the present work, the as-prepared GO was reduced with a nascent hydrogen reduction mechanism using metallic zinc obtained as a waste by-product from an industry. The rGO formed then analyzed with XRD, UV-vis, SEM, and TEM. The peak shift from 10.8 to 24.5° in the XRD pattern and the redshift in the UV-vis absorption spectra from 230 to 267 nm confirms the complete reduction of GO to rGO. In addition to this, ZnO nanoarchitectures with various morphologies were prepared using carbohydrate/cellulose as a bio-template. The as-prepared ZnO nanoarchitectures were used to decorate rGO sheets, which results in the ZnO@rGO nanocomposite. Due to the synergistic effect of ZnO and rGO, the prepared ZnO@rGO nanocomposite was found to be an excellent probe for the nonenzymatic electrochemical sensing of urea and glucose. The electrochemical studies revealed that the fabricated electrode was sensitive to urea in the concentration range of 0.02x10⁻³-7.2x10⁻³ mM with a detection limit of 0.012 μM. The developed nonenzymatic sensor electrode was sensitive to glucose in the concentration range of 0.02x10⁻³-18x10⁻³ mM with a detection limit of 0.008 μM. The developed sensor exhibited ultra-high sensitivity of 682.8 μA mM⁻¹ cm⁻² towards urea and 481 μA mM⁻¹ cm⁻² towards glucose.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the Director, CSIR-National Institute of Science and technology (NIIST) for providing the laboratory facilities to carry out the experiments. K. B. Babitha is thankful to CSIR, India for providing the Senior Research Fellowship (SRF). R. B. Rakhi is
thankful to DST-SERB for the Ramanujan Fellowship (SB/S2/RJN-098/2015). Authors also thank M/s Binani Zinc Limited for the Zinc dust which was used in the reduction of GO. The authors also thank Mr. Prithviraj for XRD, Mr. Kiran Mohan for TEM, Mrs. Soumya and Mr. V. Harish Raj for SEM, and Mr. George for FTIR analysis. All the members of the Materials Science and Technology Division are acknowledged for providing general support.

References

1 D. Dutta, S. Chandra, A. K. Swain and D. Bahadur, *Anal. Chem.*, 2014, **86**, 5914-5921.
2 R. C. Bianchi, E. R. D. Silva, L. H. Dall'Antonia, F. F. Ferreira and W. A. Alves, *Langmuir*, 2014, **30**, 11464-11473.
3 O. O. Soldatkin, I.S. Kucherenko, S.V. Marchenko, K. B. Ozansoy, B. Akata, A. P. Soldatkin and S.V. Dzyadevych, *Mater. Sci. Eng. C*, 2014, **42**, 155-160.
4 M. Arain, A. Nafady, Sirajuddin, Z. H. Ibupoto, S. T. H. Sherazi, T. Shaikh, H. Khan, A. Alsalme, A. Niaz and M. Willander, *RSC Adv.*, 2016, **6**, 39001-39006.
5 G. N. Dar, A. Umar, S. A. Zaidi, S. Baskoutas, S. H. Kim, M. Abaker, A. Al-Hajry and S. A. Al-Sayari, *Sci. Adv. Mat.*, 2011, **3**, 901-906.
6 C. Chen, Q. Xie, D. Yang, H. Xiao, Y. Fu, Y. Tan and S. Yao, *RSC Adv.*, 2013, **3**, 4473-4491.
7 V. K. L. Shanbhag and K. S. Prasad, *Anal. Methods*, 2016, **8**, 6255-6259.
8 T. R. Kumar, K. J. Babu, D. J. Yoo, A. R. Kim and G. G. Kumar, *RSC Adv.*, 2015, **5**, 41457-41467.
9 J. Jiang, P. Zhang, Y. Liua and H. Luo, *Anal. Methods*, 2017, **9**, 2205-2210.
10 P. T. Yin, T. H. Kim, J. W. Choi and K. B. Lee, *Phys. Chem. Chem. Phy.*, 2013, **15**, 12785-12799.
11 Y. Zhao, L. Fan, B. Hong, J. Ren, M. Zhanga, Q. Queb and J. Jib, *Sens. Actuators B*, 2016, **231**, 800-810.
12 X. Gao, J. Jang and S. Nagase, *J. Phy. Chem. C*, 2010, **114**, 832-842.
13 P. Cui, J. Lee, E. Hwang and H. Lee, *Chem. Comm.*, 2011, **47**, 12370-12372.
14 V. H. Pham, H. D. Pham, T. T. Dang, S. H. Hur, E. J. Kim, B. S. Kong, S. Kim and J. S. Chung, *J. Mater. Chem.*, 2012, **22**, 10530-10536.
15 O. Akhavan, E. Ghaderi, S. Aghayee, Y. Fereydoonia and A. Talebia, *J. Mater. Chem.*, 2012, **22**, 13773-13781.
16 R. S. Dey, S. Hajra, R. K. Sahu, C. R. Raj and M. K. Panigraphic, *Chem. Comm.*, 2012, **48**, 1787-1789.
17 M. B. M. Krishna, N. Venkatramaiah, R. Venkatesan and D. Narayana Rao, *J. Mater. Chem.*, 2012, **22**, 3059-3068.
18 K. B. Babitha, S. Nishanth Kumar, V. Pooja, B. S. Dileep Kumar, A. Peer Mohamed and S. Ananthakumar, *Chem. Eng. J.*, 2017, **324**, 154-167.
19 K. B. Jaimy, K. V. Baiju, S. K. Ghosh and K. G. K. Warrier, *J. Solid State Chem.*, 2012, **186**, 149-157.
20 K. Jayanthi, S. Chawla, A. G. Joshi, Z. H. Khan and R. K. Kotnala, *J. Phy. Chem. C*, 2010, **114**, 18429-18434.
21 S. Balanand, K. B. Babitha, M. Jeen Maria, A. A. Peer Mohamed and S. Ananthakumar, *ACS Sustain. Chem. Eng.*, 2018, **6**, 143-154.
22 M. S. A. S. Shah, A. R. Park, K. Zhang, J. H. Park and P. J. Yoo, *ACS Applied Materials and Interfaces*, 2012, **4**, 3893-3901.
23 T. Lv, L. Pan, X. Liu and Z. Sun, *Cat. Sci. Tech.*, 2012, *2*, 2297-2301.
24 C. K. Chua and M. Pumera, *Chem. Soc. Rev.*, 2014, *43*, 291-312.
25 D. Pradhan and K. T. Leung, *Langmuir*, 2008, *24*, 9707-9716.
26 K. S. Bhat and H. S. Nagaraja, *Mater. Res. Innov.*, 2019, 1-24.
27 R. M. Shereema, S. R. Nambiar, S. S. Shankar and T. P. Rao, *Anal. methods*, 2015, *7*, 4912-4918.
28 S. SoYoon, A. Ramadoss, B. Saravanakumar and S. J. Kim, *J. Electroana. Chem.*, 2014, *717–718*, 90-95.
29 G. Li, H. Huo and C. Xu, *J. Mater. Chem. A*, 2015, *3*, 4922-4930.
30 P. Subramanian, J. Niedziolka-Jonsson, A. Lesniewski, Q. Wang, M. Li, R. Boukherroub and S. Szunerits, *J. Mater. Chem. A*, 2014, *2*, 5525-5533.
31 H. Huo, C. Guo, G. Li, X. Han and C. Xu, *RSC Adv.*, 2014, *4*, 20459-20465.
32 M. Sreejesh, S. Dhanush, F. Rossignol and H. S. Nagaraja, *Ceram. Int.*, 2017, *43*, 4895-4903.
33 A. Ali, A. A. Ansari, A. Kaushik, P. R. Solanki, A. Barik, M. K. Pandey and B. D. Malhotra, *Mater. Lett.*, 2009, *63*, 2473-2475.
[34] A. A. Ensafi, R. Noroozi, N. Z. Atashbar and B. Rezaei, *Sens. Actuators B*, 2017, *245*, 980-987.
[35] N. Zhang and J. Zheng, *J Mater Sci: Mater Electron*, 2017, *28*, 11209–11216.
GO dispersed in water

Zn dust (2 g) + conc. HCl

Stir 12 hrs.

rGO settled in water

rGO

170x77mm (600 x 600 DPI)
Step I

1. Add 10 wt. % LiOH to a solution of Zn(NO₃)₂.
2. Stir for 1 hour at 80°C with 300W microwave for 30 minutes.
3. Centrifugation and washing.

Step II

1. Sonicate rGO in DMF for 1 hour.
2. Stir for 1 hour.
3. Centrifugation and washing.

ZnO@rGO

170x108mm (600 x 600 DPI)
170x141mm (600 x 600 DPI)
170x128mm (600 x 600 DPI)
170x66mm (600 x 600 DPI)
170x127mm (600 x 600 DPI)
170x170mm (600 x 600 DPI)
Volume adsorbed (STP cm$^3$ g$^{-1}$) vs. Relative pressure ($P/P_0$)

83x64mm (600 x 600 DPI)
170x130mm (600 x 600 DPI)
170x100mm (300 x 300 DPI)
170x129mm (600 x 600 DPI)
| Samples | $D_{XRD}$ (nm) | Lattice parameter (nm) | $\lambda_{\text{max}}$ | Morphology | $D_{\text{TEM}}$ |
|---------|----------------|------------------------|----------------------|------------|------------------|
|         |                |                        |                      |            |                  |
| ZD      | 43.99          | 0.32406                | 0.5291               | 1.6327     | 372.95           | Rods, $L=800.8$, $W=140.5$ |
| ZS      | 27.77          | 0.32385                | 0.52875              | 1.6327     | 367.84           | spheres, 109.72 |
| ZSs     | 26.62          | 0.32379                | 0.52865              | 1.6326     | 344.9            | aggregates, 50 |
| ZC      | 33.75          | 0.32386                | 0.52877              | 1.6327     | 370.4            | Square, 188.19 |

Table 1. Crystallite size ($D_{XRD}$), lattice parameters (a and c), absorption maxima ($\lambda_{\text{max}}$), and morphology of ZnO samples prepared using different carbohydrate/cellulose.
Table 2. Crystallite size ($D_{\text{XRD}}$), lattice parameters (a and c), absorption maxima ($\lambda_{\text{max}}$), and morphology of ZnO@1rGO samples.

| Samples  | $D_{\text{XRD}}$ (nm) | Lattice parameter (nm) | $\lambda_{\text{max}}$ | Morphology | $D_{\text{TEM}}$ |
|----------|-----------------------|------------------------|------------------------|------------|------------------|
| ZD@1rGO  | 38.17                 | 0.3236                 | 0.52834                | 1.6326     | 375.77          |
|          |                       |                        |                        |            | Rods             |
|          |                       |                        |                        |            | L=780, W=140     |
| ZS@1rGO  | 25.32                 | 0.3236                 | 0.52829                | 1.6325     | 373.71          |
|          |                       |                        |                        |            | spheres          |
|          |                       |                        |                        |            | 102.5            |
| ZSs@1rGO | 23.61                 | 0.3232                 | 0.52765                | 1.6325     | 362.75          |
|          |                       |                        |                        |            | aggregates       |
|          |                       |                        |                        |            | 50               |
| ZC@1rGO  | 30.12                 | 0.3236                 | 0.52833                | 1.6326     | 373.71          |
|          |                       |                        |                        |            | Square           |
|          |                       |                        |                        |            | 187.8            |
Table 3. Comparison of the sensing characteristics of the developed urea and glucose sensors using ZSs@IrGO with the other nonenzymatic sensors.

| Electrode material | Analyte | Linear range (mM) | Lowest detection limit (µM) | Sensitivity (mA mM⁻¹ cm⁻²) | Reference |
|--------------------|---------|-------------------|----------------------------|-----------------------------|-----------|
| ZnO NRs            | glucose | -                 | 0.5                        | 5.601                       | [5]       |
| Cu/CuO/ZnO        | glucose | 0.1-1             | 18                         | 408                         | [28]      |
| Ni₀.₃₁Co₀.₆₉S₂/rGO | glucose | 0.001-5, 5-16     | 0.078                      | 1753, 954.7                 | [29]      |
| Ni(OH)₂-rGO       | glucose | 15-30             | 15                         | 11.4                        | [30]      |
| Cu@Cu₂O/rGO      | glucose | 0.005-7           | 0.5                        | 0.1452                      | [31]      |
| ZnO/rGO           | glucose | 0-33.5 x10⁻³      | 0.0002                     | 39.78                       | [32]      |
| ZSs@1rGO          | glucose | 0.02x10⁻³-18x10⁻³ | 0.008                      | 481                         | Present work |
| nanoZnO           | urea    | 0.6-4.4           | 0.1527                     | 0.0259                      | [33]      |
| NiO                | urea    | 0.1-1.1           | 10                         | -                           | [4]       |
| ZSs@1rGO          | urea    | 0.02x10⁻³-7.2x10⁻³ | 0.012                      | 682.8                       | Present work |
Graphical abstract

Development of ZnO@rGO based nonenzymatic urea and glucose sensor