1. Introduction

Diabetes, a global health problem affecting over 200 million people, can cause disorders of the kidney, heart, neural system and retina. Hence, the monitoring of blood glucose levels is essential to prevent diabetic complications such as diabetes from becoming more prevalent in modern society. Conventional glucose sensors use glucose oxidase immobilized on a solid electrode, to catalyze the oxidation of glucose in the presence of oxygen to produce hydrogen peroxide and selectively monitor the glucose levels. Although such enzymatic glucose sensors are available commercially, they suffer from some limitations such as complex enzyme immobilization procedures, instability due to the intrinsic nature of enzymes, sensitivity to the chemical environment (e.g. pH), and temperature. Besides, long-term monitoring of the blood glucose levels using an enzyme-based electrode is typically hampered by surface fouling by the absorption/passivation of the products. The surface fouling inevitably limits the selectivity and sensitivity towards glucose oxidation over time. As a result, development of non-enzymatic glucose (NEG) sensors is becoming essential.

Various nanostructured metals (e.g., Au, Pt, Pd, metal oxides (e.g., NiO2, Co3O4, CuO2), their composites (e.g., CuO–SWCNT)), and nanocomposites (Cu based multicomponent nanobead), BiOCl–G nanohybrid sheets, CuO–MWCNT have been used to fabricate NEG sensors. A comprehensive review has been published on the fabrication of NEG sensors using various nanomaterials. Among the metal oxide nanostructures based sensors, TiO2 nanostructures have attracted much interest due to their combinational properties such as high surface area, electrocatalysis, non-toxicity, biocompatibility, and oxygen storage capacity. However, pristine TiO2 electrodes usually have poor electrochemical activity because of the low conductivity of TiO2. Nanocomposites of TiO2 such as TiO2 modified with metal nanoparticles, are thus promising in NEG sensors. Several binary composites based on TiO2 such as TiO2–G, NiO–TiO2, TiO2/CuO and TiO2/Pd, TiO2/Co3O4 (ref. 25 and 26) were used for the fabrication of NEG sensors. One dimensional (1D) nanostructures of TiO2, specifically...
nanowires (NW), possess essentially the common physical characteristics as that of 2D and 3D nanostructures of TiO₂, but geometrically offer the additional advantages like good transport of electrons and mechanical stability. ¹⁷ ¹D TiO₂ NWs, could also be integrated with other materials or nanomaterials to improve the surface area and electron transport properties. Our recent research studies demonstrated that TiO₂ based nanocomposite can serve as the highly sensitive electrode for the detection of cholesterol and nitrate ions.⁴⁻⁵ ¹¹ However, studies on the use of TiO₂ NW in combination with a glucose selective polymer towards NEG sensor has not been reported so far.

Boronic acid is well known to interact with 1,2- or 1,3-diols, at physiological pHs or above, and form reversible covalent bonds to generate or six-membered cyclic complexes.¹² The chemical interactions between boronic acid and diols have been utilized for the detection of diol-containing biomolecules, such as sugars, dopamine, glycoproteins, and bacteria.¹³⁻¹⁵ Boronic acid groups containing polymers such as poly(3-aminophenyl boronic acid) (PAPBA) have exhibited good operational stability and selectivity towards detection of glucose levels as compared to glucose oxidase and hence utilized for the fabrication of NEG sensors.¹⁶⁻¹⁷ Due to their fascinating electrical and catalytic properties, gold nanoparticles (Au NPs) have been utilized widely in electrochemical applications.¹⁸⁻¹⁹ Au NPs in combination with G (carbon 98, 90 (2016)); calix⁴ arane/boronic acids²⁰ were used to improve the performance of NEG sensors.

In this background, we have constructed the NEG sensor based on a new ternary nanocomposite (TNC) comprised of TiO₂ NW, Au NPs and PAPBA (designated as TiO₂ NW/PAPBA–Au TNC) (Scheme 1). Firstly, 1D TiO₂ NWs were synthesized by electrospinning and hydrothermal processes.²¹ Followed by the synthesis of TiO₂ NWs, Au NPs distributed PAPBA NC was formed on the surface of TiO₂ NW by a one-step polymerization of 3-APBA using auric chloride (HAuCl₄) as the oxidizing agent. The morphology and electrochemical properties of TiO₂ NW/PAPBA–Au TNC were investigated by field emission scanning electron microscopy (FE-SEM) electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The fabricated NEG sensor based on GCE/TiO₂ NW/PAPBA–Au TNC electrode exhibited excellent performances towards electrochemical glucose detection (Scheme 1), including high sensitivity and good selectivity in the presence of common interfering species as compared to the pristine components, PAPBA and TiO₂ NW, as well over the glucose sensing performances based on other TiO₂ based materials reported in literature (Table 1). Moreover, the capability of utilizing GCE/TiO₂ NW/PAPBA–Au TNC electrode for determination of glucose levels in human serum is demonstrated, suggesting the potential of the fabricated NEG sensor for practical diabetes diagnosis.

### Scheme 1
Schematic diagram of the preparation of TiO₂ NW/PAPBA–Au TNC and electrochemical performance towards glucose detection.

### Table 1
Comparison of glucose sensor analytical performances between GCE/TiO₂ NW/PAPBA–Au TNC, PAPBA–Au NC electrodes fabricated in this work and other glucose sensors.

<table>
<thead>
<tr>
<th>Glucose sensor</th>
<th>Sensitivity [µA cm⁻² mM⁻¹]</th>
<th>Linear range [mM]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOx/PANI-NF/GCE</td>
<td>—</td>
<td>0.01–1.0</td>
<td>44</td>
</tr>
<tr>
<td>Cyt c/AuNPs/PANI-NS</td>
<td>63.1</td>
<td>0.01–3.2</td>
<td>45</td>
</tr>
<tr>
<td>PANI-NT/GOx</td>
<td>4.62</td>
<td>0.01–5.5</td>
<td>46</td>
</tr>
<tr>
<td>GOx/n-TiO₂/PANI/GCE</td>
<td>6.31</td>
<td>0.02–6.0</td>
<td>47</td>
</tr>
<tr>
<td>Pt/CNTs/TiO₂ NTAs</td>
<td>0.24</td>
<td>0.006–1.5</td>
<td>48</td>
</tr>
<tr>
<td>GOx/TiO₂/CNTs</td>
<td>11.3 ± 1.3</td>
<td>Up to 3.0</td>
<td>49</td>
</tr>
<tr>
<td>TiO₂–SWCNT NWS</td>
<td>5.32</td>
<td>0.010–1.42</td>
<td>50</td>
</tr>
<tr>
<td>Cu₄O/TiO₂</td>
<td>14.56</td>
<td>3.0–9.0</td>
<td>51</td>
</tr>
<tr>
<td>GOx/Ag/TiO₂ NTAs</td>
<td>0.39</td>
<td>0.1–4.0</td>
<td>52</td>
</tr>
<tr>
<td>GOx/Pt/Gr/TiO₂ NTAs</td>
<td>0.94</td>
<td>0.1–8.0</td>
<td>53</td>
</tr>
<tr>
<td>AuNPs–TiO₂ NT</td>
<td>—</td>
<td>0.40–8.0</td>
<td>54</td>
</tr>
<tr>
<td>TiO₂–GR</td>
<td>6.20</td>
<td>0.8–8.0</td>
<td>21</td>
</tr>
<tr>
<td>Chitosan–AuNPs</td>
<td>—</td>
<td>0.006–0.14</td>
<td>55</td>
</tr>
<tr>
<td>GOD/1DH S–TiO₂</td>
<td>9.9</td>
<td>0.2–1.0</td>
<td>56</td>
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<tr>
<td>GOD/HNF–TiO₂/GC</td>
<td>32.6</td>
<td>0.002–3.17</td>
<td>57</td>
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<td>Nafion-silica/MWCNTs–PANI/GOx</td>
<td>3.01</td>
<td>1–10</td>
<td>58</td>
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<tr>
<td>GCE/PAPBA–Au NC</td>
<td>34.6</td>
<td>0.5–11.0</td>
<td>This work</td>
</tr>
<tr>
<td>GCE/TiO₂ NW/PAPBA–Au NC</td>
<td>66.8</td>
<td>0.5–11.0</td>
<td>This work</td>
</tr>
</tbody>
</table>
2. Experimental details

2.1. Chemicals

HAuCl₄, p-toluenesulfonic acid (p-TSA), 3-APBA, Ti(IV) isopropano-oxide, polyvinylpyrrolidone (PVP, molecular weight < 40,000, Fluka) acetic acid, glucose and human serum (from human male AB plasma, USA origin, sterile-filtered) were purchased from Sigma-Aldrich, South Korea and used as received. Ammonium peroxysulfate (APS) was obtained from Samchum Chemicals, South Korea and used as received. Glucose and human serum (from human male AB plasma, USA origin, sterile-filtered) were purchased from Sigma-Aldrich, South Korea and used as received. Ammonium peroxysulfate (APS) was obtained from Samchum Chemicals, South Korea and used as received. Glucose and human serum (from human male AB plasma, USA origin, sterile-filtered) were purchased from Sigma-Aldrich, South Korea and used as received. Ammonium peroxysulfate (APS) was obtained from Samchum Chemicals, South Korea and used as received.

2.2. Formation of TiO₂ NW/PAPBA

The formation stages of TiO₂ NW/PAPBA were similar to that reported in our previous publication.⁴² In a typical procedure for the preparation of TiO₂ NW, firstly, the composite titanate nanofibers were obtained by electrospinning a sol-gel-transformed electrospinning dope. The electrospinning dope was prepared by dispersing 2 mg of the respective electrode modifying the material in 0.1 mL of isopropyl alcohol and NaF (3 : 2 v/v) solution. The mixture was sonicated for 10 min to obtain an ink. About, 6 μL of the ink was dropped on the surface of polished glassy carbon electrode (GCE, area = 0.07065 cm²) and dried at room temperature.

2.4. Morphological characterization

Field emission scanning electron microscopy (FE-SEM) coupled with energy dispersive X-ray (EDX) (Hitachi S-4300, Japan) analysis was used to study morphology and elemental composition. The crystal structure of the prepared materials was investigated by X-ray diffraction (XRD, Quanterra SXM, ULVAC-PHI, Japan) using Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 20–85°.

2.5. Electrochemical properties and NEG sensing

Electrochemical measurements were performed using Ivium-Stat (Netherland) electrochemical interface with PC-controlled analyzer workstation. A conventional three-electrode cell assembly was used. The modified electrode was used as the working electrode. Ag/AgCl and platinum wire were used as reference and counter electrodes, respectively. The electroactivity of the modified electrodes was evaluated using cyclic voltammetry in 0.1 M PBS (pH 7). The glucose detection experiments were carried out using differential pulse voltammetry measurements at a scan rate of 0.05 V s⁻¹ with a pulse amplitude of 0.05 V, pulse rate of 0.5 s and pulse width of 50 ms for various glucose concentrations in an electrochemical cell containing a magnetically stirred PBS electrolyte.

3. Result and discussion

3.1. Morphology and structural characterization

The morphologies of the as-prepared TiO₂ NW/PAPBA–Au TNC, PAPBA–Au NC, TiO₂ NW/PAPBA NC and pristine PAPBA were characterized by FE-SEM analysis. As shown in the FE-SEM image of TiO₂ NW/PAPBA–Au TNC (Fig. 1a), the smooth surface of TiO₂ NW (Fig. 1a, inset) was transformed into an uneven and bumpy surface, suggested that the surface of TiO₂ NW was completely covered with PAPBA–Au NC. On close perusal of the surface of TiO₂ NW/PAPBA–Au TNC (Fig. 1a), one can identify two kinds of materials, spherical bright dots (Au NPs) and the dark puffy mass (PAPBA). It is clear that Au NPs were distributed within PAPBA matrix and existed on the surface of TiO₂ NW. EDAX analysis of the TiO₂ NW/PAPBA–Au TNC informed that nearly 17.63 wt% of elemental Au is present in (Fig. 2). Thus, the treatment of HAuCl₄ with 3-APBA in the presence of TiO₂ NW modified the TiO₂ NW surface with a PAPBA–Au shell layer. FESEM image of TiO₂ NW/PAPBA NC (Fig. 1b) also reveals the modification of the surface of TiO₂ NW. In this case, a much increased (about 150 nm thick) shell layer of PAPBA was formed on TiO₂ NW surface. Fig. 1c displays the image of PAPBA–Au NC with the distribution of larger sized spherical Au NPs (diameters in the range 130–200 nm) on the
amorphous host matrix of PAPBA with minimum aggregations. The pristine PAPBA had a granular morphology (Fig. 1d).

Fig. 3 shows the XRD patterns of the TiO$_2$ NW/PAPBA–Au TNC (Fig. 3a), PAPBA–Au NC (Fig. 3b). The XRD pattern of TiO$_2$ NW/PAPBA–Au TNC (Fig. 3a) exhibits peaks centered at 2\(\theta\) = 27.48°, 36.18°, 38.24°, 54.46°, 56.68°, 62.96°, 69.08° and 69.86° that correspond to (110), (103), (004), (211), (220), (204), (116) and (112) reflections of anatase TiO$_2$, peaks corresponding to the atomic planes of Au [2\(\theta\) = 44.56° (200), 64.82° (220), and
77.68° (311)] and a broad band around 10–25°. The XRD pattern of PAPBA-Au NC (Fig. 3b) comprises of an intense broadband around 2θ = 10–25° (PAPBA) that is attributed to the periodically parallel chain of amorphous polymers of PAPBA and a sharp peak Bragg reflection peak at 2θ = 44.56° (Au (200)). The Au reflection peaks at 38.24° (100) and 64.8° (220) are less intense as compared to XRD pattern of the TiO2 NW/PAPBA-Au TNC (Fig. 3a). Thus, XRD pattern of TiO2 NW/PAPBA-Au TNC (Fig. 3a) corroborates with the coexistence of crystalline TiO2, Au atomic planes, and amorphous PAPBA.

3.2. Electrochemical properties

3.2.1. Electroactivity. The electroactivity, in terms of efficiency of the electron transport across the electrode/modifying material interface, was monitored for the fabricated modified electrodes using the bench mark redox couple Fe(CN)6^{3-/4-} by recording cyclic voltammograms (CVs) in the potential range from −0.20 V to 0.60 V, over the scan rates ranging from 0.02 V s\(^{-1}\) to 0.2 V s\(^{-1}\) at the GCE/TiO2 NW/PAPBA–Au NC (Fig. 4a, GCE/TiO2 NW/PAPBA–Au NC (Fig. 4b), GCE/TiO2 NW/PAPBA–Au NC (Fig. 4c) and GCE/pristine PAPBA (Fig. 4d) electrodes. The CV of the bare GCE (Fig. 4a (inset)) in the presence of 5 mM of Fe(CN)6\(^{3-/4-}\) (0.1 M KCl) is also presented for a comparative purpose.

Typically, the modified electrodes exhibited the Fe(CN)6\(^{3-/4-}\) redox transition peaks (Fig. 4a–d) as similar to the redox transitions noticed at the bare GCE (Fig. 4a (inset)). However, there are distinct differences between the anode peak to cathode peak separation (Δ\(E_p\)) and the anodic peak current (I\(_{pa}\))/cathodic peak currents (I\(_{pc}\)). The Δ\(E_p\) of the GCE/TiO2 NW/PAPBA–Au TNC, GCE/PAPBA–Au NC, GCE/TiO2 NW/PAPBA NC and GCE/pristine PAPBA electrodes were determined to be 0.04 V, 0.09 V, 0.27 V and 0.26, respectively, at a scan rate 20 mV s\(^{-1}\). And, the GCE/TiO2 NW/PAPBA–Au TNC electrode (I\(_{pa}\) = 3.124 µA) exhibited nearly 1.8, 1.44 and 1.66 times higher I\(_{pa}\) as compared to GCE/PAPBA–Au NC, GCE/TiO2 NW/PAPBA NC, and GCE/pristine PAPBA electrode, respectively. The I\(_{pa}\)/I\(_{pc}\) linearly increased with the scan rate in the range of 0.02 to 0.2 V s\(^{-1}\) (Fig. 4, insets) and accompanied with a positive shift in the anodic peak and the negative shift in the cathodic peak of the Fe(CN)6\(^{3-/4-}\) redox process at modified electrodes. Furthermore, with the increase in scan rate (0.02–0.2 V s\(^{-1}\)), the Δ\(E_p\) increased steadily with nearly a constant I\(_{pa}\)/I\(_{pc}\) ratio. These results suggested the quasi-reversible one-electron behavior for the Fe(CN)6\(^{3-/4-}\) redox process at the modified electrodes. The electrochemically accessible surface area is an important empirical parameter to understand the relationship between the specific electrode activity and the structure/composition of the catalytic materials. The effective electroactive surface area (A) of the modified electrodes was calculated by using the Randles–Sevick equation.\(^{29}\) The A value for the GCE/TiO2 NW/PAPBA–Au TNC, GCE/PAPBA–Au NC, GCE/TiO2 NW/PAPBA NC, GCE/pristine PAPBA was calculated to be 8.22 cm\(^2\), 5.40 cm\(^2\), 5.06 cm\(^2\) and 4.67 cm\(^2\), respectively. The A value of GCE/TiO2 NW/PAPBA–Au TNC is 1.55, 1.62 and 1.76 times higher than that of GCE/PAPBA–Au NC, GCE/TiO2 NW/PAPBA NC, GCE/pristine PAPBA. Based on the results on

![Fig. 4](image-url) CV curves for 5 mM of Fe(CN)6\(^{3-/4-}\) (0.1 M KCl) at different scan rate from 0.02 V s\(^{-1}\) to 0.20 V s\(^{-1}\) at the modified electrodes GCE/TiO2 NW/PAPBA–Au TNC (a), GCE/PAPBA–Au NC (b), GCE/TiO2 NW/PAPBA NC (c), GCE/pristine PAPBA (d) and bare GCE (a, inset).
3.2.2. Interfacial properties. Electrochemical impedance spectroscopy (EIS) is an important electrochemical tool, which can be useful to understand the charge transfer resistance at the electrode and electrolyte interface of the modified electrodes. The diameter of the semicircle in a Nyquist plot is a direct measure of charge transfer resistance ($R_\text{ct}$). Fig. 6 presents of Nyquist plots of GCE/TiO$_2$ NW/PAPBA–Au TNC (Fig. 6a), GCE/PAPBA–Au NC (Fig. 6b), GCE/TiO$_2$ NW/PAPBA NC (Fig. 6c) and GCE/pristine PAPBA (Fig. 6d) electrodes recorded in 5 mM of Fe(CN)$_6^{3-/4-}$ (0.1 M KCl). Fig. 5 clearly informs that the GCE/TiO$_2$ NW/PAPBA–Au TNC electrode has the lowest ($R_\text{ct}$ (31.8 k$\Omega$)) among the other electrodes; GCE/PAPBA–Au NC (41 k$\Omega$, Fig. 6b), GCE/TiO$_2$ NW/PAPBA NC (46 k$\Omega$, Fig. 6c) and GCE/pristine PAPBA (97 k$\Omega$, Fig. 6d), suggesting that the TiO$_2$ NW/PAPBA–Au TNC film significantly improves the conductivity and electron transfer process. Therefore, the GCE/TiO$_2$ NW/PAPBA–Au TNC electrode was selected as the most suited modified electrode for electrochemical detection of glucose.

3.3. NEG sensor performances

3.3.1. Electrocatalytic oxidation of glucose. As compared to cyclic voltammetry, the other electrochemical technique, differential pulse voltammetry, is less likely to get affected by the capacitive current. Differential pulse voltammetry measures only the difference between the current at the beginning and end of each pulse. We employed differential pulse voltammetry to monitor the faradaic current response of modified electrodes in the presence and absence of glucose (Fig. 7) at the optimized differential pulse voltammetric conditions. Fig. 7 depicts the differential pulse voltammograms (DPVs) obtained at the GCE modified with TiO$_2$ NW/PAPBA–Au TNC, PAPBA–Au NC, TiO$_2$ NW/PAPBA NC, and pristine PAPBA in the presence of 1 mM glucose (Fig. 7a’–d’ curves) and absence of glucose (Fig. 7a–e curves) of GCE/TiO$_2$ NW/PAPBA–Au TNC (a and a’), GCE/PAPBA–Au NC (b and b’), GCE/TiO$_2$ NW/PAPBA NC (c and c’), GCE/pristine PAPBA (d and d’) and bare GCE (e) in 1 mM glucose + 0.1 M PBS solution (solid lines; a’–d’) and absence of glucose (dashed lines; a–e). Scan rate: 0.05 V s$^{-1}$, pulse amplitude: 0.05 V, pulse width: 50 ms.

3.3.3. Neg sensor performances

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curves) in 0.1 M PBS PBS solution (pH 7.0) at scan rate 0.05 V s\(^{-1}\). The modified electrodes GCE/TiO\(_2\) NW/PAPBA–Au TNC, GCE/PAPBA–Au NC, GCE/TiO\(_2\) NW/PAPBA NC, and GCE/pristine PAPBA show much higher peak currents (beyond the potential of +0.25 V) as compared to the current responses in the absence of glucose. Especially, the as-prepared GCE/TiO\(_2\) NW/PAPBA–Au TNC (Fig. 7a) modified electrode exhibited an extraordinarily higher current response towards glucose oxidation than noticed at GCE/PAPBA–Au NC (Fig. 7b), GCE/TiO\(_2\) NW/PAPBA NC (Fig. 7d) and GCE/pristine PAPBA (Fig. 7f) modified electrodes. Typically, two distinct oxidation peaks were observed at around 0.20 V and 0.47 V for the GCE/TiO\(_2\) NW/PAPBA–Au TNC electrode that corresponds to the oxidation of glucose to gluconolactone and oxidation of gluconolactone to the product, respectively. The DPV of the bare GCE (Fig. 7e) in the presence of glucose was featureless and informed that the bare GCE was completely electro inactive towards glucose oxidation in the potential range of interest. DPVs of the different concentrations of glucose, prepared by the proper dilution of stock glucose solution, were evaluated at GCE/TiO\(_2\) NW/PAPBA–Au TNC (Fig. 8a) and GCE/PAPBA–Au NC (Fig. 8b). The size of the wave around 0.30 V to 0.50 V progressively increased and became sharper as the concentration of glucose increased for both modified electrodes (Fig. 8a and b). The height of peak current at +0.47 V was taken as the measure of quantifying the concentration of glucose. The exact current values at the GCE/TiO\(_2\) NW/PAPBA–Au TNC (+0.47 V) were generated from the potentiostat. A good correlation was found between the concentrations of glucose and peak currents (Fig. 8c). Typically, the glucose oxidation peak current showed a linear increase with glucose concentration for the range between 0.5 and 11 mM at GCE/TiO\(_2\) NW/PAPBA–Au TNC (Fig. 8c[i]) and GCE/PAPBA–Au NC (Fig. 8c[ii]) with correlation coefficients (\(R^2\)) as 0.9923 and 0.9917, respectively. The lowest detection limits for glucose as estimated based on three times of standard deviation from the blank were 9.3 \(\mu\)M and 23.4 \(\mu\)M for the GCE/TiO\(_2\) NW/PAPBA–Au TNC (Fig. 8c[i]) and GCE/PAPBA–Au NC (Fig. 8c[ii]) electrodes, respectively. The new ISO 15197:2013 standard (as applicable from May 2016 onwards) suggests the accuracy of blood glucose test strips within ±20% of laboratory results for glucose concentrations > 5.6 mM and within ±0.83% for glucose concentrations < 5.6 mM. The ISO 15197:2013 fixes a limit of detection as 166 \(\mu\)M for glucose concentration levels below 5.6 mM. The lowest detection limit for glucose at the GCE/TiO\(_2\) NW/PAPBA–Au TNC is 9.3 \(\mu\)M, which satisfies the 15197:2013 requirement for a strip glucose sensor. The sensitivity of GCE/TiO\(_2\) NW/PAPBA–Au TNC (66.8 \(\mu\)A cm\(^{-2}\) mM\(^{-1}\); Fig. 8c(ii)) electrode was ~2 times higher than the sensitivity at PAPBA–Au NC (34.6 \(\mu\)A cm\(^{-2}\) mM\(^{-1}\); Fig. 8c(ii)) electrode. The sensitivity, and linear range of the GCE/TiO\(_2\) NW/PAPBA–Au TNC based glucose sensor are much superior to that of other reported glucose sensors based on TiO\(_2\), Au NP, PANI and enzyme and its composites (Table 1). Our results reveal that TiO\(_2\) NW/PAPBA–Au TNC exhibits superior electroactivity, higher electrochemical surface area, faster electron transfer kinetics, and interfacial characteristics as compared to the pristine components. Also, it exhibits the highest glucose sensing performances as compared to the TiO\(_2\) based materials reported in the literature (Table 1). We attribute
Human serum samples 0 4.44
result suggested that TiO2 NW/PAPBA
respect to the current corresponding to 1 mM glucose. The
TiO2 NW/PAPBA glucose sensor. We evaluated the selectivity of the proposed
tual requirement for the practical application of electrochemical
serum sample having a glucose concentration of 4.44 mM
prepared under the same conditions were tested to detect the
substances contribute nearly 0.5
interfering species. The results inform that the interfering
groups to selectively bind glucose.

Table 2 Recovery of glucose in human serum samples at the GCE/TiO2 NW/PAPBA–Au TNC electrode

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added glucose [mM]</th>
<th>Determined by glucometer</th>
<th>Determined at the fabricated electrode</th>
<th>Recovery [%]</th>
<th>RSD\textsuperscript{a} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human serum samples</td>
<td>0</td>
<td>4.44 ± 0.01</td>
<td>4.43 ± 0.04</td>
<td>99.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.415 ± 0.06</td>
<td>5.412 ± 0.01</td>
<td>99.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.44 ± 0.02</td>
<td>5.43 ± 0.05</td>
<td>99.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.43 ± 0.07</td>
<td>5.413 ± 0.04</td>
<td>99.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.43 ± 0.03</td>
<td>6.425 ± 0.07</td>
<td>99.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.36 ± 0.01</td>
<td>6.358 ± 0.02</td>
<td>99.97</td>
<td></td>
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<tr>
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<td>2</td>
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<td>6.38 ± 0.03</td>
<td>99.95</td>
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<tr>
<td></td>
<td>3</td>
<td>7.388 ± 0.3</td>
<td>7.37 ± 0.01</td>
<td>99.75</td>
<td>2.84</td>
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<tr>
<td></td>
<td>3</td>
<td>7.34 ± 0.03</td>
<td>7.35 ± 0.07</td>
<td>100.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.442 ± 0.04</td>
<td>7.31 ± 0.06</td>
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<tr>
<td></td>
<td>4</td>
<td>8.41 ± 0.01</td>
<td>8.43 ± 0.02</td>
<td>100.23</td>
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<tr>
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<tr>
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<td>8.4 ± 0.04</td>
<td>100.26</td>
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<td>100.11</td>
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<tr>
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<td>9.388 ± 0.04</td>
<td>99.97</td>
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<tr>
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<td>5</td>
<td>9.41 ± 0.05</td>
<td>9.414 ± 0.03</td>
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</table>

\textsuperscript{a} Number of measurements = 3.

a multisource synergistic electrocatalytic effect for TiO2 NW/
PAPBA–Au TNC arising from the catalytic activity of TiO2 NW in
axial and radial directions and deliberate dispersion of electrocatalytic nanosized Au particles onto the electron mediating
conducting polymer (PAPBA) having boronic acid binding
groups to selectively bind glucose.

3.3.2. Selectivity. The selectivity of the sensor in an essential
requirement for the practical application of electrochemical
glucose sensor. We evaluated the selectivity of the proposed
TiO2 NW/PAPBA–Au TNC sensor towards 1 mM of glucose
current response upon addition of 0.1 M of the commonly co-
existing interfering species such as ascorbic acid (AA), uric
acid (UA) dopamine (DA), fructose (Fru), lactose (Lac), sucrose
(Suc) and mannose (Mon). The current responses were
measured at 0.47 V. As shown in Fig. 9, it can be noticed that
GCE/TiO2 NW/PAPBA–Au TNC electrode exhibited nearly
negligible current response with the addition of 0.1 mM of each
interfering species. The results inform that the interfering
substances contribute nearly 0.5–2.2% of the \( \Delta I \) value with
respect to the current corresponding to 1 mM glucose. The
result suggested that TiO2 NW/PAPBA–Au TNC possessed
excellent selectivity for the glucose detection.

3.3.3. Real sample analysis. In order to validate the GCE/TiO2 NW/PAPBA–Au TNC electrode for the practical application
of glucose monitoring in blood serum samples, the fabricated
sensor was used for the detection of glucose in human blood
serum samples. The glucose level in the human blood serum
sample was pre-determined as 4.44 mM through a commercial
glucometer (CareCens\textsuperscript{™} N, GM5051A, I-SENS, Inc., Korea)
using a glucose strip. To evaluate the reproducibility of GCE/TiO2 NW/PAPBA–Au TNC electrode, three different electrodes
prepared under the same conditions were tested to detect the
serum sample having a glucose concentration of 4.44 mM
(against commercial glucometer). The average relative standard
device (% RSD) was estimated to be less than 5%. Similarly,
we tested sensor performance of the particularly fabricated
sensor for the determination of glucose in serum for three
times using the DPV calibration curve (Fig. 8c(i)). The previously
tested sensor was gently rinsed with the buffer solution after
each measurement. The results showed an average glucose
concentration of 4.43 ± 0.04 mM with an RSD = 2.68%. Besides,
the accuracy of the fabricated sensor was tested for the serum
samples spiked with 1 mM, 2 mM, 3 mM, 4 mM and 5 mM of
standard glucose independently to the serum samples (Table 2).
Each serum sample was spiked for three times. A good recovery
(98.2–100.26% with an RSD = 2.84%) towards glucose was
obtained at GCE/TiO2 NW/PAPBA–Au TNC electrode. We
compared the determination results in blood samples detected
from our experiments with those measured by the commercial
glucometer and results are listed in Table 2. This comparison
indicates that the results obtained by electrochemical detection
at the GCE/TiO2 NW/PAPBA–Au TNC electrode match well with
those obtained by a routine commercially available glucose
strip. Thus, we demonstrate the reproducibility and accuracy of
GCE/TiO2 NW/PAPBA–Au TNC electrode for the detection of
glucose practical samples.

4. Conclusion
The ternary nanocomposite (TNC), comprising of the surface
area enriched 1D TiO2-NWs, a glucose binding conducting
polymer (PAPBA) and electrocatalytic Au NPs materials was
utilized for the construction of a sensitive non-enzymatic
glucose sensor. The TiO2 NW/PAPBA–Au TNC exhibited good
sensor characteristics towards electrochemical detection of
glucose. The TiO2 NW/PAPBA–Au TNC sensor outperforms the
reported TiO\textsubscript{2} based glucose sensors. The peak current for glucose oxidation showed a linear dependence with a concentration of glucose in a wider range, 50 \mu M to 11 mM with a high sensitivity (66.8 \mu A cm\textsuperscript{-2} mM\textsuperscript{-1}). The excellent sensor performances (high sensitivity and wider linear range) at TiO\textsubscript{2} NW/PAPBA-Au TNC are due to synergistic roles of the components (TiO\textsubscript{2} NW, PAPBA, and Au NPs) in the newly synthesized TNC. Importantly, the peak current of glucose oxidation current was not influenced at TiO\textsubscript{2} NW/PAPBA-Au TNC in the presence of electrochemical interfering substances, such as ascorbic acid (AA), uric acid (UA) dopamine (DA), fructose (Fru), lactose (Lac), sucrose (Suc) and mannose (Mon). To note, TiO\textsubscript{2} NW/PAPBA-Au TNC sensor exhibited a remarkable performance in the human serum sample and signifies its utility for practical blood glucose detection.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**References**