Graphene, the two-dimensional (2D) form of sp²-bonded carbon atoms, has garnered much interest in energy storage and conversion, biosensing, and catalysis due to its outstanding electrical conductivity, an all-surface nature, and excellent electrocatalytic activity.1 Of late, a wave of various innovative graphene-based architectures in forms of hydrogels, foams, sponges and aerogels has emerged.2 These structures have enticed vast attention as they inherently possess structural interconnectivity and high porosity, and at the same time, all of the outstanding properties of graphene itself including low density, large surface area, unparalleled mechanical properties, biocompatibility, and excellent mass and electron transport.3

Three-dimensional graphene (3DG) architectures can be fabricated either by self-assembly of graphene-based nanosheets (template-free methods) or template-assisted procedures such as chemical vapor deposition (CVD) and annealing.4 While the template-free methods are technologically less complex and relatively cheaper, the obtained 3DG materials suffers from low electrical conductivity because of the low quality and high inter-junction sheets of chemically driven nanosheets.5 Direct synthesis of 3DG networks by template-directed CVD provides large and fixable interconnected structure with high quality and electrical conductivity, which can be utilized as a platform for the fabrication of biosensors with quality sensitivity.

To enhance electrochemical performance of 3DG architectures for biosensing applications, many studies have employed nanoparticles (NPs) with different compositions, sizes and morphologies. This approach can be implemented in various ways; encapsulation of NPs by 3DG structures,6,7 embedding catalytic NPs into 3DG via one-pot chemical synthesis methods,8 and decoration of 3DG with NPs to form hybrid structures,9 to name but a few. Noble metal NPs have extensively been utilized for the fabrication of electrochemical biosensors; however, high cost and scarcity of noble metals, their high working potentials, and poor selectivity are drawbacks.10 To develop cost-effective substrates that can work at low negative potentials, metal oxide nanomaterials have been found of great interest during the last decade.11 Among various metal oxides, cerium oxide, a wide bandgap semiconductor, is a promising candidate. In this oxide, Ce³⁺ and Ce⁴⁺ states can coexist on the surface. This is particularly important as it provides ceria with electrocatalytic ability (strongly related to the two oxidation states of CeO₂, Ce³⁺ and Ce⁴⁺), redox activity, high oxygen storage capacity, free-radical scavenging properties, biocompatibility, and quick transition between oxidation states.12–17

To the best of our knowledge, there has been no report on the combination of CeO₂ NPs with 3DG networks prepared by template-directed CVD for detection of H₂O₂. Herein, we present high-quality interconnected 3DG networks comprising CeO₂ nanoparticles for non-enzymatic H₂O₂ sensing at low potentials with satisfying sensitivity. It is important to note that oxygen vacancies in CeO₂ are crucial for sensitive and selective detection of H₂O₂ because Ce³⁺ triggers the reduction of hydrogen peroxide at less negative potentials.18 H₂O₂ is an important chemical product in many fields such as pharmaceutical, clinical and environmental area.25,26 Furthermore, it is a common reactive oxygen species (ROS) and a by-product of numerous oxidative metabolic pathways.27,28 ROS play critical roles in some signaling cascades present in living systems. At higher concentrations, ROS cause negative effects in living systems. Herein, hydrogen peroxide is important because of its stability and its links to a wide range of serious
Table I. Figure of merit for non-enzymatic H2O2 detection by different biosensors.

| Electrodes               | Liner range (μM) | Limit of detection (μM) | Reference |
|-------------------------|------------------|------------------------|-----------|
| Cytomel-type             | 100–6900         | 2.0                    | 23        |
| MnO2/CPE                | 20–9670          | 3.2                    | 24        |
| Mn00H/CC                | 96–8880          | 25                     | 25        |
| PAN-PAA                 | 40–12000         | 20                     | 26        |
| Grass-like CuO (RGO/Au@PB paper electrode) | 1–30 | 0.1                   | 28        |
| Pd/cu SPCE              | 500–1100         | 0.7                    | 29        |
| Fe3O4–RGO               | 100–6000         | 3.2                    | 30        |
| HRP/DNA/Au              | 10.0–9700        | 50.0                   | 51        |
| Ag NPs/graphite substrate | 250–2500       | 1.0                    | 52        |
| TiO2/HRP gold nano-seeds/GCE | 41–630 | 5.9                     | 53        |
| GO/Au/NPs/CS            | 200–4200         | Not reported           | 54        |
| Se/Pt                   | 10–1500          | 3.1                    | 55        |
| CuO/GNs                 | 300–3300         | 3.3                    | 56        |
| Cu–CuO hollow microsphere | 220–10890       | 0.05                   | 57        |
| CuO NPs                 | 50–1100          | 47.2                   | 58        |
| CuO-rGO                 | 30–12500         | 21.7                   | 59        |
| GCE/ carbon nanohorns and poly(2-aminopyridine) | 50–800 | 3.6 | 46 |
| G/PAM                   | 250–2250         | 35                     | 60        |
| CDE                     | 20–1500          | Not reported           | 61        |
| CeO2 NPs/3DG/NF         | 2.50–160         | 1.0                    | This work |

HRP: horseradish peroxidase, Au: Gold electrode, CPE: Carbon paste electrode, GCE: Glassy carbon electrode, SPCE: Screen printed carbon electrode, GO: Graphene oxide, CS: chitosan, rGO: reduced graphene oxide, PAn-PAA: polyaniline-polyacrylic acid, G/PAM: graphene-polyacrylamide, PB: Prussian Blue; CC: carbon cloth, G: graphene, CDE: copper disk electrodes.

Materials characterization.—The prepared structures were characterized by Raman spectroscopy (Teksan Takram, 532 nm excitation wavelength) at up to 10 points across the samples. X-ray diffractionmetry (XRD) was performed in a Philips diffractometer with Cu Kα radiation (λ = 0.1541478 nm). Field-emission scanning electron microscopy (FESEM; TESCAN–Mira3) was used to investigate the microstructural characteristics and growth morphological features of 3DG and the hybrid electrode. The instrument was equipped with an energy-dispersive X-ray (EDX) spectrometer which was used for compositional analysis and elemental distribution mapping in the regions of interest across the sample.

Electrochemical measurements.—Electrochemical measurements were carried out by employing an AutoLab PGSTAT320N electrochemical workstation (Eco-Chemie, Netherlands) in combination with a standard three-electrode system consisting of a working electrode, an Ag/AgCl electrode (saturated KCl) as reference electrode, and a platinum wire as counter electrode. Freshly-prepared phosphate-buffered saline (PBS, 0.1 M, pH 7.4) was used as the supporting electrolyte. All the electrochemical studies were performed under deaerated atmosphere (using high purity N2). Before electrochemical measurements, the 3D substrates were treated by cyclic voltammetric scanning over 0.0 V to −1.0 V at a scan rate of 50 mV s−1. The electrochemical activity of the CeO2-modified 3DG electrode was compared with NF and 3D graphene network.

Results and Discussion

Structure and composition of the 3DG hybrid architecture.—Figure 1 represents the results of the SEM investigation of microstructural and compositional characteristics of the sample, from the bare NF through the final 3D hybrid structure. As can be viewed in Fig. 1a, the Ni template is highly porous (>90%) with an interconnected pore structure and channel diameter of >500 μm. The struts have a size of about 100 μm and consist of a cellular structure with an average grain size of ~8 μm (Figs. 1b, 1c). It is also noted that the Ni template (as-received) has a rough surface with elevated features being detectable in both the medium and high magnification SEM images (Figs. 1b, 1c). Figs. 1d–1f show the SEM images of the sample after the CVD growth process at the same magnifications as images (a–c). Most notably, it can be clearly seen that unlike the bare NF (Fig. 1b), no raised features are detectable in 3DG/NF hybrid structure and the surface is much smoother (Figs. 1e, 1f). This is attributed to the annealing step of the CVD process performed before the growth, rendering a smooth surface suitable for uniform growth of graphene. After graphene growth, equixed grains are covered with graphene layers, displaying a morphology that resembles a parched desert. The grown graphene is majorly continuous but of multilayer nature and has conformed to the underlying grain structure of Ni substrate. Fig. 1g shows the EDX spectrum and embedded oxygen and cerium maps.
Figure 1. Step-by-step SEM/EDX studies of the microstructural evolutions at different stages of specimen preparation process. (a-c) SEM images of the bare NF, indicating the open cell structure of nickel template and its fine cellular structure. (d-f) SEM images of 3DG/NF structure, revealing the grain growth of nickel during the CVD process and formation of parched desert features. (g) SEM image, EDX spectrum and elemental mapping of the final 3DG hybrid structure, showing the successful deposition of cerium oxide nanoparticles on the strut surfaces, and elemental mapping determining that NPs are uniformly distributed over the surface. (h) XRD measurement further signifies the presence of CeO2 on the surface of the 3DG/NF structure.

of the 3DG/NF structure after drop-casting of the colloidal suspension of cerium oxide. The EDX spectrum consists of various Ni edges as the main constituent of the hybrid structure, oxygen core edge peak, and edges of cerium, though weaker in comparison to other peaks (the concentration of C, O and Ce from EDX measurement are 47.9 ± 7 at%, 12.9 ± 7.12 at% and 1.2 ± 0.2 at%, respectively). Considering that the Ni surface is covered with graphene, the observed O and Ce edges in the spectrum are ascribed to CeO2 nanoparticles and not nickel oxide. Furthermore, the elemental distribution maps (embedded images), demonstrates the presence of CeO2 NPs on the surface, and that Ce is uniformly distributed on the surface, with a slightly higher density of oxygen as expected in CeO2. XRD measurement was also carried to complement the SEM/EDX analyses. The XRD pattern (Fig. 1h) comprises of strong diffraction peaks of FCC Ni (2θ = 44.5°, 51.8° and 76.3° associated with the (111), (220) and (200) planes; JCPDS card No. 40-0850) and not those of nickel oxide, and weak hint of ceria (2θ = 47.7° associated with (220) plane of cubic fluorite structure; JCPDS card No. 01-0800). It is noted that the low intensity of the characteristic peaks is attributed to its low concentration and ultrafine crystal structure as well as strong and close peaks of nickel.

Electronic coupling between graphene and CeO2 NPs.—In order to evaluate the quality of the 3D graphene architecture and possible electronic coupling with CeO2 NPs, Raman spectroscopy was employed (Fig. 2). Raman spectra show two prominent peaks at 1582 cm⁻¹ (G peak) and 2706 cm⁻¹ (2D peak) for the laser excitation wavelength used in this work. The linewidth of the 2D peak together with the I_G/I_2D intensity ratio provide a fast estimation of the number of layers in graphene. The full width at half maximum (FWHM) of 2D peak was measured to be ~40 cm⁻¹ and the I_G/I_2D was ~0.8, suggesting the presence of few-layer graphene. The G and 2D bands of graphene are evidently red-shifted from 1582 cm⁻¹ to 1566 cm⁻¹, and from 2706 cm⁻¹ to 2650 cm⁻¹, respectively. Since the Raman spectra were taken at several locations within the same and different samples, and
always the same Raman behavior was observed, the lack of uniformity effect on the observed significant frequency shifts is ruled out.

One of the possible reasons for these significant Raman shifts could be charge transfer between graphene and ceria NPs. It should be noted that the 2D peak position increases for p-doping, while it decreases for n-doping; and the G peak up-shifts for both types of doping. Therefore, the strong redshift of G and 2D peaks observed in this work cannot only be explained by doping, and some other mechanism should be in play. The Raman spectrum of the hybrid electrode contains an additional feature, the F\textsubscript{g} band, which is the Raman peak of the bulk CeO\textsubscript{2} observed at 464 cm\textsuperscript{-1}. This peak is assigned to a triply degenerate first order symmetrical breathing mode of the oxygen atoms around the cerium ions. When examining the Raman spectrum of the hybrid electrode (red curve) in the region of F\textsubscript{g} band, due to the very low concentration of CeO\textsubscript{2}, as well as the high relative intensity of G and 2D peaks in comparison to F\textsubscript{g} peak (greater by a factor of 250), the region appears as smeared out. Thus, this peak is not very reliable and is discarded for the investigation of the properties of the system.

To investigate the possible interactions between CeO\textsubscript{2} NPs and the underlying graphene, a model based on density functional theory (DFT) was developed. The local spin density approximation (LSDA) as exchange correlation with Perdew-Zunger function with Double Zeta Polarized basis was used as implemented in Siesta Package. In addition, to overcome the inaccuracy of DFT in modelling “f” orbitals, the Hubbard model on of Ce atoms were considered and defined by 5eV as reported before. Additionally, the smallest stable structure of this group was considered as Ce\textsubscript{6}O\textsubscript{8}. An optimized supercell of graphene consisting of 72 atoms is considered and Ce\textsubscript{6}O\textsubscript{8} nanoparticle transferred on it at different possible positions and the whole new structure is optimized with 10 × 10 × 1 Monkhorst-Pack k-point sampling that defined after proper convergence tests. The optimisation performed on different possible positions and the most stable one considered as the optimized structure. The mesh cut of 75Ry was defined after proper convergence test. The density of state (DOS) calculation was performed with 20 × 20 × 1 set value and the Mulliken population was studied to define the charge transfer.

Figs. 3a, 3b show the schematic representation and electron density of graphene with ceria NPs on its surface, respectively. The combination of orbitals between graphene and nanoparticles indicates that...

![Figure 2](image_url)  
**Figure 2.** Raman spectra of 3D graphene architecture with and without CeO\textsubscript{2} NPs. The Raman peak position of ceria is marked with green line.

![Figure 3](image_url)  
**Figure 3.** (a) Schematic representation of a ceria nanoparticle on the graphene. The carbon, oxygen and cerium atoms are in black, red and white colors, respectively. (b) Electron density of graphene with ceria NPs on its surface. (c) Density of state of graphene in decorated structure with ceria NPs.
there is a good bond between them, providing a platform for charge transfer. More careful analysis suggests that the orbitals near the Ce atom and graphene are combined. A slight deformation in the graphene plane due to columbic interaction of Ce$_6$O$_8$ NPs is also noticeable. Fig. 3c shows the DOS of graphene in the presence of quantum nanoparticles. The clear shift of Fermi level toward conduction band demonstrates that there is a noticeable transfer of charge from nanoparticles to graphene which increase the number of electron carriers and lead to such shift in Fermi level. Mulliken population shows this transfer of charge to the graphene is in the order of 0.28 e within the range of study, confirming the location of Fermi level. The DOS also shows the difference between spin up and down in the graphene due to Ce$_6$O$_8$. The few changes in the up spin compared with down one shows the potential of decorated graphene with Ce$_6$O$_8$ NPs for spintronic applications. Based on the results of DFT calculations, the observed red-shift of the graphene Raman peaks is ascribed to the combinatorial effect of n-doping of graphene by ceria NPs, and the created (tensile) strain through coulombic forces; the principles behind the effects of strain and doping has been previously noted by Ferrari & Basko,36 Mohiuddin et al.,41 and Ni et al.42

Electrochemical activity of 3D interconnected CeO$_2$/graphene composite was evaluated by cyclic voltammetry (CV) in PBS (2.0 mM, pH = 7.4) containing hydrogen peroxide (Fig. 4). At a constant hydrogen peroxide concentration (2.0 mM) and scan rate (100 mV s$^{-1}$), growth of graphene significantly improves the response of electrode to oxidation of H$_2$O$_2$ in comparison to the nickel substrate (Fig. 4a). Further improvement is attained by CeO$_2$ NPs deposition, owing to their active catalytic sites for electrochemical reaction. As can be seen, upon increasing the concentration of H$_2$O$_2$, cathodic current intensity is enhanced, and the electrode becomes more sensitive to the concentrations at low applied potentials. It is important to mention that; the developed electrode shows better responses to variation of H$_2$O$_2$ concentrations (Fig. 4b) in cathodic domain.

From the literature, it is suggested that on the electrode’s surface, CeO$_2$ NPs act as redox sites to adsorbed H$_2$O$_2$ and other peroxide
species coordinated onto the surface of CeO$_2$ NPs. At high H$_2$O$_2$ concentrations (millimolar range and above), a rapid color change from yellow to orange was observed, which could be attributed to an increase in the ratio of Ce$^{4+}$ to Ce$^{3+}$ in the metal oxide, similar observations were also found by Perez et al. During electrochemical reactions and applying a cathodic potential, Ce$^{4+}$ can reduce to Ce$^{3+}$. The ability of these nanoparticles to reversibly switch from Ce$^{3+}$ to Ce$^{4+}$ is a key factor for their catalytic applications. Therefore, the active centers of CeO$_2$ NPs on graphene electrode could boost cathodic current. The Ce$^{3+}$/Ce$^{4+}$ couple is regenerated during the reaction and participates in the electrochemical reaction. The suggested mechanism of the electrocatalytic reduction of H$_2$O$_2$ is expressed as following:

$$2\text{Ce}^{3+}(\text{CeO}_2 \text{ NPs}) + \text{H}_2\text{O}_{(aq)} + 2\text{H}^+ \rightarrow 2\text{Ce}^{4+}(\text{CeO}_2 \text{ NPs})$$

2Ce$^{4+}$(CeO$_2$ NPs) as an intermediate + 2e$^-$ → 2Ce$^{3+}$(CeO$_2$NPs)

This catalytic reaction combines with porous and conductive structure of 3DG which provides a low resistance and promotes the electron transfer to reduce the response time. Furthermore, it has been shown that the coordination number of Ce in the first coordination shell slightly increased after the addition of H$_2$O$_2$. Thus, peroxide species are proposed to be able to coordinate with surface Ce ions and decompose because of the intrinsic redox ability of Ce$^{3+}$/Ce$^{4+}$ pair.

Figure 4c shows CVs of the purposed electrode at different scan rates in the range of 0.05 to 0.40 V s$^{-1}$. The peak current is linearly varied with the square root of the scan rate ($\nu^{1/2}$) ($R^2 = 0.992$) as $I_{pc}(\mu A) = -33.4 \nu^{1/2} (V \cdot m^{-1}) + 42.1$. This observation may indicate a diffusion-controlled mechanism of the electroreduction.

Fig. 5a shows the amperometric response of the 3DG hybrid structure substrate upon successive and step-wise addition of H$_2$O$_2$ into 2.0 mM of PBS under stirring at a working potential of $-0.25$ V. A steep decrease in the current response is observed after H$_2$O$_2$ addition, but the current approaches to a steady-state value about 5 s. The variation of peak current versus concentration is shown in Figure 5b. The fabricated sensor exhibits a good linear response to H$_2$O$_2$ concentrations in a range from 2.8 to 20.2 $\mu$M with regression equation, $I(\mu A) = 0.06c(\mu A/\mu M) + 3.05(\mu A)$ ($R^2 = 0.97$), a detection limit of 1 $\mu$M ($S/N = 3$) and 20.0 to 160.0 $\mu$M with regression equation, $I(\mu A) = 0.026c(\mu A/\mu M) + 13.43(\mu A)$ ($R^2 = 0.99$). The attained sensitivity should be linked the oxygen vacancies in ceria and fast charge transfer in monolayer graphene.
We also examined the selectivity of the 3DG composite substrate through adding some interfering compounds (0.20 mM) which may have possible interference. Fig. 5c shows that the 3D hybrid electrode is only sensitive to a small amount of H$_2$O$_2$ (0.10 mM). It is noticeable that permitted electrode possesses higher sensitivity and larger liner range toward H$_2$O$_2$ detection in comparison to other reported structures.

In the next step, all electrodes were characterized and compared using electrochemical impedance spectroscopy (EIS). Fig. 5d shows the representative Nyquist plot of NF, 3DG/NF and CeO$_2$ NPs/3DG/NF in 5.0 mmol L$^{-1}$ [Fe(CN)$_6$]$^{3−/4−}$ solution containing 0.1 mol L$^{-1}$ KCl. In these plots, the semicircle diameter implies a high charge-transfer resistance (Rct) value. The equivalent circuit model is shown as inset in Fig. 5d. In this circuit model, the Rct is charge transfer resistance, where the diameter of the semicircle of Nyquist plot is proportional to the electron transfer resistance occurring at the electrode surface. Rct is the solution resistance and C the capacitance. The evolution of the corresponding circuit model data is interesting. Upon growth of 3D graphene on NF, the charge transfer resistance of the system increases.

It is postulated the lower Rct of NF alone could be due to its porosity that enhances the diffusion of the redox couple; and after the deposition of few-layer graphene on NF, the available surface for diffusion decreases or at least the diffusion path becomes more difficult, and as a result, the Rct increases.

Upon addition of CeO$_2$ NPs to the 3DG composite substrate, a clear decrease in Rct is observed, indicating the remarkable role of CeO$_2$ NPs as an electrocatalyst on the enhanced electron transfer rate. It is known that oxygen vacancies in cerium oxide (transition between Ce$^{4+}$ and Ce$^{3+}$) play a key role on its catalytic activity. 32,35 It has been previously reported that the activation energy for electrical conduction is lower for nanoceria. 35 Further analysis shows that CeO$_2$ NPs yields a high sensitivity within a wide liner range toward H$_2$O$_2$ detection.

**Conclusions**

The results of this work build up a comprehensive picture of the CeO$_2$-modified 3D graphene nanohybrid biosensor system from experimental and theoretical viewpoints. In general, the addition of CeO$_2$ nanoparticles lowers the charge transfer resistance of the 3D graphene/Ni foam system and provides non-enzymatic micromolar range selective detection of H$_2$O$_2$. When the electrochemical behavior of the Ni foam and 3DG/NF systems are compared, we can see that the charge transfer resistance of NF is lower than that of 3DG/NF. The DFT simulations suggest that the said increase in Rct could be due to the impaired electron tunneling mechanism for conductivity when graphene is deposited onto Ni foam. Further, DFT results may put forward a postulation for the observed Raman shifts in CeO$_2$ NPs/3DG/NF hybrid system, linking them to coulombic interaction and the resulting slight rippling of graphene. While this may be disadvantageous for some applications, one could cite the improved Rct to recommend CeO$_2$ nanoparticles modification for strain-independent applications.

While the sensing performance of CeO$_2$ NPs/3DG/NF are comparable to the common modifying entities such as Au NPs, the electrocatalytic properties of CeO$_2$ NPs such as oxygen storage capacity, multiple oxidation states and great electrocatalytic activity, a wider range of applications can be targeted using CeO$_2$-modified 3D graphene. This means that for applications where, for instance, energy storage and conversion is important, CeO$_2$ NPs are the surface modifier of choice. Ultimately, the presented experimental and theoretical study of CeO$_2$-modified CVD 3D graphene is only the beginning for sensing and energy applications. We hope that in light of this work the more common template-free synthesis and noble metal modifiers may be adapted to include CeO$_2$ NPs and its derivatives.

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**ORCID**

E. Rezvani https://orcid.org/0000-0002-3595-0036
A. Simchi https://orcid.org/0000-0002-9111-2977

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