Original Article

In situ synthesis of highly populated CeO₂ nanocubes grown on carbon nanotubes as a synergy hybrid and its electrocatalytic potential

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Interesting properties of nanostructures can be tailored to generate hybrid materials with exciting morphology and chemical compositions. Assembling of different forms, morphology, and chemical complexities of nanomaterials can lead to high performance materials. We present a study where CeO₂ nanocubes are grown on CNTs to produce a synergy hybrid. Microscopy showed the presence of the highly dense population of ceria cubes grown on the surface of carbon nanotubes. This special three-dimensional morphology provided micro cavities and pits network to facilitate improved mass transport and offered a large surface area to promote remarkable electrocatalysis. X-ray diffraction analysis confirmed high purity of the hybrid whereas, fourier transform infrared spectroscopy was employed to evaluate the presence and utilization of functional groups during the formation of hybrid. The hybrid exhibited excellent electrochemical potential for the detection of ascorbic acid and its fast oxidation occurred at very low potential (0.1 V). The lower detection limit was found to be 70 nM (S/N = 3). The three-dimensional morphology, versatile chemical composition with better catalytic properties can provide pathways to the development of high-performance functional hybrids for the determination of other specimens or analytes.

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Novelty statement

In this work, we have presented a single-step and straightforward method for the preparation of ceria nanocubes augmented carbon nanotubes hybrid. The morphology consisted of a highly dense population of cubes on the strands of tubes. The morphology and synergy of both nanomaterials lead to improved sensor design showing excellent electrocatalytic properties. This is the first report such where, such hybrids are investigated for electrocatalytic potential of biomolecules.

1. Introduction

Nanotechnology, as a very promising field, has emerged to develop functionalized nanostructures and devices for a diverse range of applications with a focus to increase the utilization of the resulting unique functional nanomaterials for enhanced performance [1]. These applications mainly exploit inherent nanostructured features, where increased surface area and quantum confinement affects mainly contribute to improved activity [2]. Such modern tools provide a gateway to assemble these exceptional nanostructures into numerous functional models [3].

Carbon nanomaterials e.g. carbon nanotubes (CNTs) and graphene have attracted great interest of the scientific community due to their excellent structural, electrical, optical and mechanical properties [4]. The exceptional properties of these materials can be combined to design applications where these hybrid materials offer better activity due to the synergistic effects of more than one nanomaterials [5]. These developed composite materials can influence the behavior by improving conductivity and offer easy methods to align for proper device fabrication, which improve sensitivity and selectivity [6,7].

In past years, many fabrication methods have been established for the development of CNTs based hybrid materials to enhance their potential applications in diverse fields. Among those approaches to fabricate such materials consist of covalent and non-covalent modification [8]. Covalent methods involve chemical functionalization with some defects, but non-covalent modification offers valuable substitution techniques to modify interfacial properties of CNTs. In these methods, nanostructures have been fabricated in the form of clusters by using CNTs as a template [7]. Metal and metal oxide/CNTs hybrids have increased their potential in different applications like advanced oxidation processes, sensors, and other catalytic processes. Some bio-reagents can be used to add functional moieties onto CNTs which induce van der Waals interactions to produce a molecular complex to enhance the loading of nanoparticles onto CNTs [9,10]. Herein, the catalytic effects of nanoparticles are combined that act as the reaction epicenter to increase the electron transfer rate, which leads CNTs to have greater interactions, consequently developing hybrid with remarkable characteristics [11].

Ascorbic acid is an essential vitamin which is a key catalyst for many important enzymatic reactions to initiate defense mechanisms against diseases [12]. It is an important medication for the treatment of minor diseases like the common flu to major diseases like cancer and AIDS [13]. The pharmaceutical, food, cosmetics, and chemical industries have used ascorbic acid tremendously for its antioxidant properties [14]. The large-scale industrial processes require stringent quality control which necessitates to develop an accurate, reliable and robust method for monitoring ascorbic acid concentrations in routine examinations. Materials with high electrical conductivity and good stability, such as, metal and metal oxide nanoparticles [15,16], graphene/CNTs [17] nanohybrids of metal nanocubes e.g. manganese, platinum, zinc and tungsten nanoparticles loaded onto CNTs as a transducer material have been reported [18] for the analysis of ascorbic acid. All of the mentioned materials revealed better performance, however, to acquire better sensitivity other nanomaterials with novel morphology are still required.

Cerium oxide (CeO₂) are rare earth metal oxides which have gained popularity owing to their structure, stable morphological orientation, chemical and optical properties in term of permeability, high porosity, extraordinary stability and large surface area [19]. Electrochemical methods are favorable platforms for the sensitive detection due the possibility of manipulating versatile transducers when combined with nanomaterials. It is especially important when already established monitoring methods are technically challenging, involving advanced equipment [20].

In this study, we investigate single step and cost-efficient method to synthesize ceria nanocubes decorated carbon nanotubes (CeO₂ NCs@CNTs) hybrid. To the best of our knowledge, this is the first work where the properties of ceria are augmented with the conductivity of CNTs and its potential for the selective detection of bioanalytes is explored. The morphology is investigated by scanning electron microscopy (SEM), transmission electron microscopy, whereas, X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) experiments were carried out for structural and functional analyses. Cyclic voltammetry (CV) studies were performed to explore the electrochemical activity of ascorbic acid. The designed materials exhibited a promising platform where the practical potential of this unique hybrid can be demonstrated for clinical diagnostics.

2. Materials and methods

2.1. Materials

All chemicals used in this work were of analytical grade. These were used as purchased from either Merck or Sigma-Aldrich and utilized without any modification. A sodium phosphate buffer solution (50 mM; pH 7.0) as a background medium was prepared for all experiments, using sodium phosphate monobasic monohydrate (0.34 g) in 50 mL of deionized water. All aqueous solutions were prepared using deionized water (Ultrapure Millipore-Milli Q system, (ρ = 18 MΩ cm).

2.2. Synthesis of CeO₂ NCs@CNTs hybrid materials

Functional moieties to generate supportive growth centers on the surface of CNTs were created with certain modification. Briefly, 0.01 g of CNTs were added into 5 mL (0.1M) of
a nitric acid solution and sonicated for 30 min. The solution was centrifuged at 4000 rpm and CNTs pellets were obtained by discarding the supernatant. The pH of the CNTs solution was maintained neutral by washing pellets comprehensively several times with deionized water. Along with CNTs pellets, 1 g of CeO₂ powder was added into 9 mL of methanol, sonicated for 30 min to make a homogenous solution, and a final volume was made by adding 1 mL of a NaOH solution (10 M). Dispersion of CNTs and CeO₂ were placed into a Teflon lining neatly and autoclaved at 180 °C for 24 h. The dispersion was kept at room temperature till it was cooled down. The precipitates were separated by centrifuging at 10,000 rpm, washed with deionized water and ethanol in turn, and then dried at 60 °C for 6 h. The obtained product was stored in desiccators for further utilization. It is denoted as CeO₂ NCs@CNTs to refer the design hybrid in this study. A schematic of the hybrid synthesis method is depicted in Fig. 1. For the preparation of CeO₂ NCs as a control, all steps were followed except the addition of the acid treated CNTs to the CeO₂ precursor.

2.3. Material characterization

The morphology of the hybrid was studied by scanning electron microscope (JEOL, JSM-7500 F), transmission electron microscope (TEM; JEOL, JSM-1010). X-ray diffraction (XRD) (Bruker D-8) was used for phase identification and provided information on unit cell dimensions. FTIR profiles of CNTs, CeO₂ NCs and CeO₂ NCs@CNTs hybrids were measured by a FTIR spectrometer in ATR (attenuate total reflection) mode. Three samples each of the study materials were prepared to obtain the information about their functional groups.

2.4. Electrochemical investigations of the CeO₂ NCs@CNTs hybrid

Firstly, the glassy carbon electrodes (GCEs) were polished by alumina slurries (1.0, 0.3, and 0.05 μm) for 1 min each, and later, rinsing thoroughly with ethanol and deionized water, to remove organic and inorganic contaminants. In order to remove adsorbed impurities, the cleaned electrodes were subjected to 10 cycles in 0.1 M H₂SO₄ solution between -0.2 to 1 V at 50 mV s⁻¹. To prepare a sensor, a suspension of hybrid was prepared by dispersing 0.5 mg in 1 mL deionized water. 10 μL out of this suspension were drop-casted on GC electrodes and dried in an oven at 60 °C for 5 min. The layers were then secured with nafion (2 μL of 5%) and all the devices were dried at room temperature for 24 h. To perform the control experiments, all preparatory steps were followed except the addition of the hybrid. Herein, 10 μL (0.5 mg mL⁻¹) each of CNTs and CeO₂ NCs dispersions in deionized water were drop casted over GCEs to obtain CNTs and CeO₂ modified control electrodes, respectively.

2.5. Sensor measurements

The electrochemical measurements were obtained using Autolab Potentiostate/Galvanostate (PGSTAT) and conventional three electrode method. A GC electrode modified with CeO₂ NCs@CNTs hybrid was employed as a working electrode, Ag/AgCl as a reference electrode and carbon rod as a counter electrode. All experiments were carried out in a sodium phosphate monohydrate solution (0.5 M). Before measurements, the background solutions were de-oxygenated with ultra-pure nitrogen gas for 2 min. The change in the peak of oxidation current was studied by running the cyclic voltammetry (CV) using a General-Purpose Electrochemical System Software (GPES version 4.9). All CV scans were analyzed at a scan rate of 50 mVs⁻¹ with a potential range (–0.2 to 1V). The final data was assembled in an excel sheet using Microsoft Excel.

3. Results and discussion

3.1. Morphology and structural characterization

The surface structure, shape, and dimension of the prepared materials were exclusively examined by field emission scanning electron microscopy (FESEM) and transmission electron
Fig. 2 – Morphology analysis; (A) FESEM image of CeO$_2$ NCs@CNTs hybrid, (B) FESEM image of CeO$_2$ NCs, (C) TEM images of CeO$_2$ NCs@CNTs hybrid, (D) TEM images of CeO$_2$ NCs.

microscopy. The resultant images are displayed in Fig. 2(A–D). The Micrograph (A) clearly shows a highly dense population of cubic structure of CeO$_2$, (CeO$_2$ NCs) 25–30 nm in size. It exposed the structural morphology of CNTs with the average size of 20–25 nm. However, at some places the aggregation was observed, which is probably due to the particles interacting with each other during solution-based treatment. This aggregation furnished porosity on the surface of CeO$_2$ NCs that increase its surface area [21] and outstanding performance can be assumed out of this morphology. When it is compared to control (Fig. 2B) it is evident that hybrid is showing the same level of population and morphology comparable to its control material. It shows the successful design of the hybrid materials with a huge population of CeO$_2$ NCs. Further the morphology was confirmed using TEM and it revealed that the average diameter of CNTs was about 20–25 nm populated with CeO$_2$ NCs (Fig. 2C). In terms of morphology and structure, both SEM and TEM results were found in close accordance.

The crystal structure and phase composition of the CNTs, CeO$_2$ nanocubes and the CeO$_2$ NCs@CNTs hybrid was investigated by using XRD (Fig. 3). The XRD spectra recorded for CNTs and as synthesized CeO$_2$ nanocubes showed sharp diffraction peaks at (002) for CNTs and (111), (200), (220), (311), and (222) for face center cubic CeO$_2$ standardized with (JCPDS card number 72-0746). The XRD pattern of CeO$_2$ NCs@CNTs hybrid displayed four peaks at 28.5, 33.1, 47.5 and 56.3°, which correspond to face center cubic CeO$_2$ [22]. The XRD peak of CNTs was not observed in the CeO$_2$ NCs@CNTs hybrid. It can be credited to the high degree of deposition of CeO$_2$ in CNTs.

The surface functionalization of pure CNTs, acid-treated CNTs and the CeO$_2$ NCs@CNTs hybrid was confirmed by FT-IR analysis (Fig. 4). Several absorption peaks can be seen for the acid treated CNTs across different regions (blue line). Absorption bands were found at 1280 cm$^{-1}$ for the carboxyl groups (C–O bond), at 1640 cm$^{-1}$ for C=O and at 3600 cm$^{-1}$ for the hydroxyl groups (O–H bond) [23]. These absorption peaks at different sites indicated that this type of acid treatment successfully added acidic groups on the surface of CNTs. The FTIR analysis of the CeO$_2$ NCs@CNTs hybrid without any absorption peaks confirmed the consumption of acidic groups due to the formation of the CeO$_2$ NCs@CNTs hybrid (black line).

3.2. Electrocatalytic performance

The electrochemical characteristics of the designed CeO$_2$ NCs@CNTs hybrid were investigated by the cyclic voltammetry method. A fine layer of material was carefully drop-casted on the surface of the neat glassy carbon electrode and the electrochemical study of the CeO$_2$ NCs@CNTs hybrid was carried out which was subjected to 0.5 mM ascorbic acid. The resulting responses are shown in Fig. 5. The GCE modified with CNTs yield greater current (40 μA) at −0.1 V (green line). In case of the hybrid, a prominent increase in current at 0.1 V was observed, with a very conspicuous and defined oxidation peak (blue line) as compared to bare and CeO$_2$ nanocubes only. It revealed very high electron transfer rate and electron cloud which generates faradic current across the hybrid modified electrode interface, however, strong oxidation at low potential (0.1 V) indicate extraordinary electrocatalytic potential. Importantly, almost three times the increase in current intensity (130 μA) confirmed the outstanding electrocatalytic activity of the hybrid in comparison to CeO$_2$ nanocubes or
CNTs. Whereas, insignificant redox peaks in response to the bare and CeO$_2$ modified GC electrode confirmed on the one hand the remarkable performance of our designed hybrid, and further shows poor electron transfer rate at the interface (purple and red line). This indicates the catalytic activity of CeO$_2$ nanocubes towards ascorbic acid. Separation of anodic (0.1 V) and cathodic (−0.2 V) potential was measured to be approximately 100 mV signifying enhanced electrode kinetics and reversibility of the process. This is the first study where CNTs are augmented with ceria nanocubes and the electrocatalytic potential is reported.

The CeO$_2$ NCs@CNTs hybrid offers several benefits such as ease in fabrication, simple assembly, and electrochemically activity. The conducting nature of hybrid belongs to oxygen vacancies present at metal oxide surface. The formation energy of metal interstitial and oxygen in CeO$_2$ NCs@CNTs hybrid is very low and these defects formed which in turn relate to experimentally elevated conductivity of hybrid [5]. The high sensitivity of the as designed material based sensor toward ascorbic acid was attributed towards high mass transfer owing to the pits and grooves of cubic shaped aggregation, good absorption, electronic communication between
CNTs and CeO$_2$ and surface roughness of the hybrid. It can be concluded that the synergy of both forms of nanomaterials has induced remarkable catalytic potential in the resulting hybrid. In the electroanalysis findings, the underlying mechanism of the observed electrochemical response can be justified. Specifically, the acidic treatment of the CNTs changes their diameter; their conductivity increases, which in turn enhances their surface energy due to carboxyl groups present onto CNTs [24]. These carboxyl groups, then act as reaction centers offering more binding domains to attach CeO$_2$ nanocubes [25]. On the other hand, the overall conductivity of the CNTs decrease due to structural impurities in the form of CeO$_2$ nanocubes but the electrocatalytic ability improved [26].

3.3. Analytical evaluation

Analytical performance of a sensor is an ability to recognize the changes of their micro environment with analytical accuracy. The CV responses of designed sensor were recorded against different concentration of ascorbic acid. A broad range of ascorbic acid concentration was covered (0.05–0.5 mM) and consequent responses are compiled in Fig. 6A. It can be seen that the current intensity gradually increased by increasing the concentration of ascorbic acid from 30 µA to 140 µA (linear regression = 0.98) (Fig. 6B). The linear relationship with a strong correlation coefficient (r = 0.98) confirmed that the ascorbic acid binding with the CeO$_2$ NCs@CNTs hybrid. The limit of detection and the limit of quantification were calculated to be 70 nM and 250 nM, respectively. The linear range and limit of detection of our designed sensors are compared with other published methods (compiled in Table 1). It manifests the analytical performance of our designed sensors is much superior as compared to other various materials. The high sensitivity and electrocatalytic efficiency of our sensor can be conferred to the outstanding morphology and chemical composition of CeO$_2$ NCs@CNTs hybrid.

![Graph](image)

**Fig. 5** – Sensor investigation; Cyclic voltammetry responses towards 0.5 mM ascorbic acid at the bare GC electrode, CeO$_2$ NCs GC electrode, CNTs GC electrode and CeO$_2$ NCs@CNTs hybrid modified electrodes; background electrolyte NaH$_2$PO$_4$·H$_2$O (0.5 M); scan rate 50 mVs$^{-1}$.

![Graph](image)

**Fig. 6** – Analytical parameter; (A) cyclic voltammetry response of the hybrid towards different concentration of ascorbic acid (0.05–0.5), (B) regression analysis the influence of ascorbic acid concentration.

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear range (mM)</th>
<th>Detection limit (nM)</th>
<th>References</th>
</tr>
</thead>
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<td>f-MWCNTs–NF–PtAu composite GCE</td>
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<td>8823</td>
<td>[28]</td>
</tr>
<tr>
<td>Graphene oxide (GO)/multiwalled carbon nanotubes (MWNTs) GCE</td>
<td>5.0–300</td>
<td>100</td>
<td>[29]</td>
</tr>
<tr>
<td>MWCNTS/CPE</td>
<td>0.6–112</td>
<td>20000</td>
<td>[30]</td>
</tr>
<tr>
<td>Pd/CNF composite GCE</td>
<td>0.05–4</td>
<td>1500</td>
<td>[31]</td>
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<tr>
<td>(AuNCs)/(AGR)/MWCNTs nanocomposite</td>
<td>10–150</td>
<td>270</td>
<td>[32]</td>
</tr>
<tr>
<td>Electrochemically reduced graphene oxide</td>
<td>0.5–0.2</td>
<td>30000</td>
<td>[29]</td>
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<tr>
<td>Reduced Graphene Oxide-ZnO composite</td>
<td>0.05–2.35</td>
<td>371</td>
<td>[33]</td>
</tr>
<tr>
<td>CeO$_2$ NCs@CNTs hybrid</td>
<td>0.05 - 0.5</td>
<td>70</td>
<td>This study</td>
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3.4. Selectivity studies

The electrochemical potential of the hybrid was further challenged by another molecule which is a structural and a functional competitor of ascorbic acid, i.e, uric acid. Electrochemical responses were measured when the modified electrode was exposed to 0.5 mM uric acid (Fig. 7). In this case, a clear and defined oxidation peak was observed at 0.5 V but with much less current intensity (30 μA as compared to 130 μA of ascorbic acid). The remarkable feature of the hybrid was its discern capability between the presence of two kinds of molecules. The peak separation between ascorbic acid and uric acid was found to be 400 mV which reveals outstanding selectivity of our sensor to recognize both analytes. In conclusion, CV responses establishes the electrochemical behavior of the sensor toward identifying both biomolecules. In fact, the chemical structure of ascorbic acid lack electronegative site (oxygen) in the ring which in turn cause rapid oxidation of molecules at lower potential with high current intensity than uric acid. Whereas, in uric acid, the ring structure contains an electronegative element (nitrogen), that require high potential to oxidize result in lesser response in peak height [27].

4. Conclusions

In summary, the different forms and chemical compositions of nanomaterials can be crafted together to incorporate parent properties in one material with enhanced functionalities. We have shown a facile method for the growth of ceria nanocubes on CNTs substrates. Microscopic studies confirmed the successful planting of the highly dense population of CeO₂ nanocubes onto functionalized CNTs. This morphology is related to the greater surface area and improved catalytic properties. Based on this CeO₂ NCS@CNTs hybrid, an electrochemical sensor was successfully designed for the detection of ascorbic acid. Highly sensitive catalytic signals were achieved yielding 70 nM as the lower limit of detection. This work opens up the possibility of combining different dimensions and compositions of nanomaterials for high performance applications.

Conflicts of interest

The authors declare no competing financial interest.

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