

Full Length Article

Selective electrochemical sensing of dopamine via solid-state hydrothermal β -cyclodextrin-functionalized selenium quantum dots-embedded with multiwall carbon nanotubes[☆]

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ARTICLE INFO

Keywords:

Electrochemical sensor
 β -CD-SeQDs-APBA-MWCNTs nanocomposite
 Carbon nanotubes
 Selenium quantum dots
 β -cyclodextrin
 Dopamine

ABSTRACT

The selective electrochemical sensor was developed based on the surface functionalized selenium quantum dots (SeQDs) by β -cyclodextrin (β -CD) and boronic acid moieties and their incorporation into the multiwall carbon nanotubes (MWCNTs) on the GCE and SPE electrodes. The prepared β -CD-SeQDs-APBA-MWCNTs nanocomposite-modified electrodes were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques for dopamine (DA) sensing. The SeQDs were synthesized using the solid-state hydrothermal approach without using solvent and demonstrated the average particle size of 6 nm. Initially, β -CD-modified SeQDs (β -CD-SeQDs) and then APBA (i.e., β -CD-SeQDs-APBA), and finally, this β -CD-SeQDs-APBA was functionalized with MWCNTs through non-covalent interactions. To the best of our knowledge, the novel β -CD-SeQDs-APBA-MWCNTs sensor was selectively detected DA in both GCE and SPE electrodes with the linear concentration ranges of 0–1000 nM and 0–5 μ M in the PBS buffer using both CV and DPV techniques, respectively. These β -CD-SeQDs-APBA-MWCNTs nanocomposite was selectively applied for DA sensing and achieved desired detection limits over both GCE; 70.9 nM and 113.38 nM and SPE; 0.76 μ M and 0.82 μ M electrodes in the PBS buffer via CV and DPV techniques, respectively. In addition, nanocomposite showed high stability, reproducibility, and improved selectivity. The practicality of the sensor was also investigated for DA sensing in real samples like human serum.

1. Introduction

Dopamine (DA), a catecholamine-based neurotransmitter, controls the central nervous system, hormonal system, renal system, and metabolism. Alzheimer's, Parkinson's, Huntington's, schizophrenia, and depression originate from its abnormalities [1]. Endogenous DA levels in the brain range from 10 nM to 1 μ M, whereas healthy persons have levels between 0.01 and 10 μ M [2]. Thus, DA detection requires high-sensitivity, high-specificity sensors. So far, a myriad of conventional detection methods is existing, which include HPLC-MS, capillary electrophoresis, chemiluminescence, fluorescence, colorimetry, and surface-enhanced Raman spectroscopy (SERS) [3–8]. Unfortunately, these DA detection devices are neither cost-effective nor time-saving. In general scenario, quantifying DA in physiological fluids aids neurological illness diagnosis. Therefore, we need targeted, precise, and simple methods for

DA determination. Among these, electrochemical sensing is a popular approach because of its sensitivity, convenience, robustness, and reproducibility. Initially, it is very crucial to achieve highly-selective electrochemical sensors for DA determination because of the co-existence of structural analogues such as epinephrine (EP) and norepinephrine (NE), which can interfere redox peak current signals at glassy carbon electrodes (GCEs). By keeping this in mind, our team has been dedicated to the designing of divergent electrochemical biosensors for DA using 1D, 2D, and 3D materials such as carbon nanotubes (CNTs), covalent organic frameworks (COFs), metal organic frameworks (MOFs), MXenes, and conjugated microporous polymers (CMPs) [9–12]. Among these materials, MOFs appear to be promising due to their multifarious potentials, such as excellent porous crystallinity, enormous surface area, tunability, and mechanical stability. Significantly, its convenient surface functionalization through adopting desirable

[☆] This article is part of a special issue entitled: 'MCARE 2024_APSUSC' published in Applied Surface Science.

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electrocatalytic features of diversified 0D and conductive materials allows them to be explored as excellent sensing materials for detecting DA at nanomolar levels [10,11].

In this context, electrochemically active surface-functionalized ligands are crucial for attaining desired sensitivity. For instance, β -cyclodextrin (β -CD) is an oligosaccharide that is composed of seven glucose units with a toroidal structure with a hydrophobic inside and a hydrophilic outside. β -CD is often used as a molecular receptor because it has a high level of molecular selectivity and enantioselectivity. This is especially true in medicine, the chemical industry, and electrochemical sensors. Till now, multifarious electrochemical sensors using β -CD have been reported for DA sensing [13–17]. Based on these studies, it is commonly believed that β -CD can enhance the dispersion and stability of various nanocomposites [18]. Especially, the host and guest recognition capabilities of hydrophobic cavities have the potential to enhance the ability of composite materials that identify each other in a distinct manner. Moreover, β -CD can contribute substantial electrochemically active surface area (EASA) and abundant active sites, and thereby accelerating the transfer of electrons between molecules and electrodes, and turning sensors into conveniently selective and sensitive devices. By forming inclusion complexes, β -CD can participate in both hydrophobic and hydrogen-bonding interactions. Thus, β -CD serves as a modulator, augmenting the sensitivity and selectivity of electrochemical sensors [19]. For instance, through host–guest interactions between β -CD and pyridoxal (PYL), our research team has previously designed an ultra-sensitive fluorescent sensor that utilizes the ability to switch on the fluorescence based on DA concentrations [20].

Semiconductor nanocrystals, or quantum dots (QDs), are nanomaterials with diameters ranging from 2 to 10 nm. These materials differ from bulk materials due to their high surface-to-volume ratio and adjustable bandgap, which are a result of quantum confinement phenomena. High photochemical stability, narrow emission spectra, and wide absorption spectra distinguish QDs as fluorescent. Their unique optical and electrical characteristics have led to applications in biology, medicine, sensing, energy, electronics, polymers, and optoelectronics. Researchers have dedicated decades to creating QD materials that combine any metal with a chalcogenide element from group VI. The common chalcogenides include selenium (Se), tellurium (Te), and sulfur (S). Numerous researchers have extensively studied compounds containing cadmium, such as CdTe and CdSe. Despite its remarkable photoluminescence and electric/optoelectronic characteristics, its hazardous toxicity prompts researchers to seek alternatives [21,22]. In this regard, several reports have already been published based on the SeQDs [23–25]. Yang et al. developed a reversible fluorescent probe based on the extensive radical scavenging property of the SeQDs. These probes exhibit superior sensitivity and selectivity in scavenging $\cdot\text{OH}$ radicals and monitoring their activities in living cells [26]. In recent times, research has been widely expanded to the synthesis of sole SeQDs, selenide-based QDs, and Se-doped nanozymes for sensing and radical scavenging applications [27–29]. For instance, Li et al., synthesized SeQDs using selenocystine as a precursor via hydrothermal method. But, the average diameters of the SeQDs were very large i.e., in the range of 20–40 nm, which attributed to their intermolecular hydrogen bonding effects [30]. In another study, researchers produced trigonal silica-SeQDs using selenous acid (H_2SeO_3) and tetraethyl orthosilicate (TEOS) as precursors by employing a solvothermal approach at 150 °C. Though, these silica-SeQDs were investigated for curcumin sensing by fluorescence approach, unfortunately, the larger average diameters (i.e., 60 and 120 nm) of the prepared silica-SeQDs are suffering for electrochemical sensing purposes [31]. Huang et al. developed sulfur/selenium-doped CQDs using sodium selenite as the selenium precursor by hydrothermal method. These selenium-codoped CQDs were exhibited a better narrow size distribution with an average size around 6 nm and exploited for radical scavenging abilities [32]. Based on the molecular structure of DA, its electrooxidation can occur by transforming hydroxyl ($-\text{OH}$) groups into ketonic ($\text{C}=\text{O}$) groups. Adding heteroatoms, like

chalcogenides, to QDs has been shown in many studies to improve their surface features, electronic structures, and charge carrier mobility. Earlier studies also suggested that the availability of redox centers from chalcogenide sites significantly enhances the electrocatalytic sensing capabilities for a diverse range of molecules [31,33–35].

According to numerous research studies, it is suggested that the QDs, or CDs, contain specific chemical moieties, such as boronic acid ($\text{B}-\text{OH}$) groups, that demonstrate an impressive capability to recognize 1,2-cis-diol-functional compounds like DA. Especially at pH around 7.4, the ($\text{B}-\text{OH}$) groups adopt a tetrahedral configuration, enhancing their ability to bind with DA. For instance, the large surface area of the CNTs significantly enhanced the density of the ($\text{B}-\text{OH}$) receptors over the electrode surfaces and immediately allowed them to specifically interact with DA [36–38].

Unfortunately, pristine multiwall carbon nanotubes (MWCNTs) aren't very selective or sensitive because there isn't much charge transfer and their inefficiency for sufficient chemical interactions with the analyte molecules. In this context, the convenient surface functionalization of the MWCNTs is allowing the enhancement of the interfacial interaction with analytes [39]. Thus, in recent times, surface functionalized MWCNTs or its integration with other nanoscale materials (i.e., nanohybrids) including 0D, 1D, and 2D materials have gotten a lot of attention owing to their unique properties, such as their high chemical stability, reasonable specificity, and chemical reactivity in electrochemical sensor applications [40–44]. Molecular partners that either donate or accept electrons are more likely to stick to nanotubes because they have polar groups on their surface, which makes for a beneficial response [45–47].

Inspired by the above discussion, our team developed a nanocomposite in this study, consisting of MWCNTs and surface-functionalized SeQDs. The SeQDs were modified in the following manner: firstly, through β -CD (i.e., β -CD-SeQDs) and then APBA (i.e., β -CD-SeQDs-APBA) moieties, and finally, β -CD-SeQDs-APBA was conjugated with MWCNTs via non-covalent interactions. To the best of our knowledge, the novel β -CD-SeQDs-APBA-MWCNTs sensor was selectively detected DA in both GCE and SPE electrodes with the linear concentration ranges of 0–1000 nM and 0–5 μM in the PBS buffer using both CV and DPV techniques, respectively (Scheme 1).

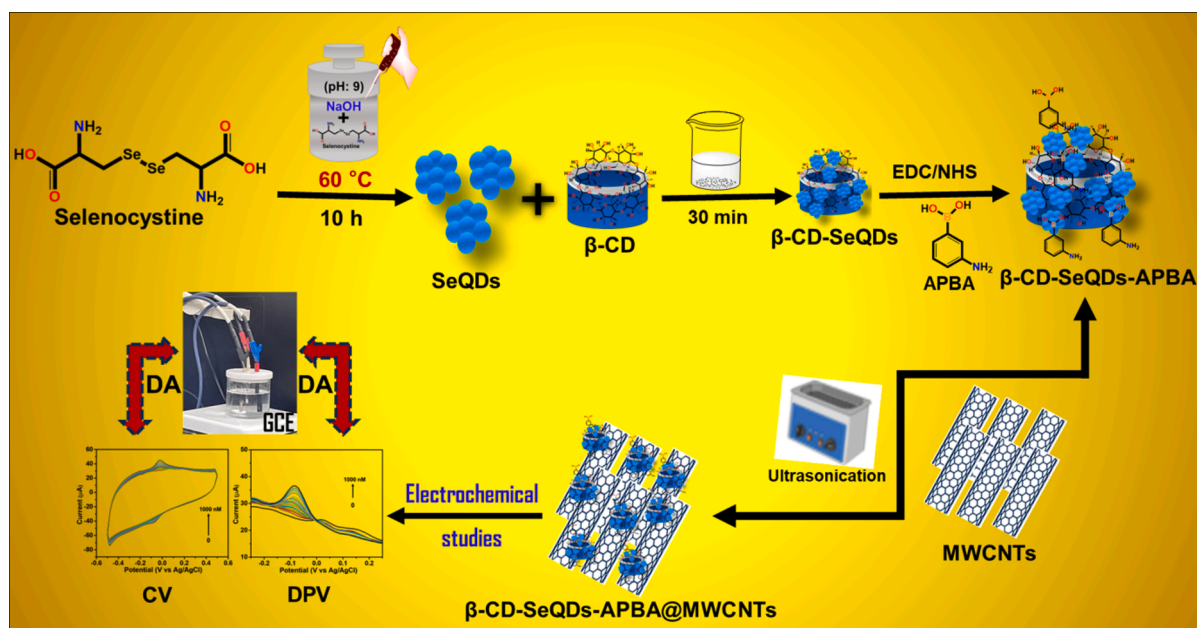
2. Experimental section

2.1. Materials and Reagents

All chemicals and solvents were purchased from commercial suppliers and used without further purification. L-Selenocystine ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{Se}_2$), dopamine hydrochloride ($\text{C}_8\text{H}_{11}\text{NO}_2\cdot\text{HCl}$), γ -aminobutyric acid ($\text{NH}_2(\text{CH}_2)_3\text{COOH}$), serotonin ($\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$), epinephrine ($\text{C}_9\text{H}_{13}\text{NO}_3\cdot\text{HCl}$), norepinephrine ($\text{C}_8\text{H}_{11}\text{NO}_3\cdot\text{HCl}$), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), L-glutamic acid ($\text{C}_5\text{H}_9\text{NO}_4$), L-cysteine hydrochloride ($\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}\cdot\text{HCl}$), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxy-succinimide (NHS), human serum (male AB plasma), and sodium hydroxide (NaOH) were obtained from Sigma Aldrich. Deionized water was used for all experiments. Hydrochloric acid (HCl) and ethanol were obtained from Duksan, South Korea. Deionized water and Phosphate-buffered saline (PBS, 10 mM, pH 7.4) was used for sensing experiments.

2.2. Characterizations

SEM images were acquired from a Hitachi S-4700 FE-SEM (Japan). For all samples, imaging was performed in a high vacuum at an emission current of 9000 nA. TEM was performed using JEM 3010, JEOL Ltd., Japan, at 300 kV. All sample solutions were treated in an ultrasonic (Branson branson ultrasonic bath) bath before the deposition to reduce aggregation. Powder X-ray diffraction (PXRD) patterns of the samples were measured using Ultima IV diffractometer (Rigaku) at the Smart



Scheme 1. Schematic illustration for the synthesis of β -CD-SeQDs-APBA-MWCNTs and its electrochemical detection of DA.

Materials Research Center for IoT (SMRCI), Gachon University under a 4-kW X-ray generator (scan range: $2\theta = 5\text{--}90^\circ$). The Fourier transform infrared spectra were recorded in the range $200\text{--}4000\text{ cm}^{-1}$ on Vertex 70, Bruker, USA. X-ray photoelectron spectra (XPS) were measured using the Thermo Scientific K-AlphaTM X-ray Photoelectron Spectrometer with a range of motion ($100\text{--}4000\text{ eV}$), 128 channel detectors, a double-focusing hemispherical analyzer (180°), and a micro-focused X-ray source (Al K α). Cyclic voltammetry and DPV were carried out in WizMac WizEIS-1200 Premium voltammeter at room temperature in a standard three-electrode cell, where a glassy carbon (GC) (area = 0.07 cm^2) is used as the working electrode, Pt wire as the counter electrode, and Ag/AgCl/KCl (sat) as reference electrode. Before each casting, GCE was polished with alumina slurry ($0.05\text{ }\mu\text{m}$) in an eight-shaped direction and cleaned with ethanol and DI water. We purchased the screen-printed carbon electrode (SPCE), Poten from Shenzhen More-Suns Electronics co. Ltd, China.

2.3. Synthesis of SeQDs

In this study, SeQDs were synthesized via solid-state hydrothermal approach. In a typical synthesis, selenocystine (100 mg) was placed in beaker and the pH was maintained at 9 by adding NaOH to enhance the solubility of selenocystine. The resulting powdered solution was taken in a Teflon-lined autoclave and heated at $60\text{ }^\circ\text{C}$ for 10 h. The as-synthesized cream-color solution of SeQDs washed thoroughly thrice using DI water and centrifuged (9000 rpm for 20 min). Further, SeQDs were dialyzed against DI water for 24 h using a dialysis membrane (MWCO: 100–500 D) and filtered through a syringe filter ($0.22\text{ }\mu\text{m}$) to remove impurities. Finally, SeQDs were dried under hot-air oven and refrigerated for further functionalization purposes. The purified SeQDs were dissolved in 100 mL DI water for further functionalization steps.

2.4. Synthesis of β -CD-SeQDs

In a typical synthesis, 20 mg of β -CD and 5 mL of SeQDs were ultrasonicated for 30 min. To the above-solution, 25 mL of PBS (10 mM, pH 7.4) was added and finally obtained the β -CD-SeQDs. The β -CD-SeQDs were rinsed, washed thrice using DI water and centrifuged (9000 rpm for 20 min). Further, β -CD-SeQDs were dialyzed against DI water for 24 h by employing a dialysis membrane (MWCO: 100–500 D) and filtered

through a syringe filter ($0.22\text{ }\mu\text{m}$) to remove un-reacted β -CD moieties and allied impurities. Finally, β -CD-SeQDs were freeze-dried and refrigerated for further characterization and electrochemical sensing experiments.

2.5. Synthesis of β -CD-SeQDs-APBA

The β -CD-SeQDs-APBA was prepared by EDC/NHS coupling reaction. Herein, 15 mg of EDC was added to 20 mL of PBS and thoroughly shaken for 30 min and obtained a white-colored solution. To this solution, 10 mg of NHS was added and stirred for 2 h and finally 10 mg of APBA was mixed and continuously stirred for 3 h under room temperature. The resulting β -CD-SeQDs-APBA was rinsed and washed thrice with DI water and centrifuged thrice (9000 rpm for 20 min). Further, β -CD-SeQDs-APBA was dialyzed against DI water for 24 h using a dialysis membrane (MWCO: 100–500 D) and filtered using a syringe filter ($0.22\text{ }\mu\text{m}$) to purify un-reacted APBA and β -CD-SeQDs. Finally, β -CD-SeQDs-APBA was freeze-dried and refrigerated for further characterization and electrochemical studies.

2.6. Synthesis of β -CD-SeQDs-APBA@MWCNTs nanocomposite

In a typical synthesis of final nanocomposite (β -CD-SeQDs-APBA@MWCNTs), 10 mg of MWCNTs were dispersed in DI water (25 mL) and the solution was ultrasonicated for 1 h. Later, 10 mg of β -CD-SeQDs-APBA was added to the dispersed solution of MWCNTs and ultrasonicated for 2 h. Consequently, black-colored nanocomposite of β -CD-SeQDs-APBA@MWCNTs was obtained in the form of dispersed suspension. The nanocomposite was washed thrice with DI water and centrifuged thrice (9000 rpm for 20 min) to remove un-reacted pristine MWCNTs and β -CD-SeQDs-APBA moieties. Further, nanocomposite was freeze-dried and refrigerated for further characterization and electrochemical studies. The corresponding digital photographs of the powdered forms of precursors and the resulting SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs are illustrated in Fig. S1.

2.7. Electrochemical characterization of modified GCEs and SPEs for DA sensing performance

Our research team has investigated the electrochemical sensing response of DA by employing different modified electrodes such as GCEs and SPEs at a pH of 7.4 via CV and DPV techniques. Furthermore, we studied the comparison of electrochemical behavior for the different modified electrodes, including SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs-GCEs and -SPEs, at a fixed concentration of DA in PBS. We used 1 mM PBS (pH = 7.4) for obtaining the impedance response from SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs-GCEs and -SPEs in frequency ranging from 0.1 Hz to 10^6 Hz with an amplitude of 10 mV. The 0.5 mg of β -CD-SeQDs-APBA@MWCNTs was dispersed in 1 mL of ethanol and further we added 30 μ L of nafion solution and sonicated for 15 min. From the above solution, 10 μ L of sample was coated on the GCE and SPE, and finally, we conducted electrochemical experiments using CV and DPV techniques in the range from -0.5 to $+0.5$ V.

3. Results and discussion

3.1. Materials characterization

The morphological features of the prepared SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs were investigated by TEM and SEM techniques. The as-synthesized SeQDs exhibited a uniform dispersion with spherical shape with an average particle size of 6 nm [Fig. 1. a, b (inset)] [32]. After the modification of SeQDs through the β -CD (i.e., β -CD-SeQDs), the sheet like appearance can be visible over the surfaces of SeQDs (Fig. 1. c). This appearance is results from the β -CD moieties and corroborated with the previous β -CD-modified CDs [20]. However, a slight increase in the aggregation of SeQDs can be observed, which has been resulted from the β -CD moieties.

Further, the final nanocomposite (β -CD-SeQDs-APBA@MWCNTs) has shown the long tubular coil-like morphologies with an average diameter of 60.4 nm, where the spherical nanostructures of the prepared β -CD-SeQDs-APBA were embedded on the surfaces of the final nanocomposite [Fig. 1. d, e (inset)]. These results are consistent with the morphological features of the formerly reported covalently functionalized MWCNTs with selenium-derivatives [46]. Further, morphologies of β -CD-SeQDs-APBA@MWCNTs were investigated through the TEM images at other magnifications, which again confirmed the similar morphology (Fig. S2). In addition, SEM images of β -CD-SeQDs-APBA@MWCNTs were analyzed at different magnifications, which demonstrated the similar morphology as seen from TEM images [Fig. 1. f (inset)]. The obtained morphologies of the final nanocomposite are highly corroborated with the earlier synthesized nanohybrids [41,46]. The EDX-elemental mapping analysis for the SeQDs has exhibited mainly carbon (C), oxygen (O), and selenium (Se) elements (Fig. S3a-c). Further, it is confirmed with the EDX spectral analysis, as shown in Fig. S4. From the SEM images of β -CD-SeQDs, it is signified that the aggregation of SeQDs has resulted from the β -CD moieties (Fig. S5). However, as compared to the morphology of β -CD-SeQDs, high existence of the spherical nature was observed in the β -CD-SeQDs-APBA, which suggests that the APBA moieties were embedded well all over the surfaces of β -CD-SeQDs (Fig. S6). Further, the EDX-elemental mapping analysis and the SEM-EDX spectral analysis reveals the presence of elements including C, O, and Se (Fig. S7a-c and Fig. S8). Further, the EDX-elemental mapping analysis and the EDX spectral analysis showed the elements C, O, Se, N, and Na (Fig. S9a-c and Fig. S10).

The phase composition of the pristine MWCNTs, SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs were thoroughly investigated through the powder XRD technique (Fig. 2a). The XRD pattern for the pristine MWCNTs has shown two distinct peaks at 25.94° and 43.81° , which corresponds to the graphitic planes of (002) and (100), respectively (black curve) [39]. The XRD pattern of the prepared

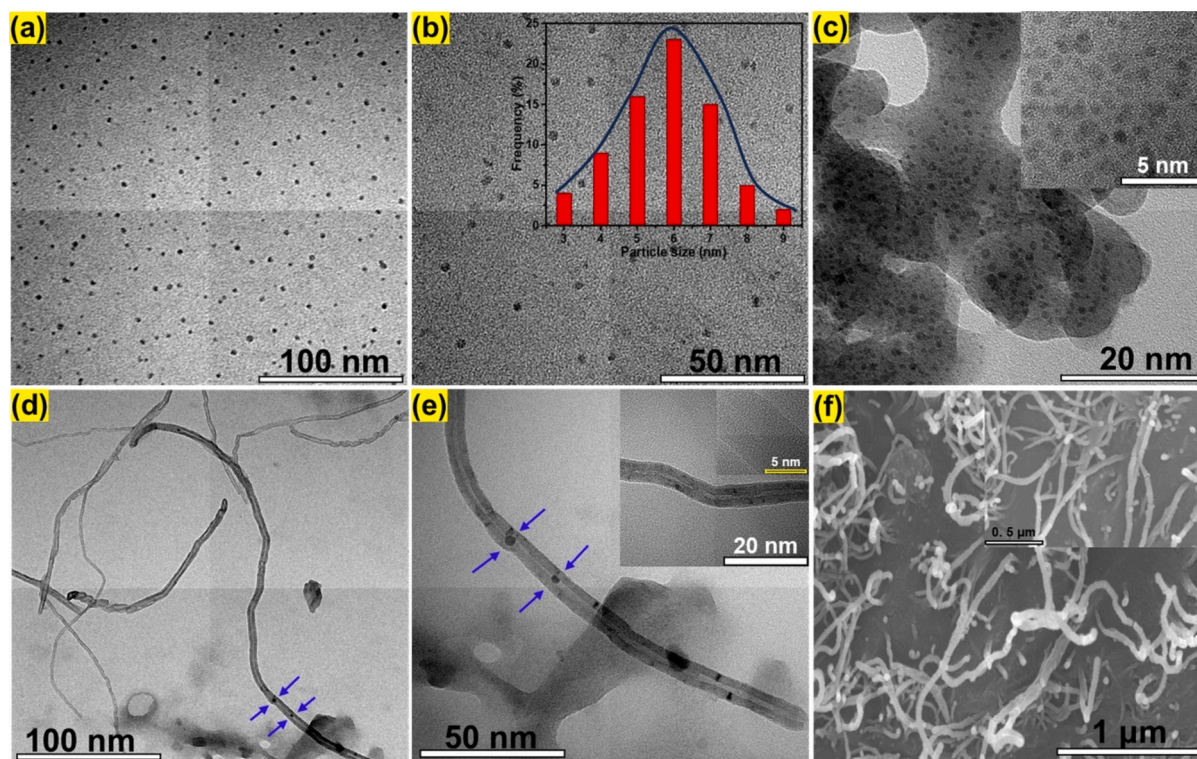


Fig. 1. (a, b) TEM images of SeQDs. The inset (b) shows the particle size histogram of SeQDs. (c) Low-resolution TEM image of β -CD-SeQDs. The inset (c) shows the high-resolution TEM image of β -CD-SeQDs. (d, e) TEM images of β -CD-SeQDs-APBA@MWCNTs. The inset (e) shows the low and high-resolution TEM images of β -CD-SeQDs-APBA@MWCNTs. (f) SEM image of β -CD-SeQDs-APBA@MWCNTs. The inset (f) representing the high-resolution SEM image of β -CD-SeQDs-APBA@MWCNTs. Scale bars: 1 μ m and 0.5 μ m, respectively.

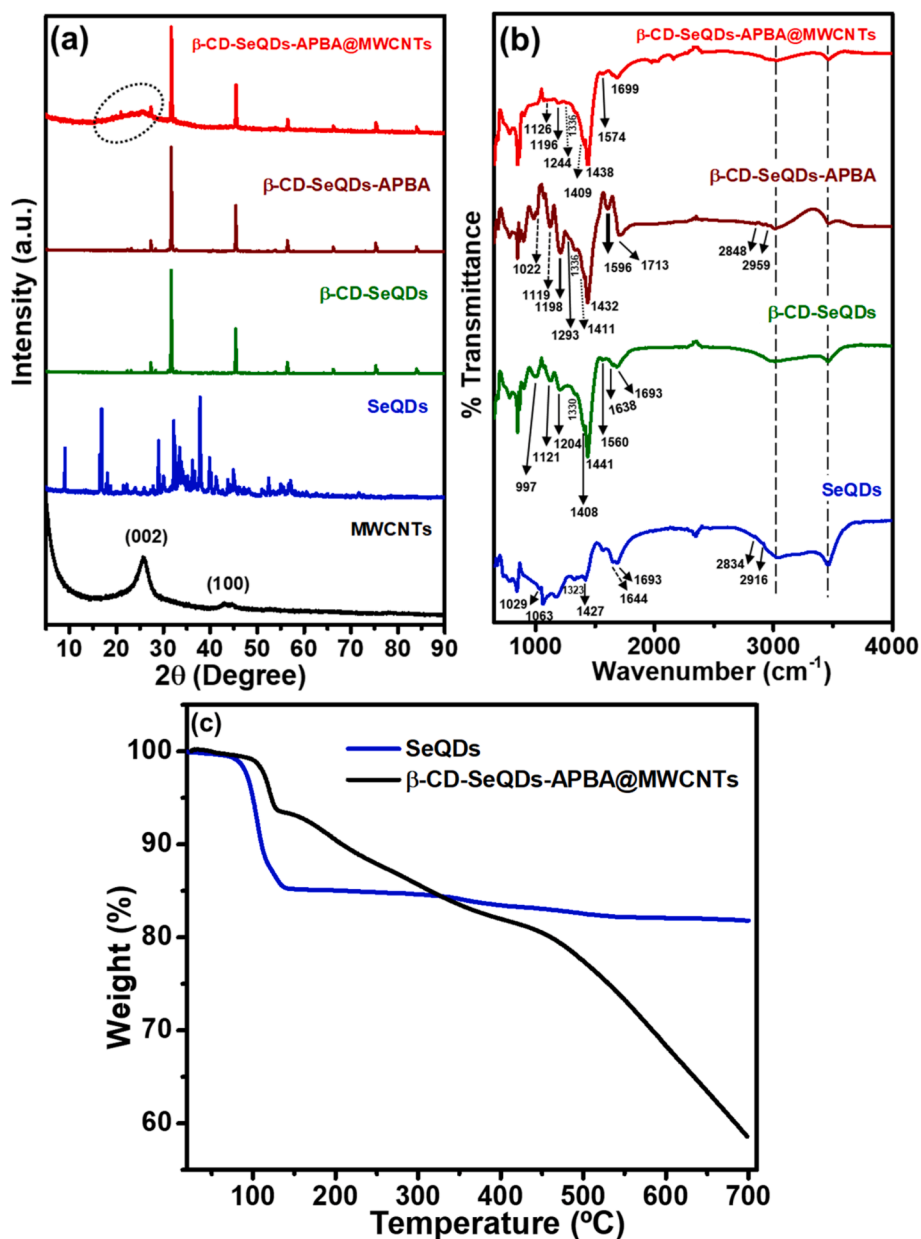


Fig. 2. (a) XRD patterns of the pristine MWCNTs, SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs, (b) FT-IR spectra of the SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs, and (c) TGA plots for the SeQDs and β -CD-SeQDs-APBA@MWCNTs.

SeQDs has shown the multiple sharp peaks at 26° , 28.88° , 41.26° , 44.97° , 48.12° , 52.41° , 55.08° , 60.30° , 62.59° , 64.98° , and 71.63° corresponding to the (100), (101), (110), (102), (111), (201), (112), (103/202), (210), (211), and (113), respectively (blue curve). These lattice planes were attributed to the bulk selenium, and signify the formation of trigonal SeQDs as indexed from the formerly reported similar XRD patterns (JCPDS card no. 06-0362) [31,48]. The other short-intense peaks were observed in the region between 20 and 25° are responsible for the carbonization while formation of the SeQDs [49]. Further, XRD pattern of β -CD-SeQDs has shown moderately sharp peaks at 27.2° and 28.02° . The high intensity sharp peaks were observed at 31.76° , 45.45° , 56.27° , 66.20° , 75.23° , and 83.74° , which are resulted from the SeQDs (green curve). Interestingly, XRD patterns of β -CD-SeQDs-APBA has also shown the similar sharp peaks, which suggests that the boronic acid-functionalization of the β -CD-SeQDs does not affect the crystal phase of native SeQDs (brown curve). In the XRD patterns of β -CD-SeQDs-APBA@MWCNTs, the peak at portion between 20 and 30°

is apparently broadening, where a graphitic plane of (002) was observed at 25.77° , which resulted from the pristine MWCNTs [39]. Meanwhile, the other portion following the very similar XRD patterns of β -CD-SeQDs-APBA (red curve). These results are highly consistent with the earlier reported XRD patterns of covalently functionalized MWCNTs by selenium-derivatives [46]. Overall, these results are highly signifying that the final nanocomposite was successfully synthesized from the two different nanomaterials i.e., MWCNTs and SeQDs.

Fig. 2b shows the FT-IR spectra of the prepared SeQDs, β -CD-SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs, which demonstrated their chemical environment and divergent functional groups. The FT-IR spectrum of SeQDs has shown typical (–OH) stretching vibrations around 3020 and 3456 cm^{-1} . The bands at 1029 , 1063 , 1644 , and 1693 cm^{-1} are responsible for the (C–O), (C–C), (C = C), and (C = O) stretching vibrations, respectively [2]. The two bands at 2834 and 2916 cm^{-1} are attributed to (C–H) stretching vibrations. The bending vibrations of (C–O) and (C–H) groups were identified at 1323 and 1427

cm^{-1} . In the FT-IR spectrum of β -CD-SeQDs, stretching vibrations of (C–O), (C–N), (C = C), and (C = O) groups were observed at 1204, 1330, 1638, and 1693 cm^{-1} , respectively. The bending vibrations of (C = C), (C–H), and (N–H) groups were observed at 997, 1441, and 1560 cm^{-1} , respectively. The peak at 1408 cm^{-1} is assigned for the asymmetric stretching vibrations of (COO[−]) groups. Significantly, the broadening of the band was observed at 3009 and 3460 cm^{-1} , which implied the presence of typical (–OH) stretching vibrations. The typical band at 1121 cm^{-1} is responsible for the stretching vibrations of (C–O–C), which formed from the β (1,4)- glycosidic bonds from β -CD structure [20,50]. These results are corroborating with the similar chemical environments of the earlier β -CD-modified CDs and thereby suggesting that the SeQDs were functionalized with the β -CD moieties [13,20]. Further, the APBA-functionalization of the β -CD-SeQDs was confirmed by the presence of multiple peaks at 1022, 1293, 1336, 1411, and 1713 cm^{-1} , which are responsible for the (B–O–H) deformation, (C–B), (C–N), (B–O), and (C = O) stretching vibrations, respectively [51]. The peaks at 1119 and 1198 cm^{-1} are ascribed to the B–O–H bending vibrations. The bands at 1432 and 1596 cm^{-1} are attributed to the bending vibrations of (C–H) and (N–H) groups, respectively [52]. In addition, the two bands at 2848 and 2959 cm^{-1} are responsible for the (C–H) stretching vibrations. The absorption bands were slightly shifted to 3002 and 3455 cm^{-1} , which signifies the existence of (–OH) stretching vibrations. The existence of (C = O), (N–H), and (–OH) groups on the surface of β -CD-SeQDs-APBA nanostructures signify the formation of amide (O = C–N–H) bond through the EDC/NHS coupling reaction [53]. The FT-IR spectrum of the final nanocomposite i.e., β -CD-SeQDs-APBA@MWCNTs has demonstrated two bands at 1126 and 1196 cm^{-1} , which are ascribed to B–O–H bending vibrations. The bands at 1244, 1336, 1411, and 1699 cm^{-1} are attributed to (C–B), (C–N), (B–O), and (C = O) stretching vibrations, respectively. The bands at 1438 and 1574 cm^{-1} are responsible for the bending vibrations of (C–H) and (N–H) groups, respectively. The peak at 1409 cm^{-1} is assigned for the asymmetric stretching vibrations of (COO[−]) groups. Both absorption bands of (–OH) stretching vibrations from the FT-IR spectrum of β -CD-SeQDs-APBA were slightly shifted to 3040 and 3458 cm^{-1} .

The thermal stability for the SeQDs and β -CD-SeQDs-APBA@MWCNTs was studied using the TGA analysis (Fig. 2c). The initial weight losses (14.8 % and 6.4 %) were observed from the SeQDs and β -CD-SeQDs-APBA@MWCNTs at temperatures 139° and 132°, respectively. These weight losses are responsible for the degradation of hydroxyl (O–H) moieties on the surfaces of both SeQDs and final nanocomposite. More importantly, in the temperature range between 139°–700°, SeQDs exhibited high thermal stability with a low weight loss of 3.27 %. This also imply that the synthesized SeQDs comprising of possibly elemental selenium rather than in ionic form, which accounted for its high thermal stability [54]. While in the case of β -CD-SeQDs-APBA@MWCNTs, the temperature range between 132°–396°, further weight loss (11.50 %) was occurred. Significantly, at the temperature above 350°, the degradation of β -CD moieties will occur due to the depolymerization of its glycosidic linkages [55]. Around the temperature range of 396° to 700°, the final weight loss of 17.98 % was observed in the β -CD-SeQDs-APBA@MWCNTs. This is mainly due to the decomposition of aromatic conjugated heteroatom organic moieties; (C = O) (C–N), and (B–OH). In addition, the decomposition of carbon backbone of MWCNTs from the β -CD-SeQDs-APBA@MWCNTs was also contributed to the final weight loss [56]. The overall weight losses of 18.07 % and 41.59 % were observed in the SeQDs and final nanocomposite, respectively (blue and black curves). The overall less weight loss% of SeQDs in contrast to the final nanocomposite is believed to be the formation of highly stable carbonized SeQDs. Again, these results are suggesting that that the final nanocomposite is properly constructed with functionalized β -CD-SeQDs-APBA and MWCNT nanostructures.

The chemical valence states of the SeQDs, β -CD-SeQDs-APBA, and β -CD-SeQDs-APBA@MWCNTs were studied by employing XPS technique. The total survey spectrum of SeQDs showed different elements

including Se 3d, C 1 s, Na KLL, O1s, and Na 1 s with binding energies of 61.71, 284.69, 495.7, 530.65, and 1072.33 eV, respectively (Fig. S11a). The corresponding individual high-resolution XPS spectra for the SeQDs are shown in Fig. S11b–e. The high-resolution XPS spectra of Se 3d show two main deconvoluted peaks at 53.73 and 59.03 eV indicating Se 3d_{5/2} and Se 3d_{3/2}, respectively (Fig. S11b) [57]. The high-resolution XPS spectra of C 1 s show binding energies of 285.11 and 288.89 eV, which are responsible for the (C–C/C = C/C–Se) and (O–C = O), respectively (Fig. S11c) [27]. The XPS spectra of the O 1 s demonstrate four distinct peaks attributed to the (C–O), (C–OH/C–O–C), (Na KLL), and (O–C = O) functional groups at 529.86, 531.31, 532.66, and 534.16 eV, respectively (Fig. S11d). The XPS spectrum of Na 1 s revealed a typical peak at 1071.50 eV (Fig. S11e).

Furthermore, the valence states of the different chemical species were investigated for the as-functionalized β -CD-SeQDs-APBA using XPS analysis. The total survey spectrum of β -CD-SeQDs-APBA revealed a myriad of elements including Se 3d, B 1 s, C 1 s, N 1 s, O 1 s, and Na 1 s at 54.12, 191.14, 285.05, 532.45, and 1072.35 eV, respectively (Fig. S12a). The corresponding individual high-resolution XPS spectra for the β -CD-SeQDs-APBA are shown in Fig. S12b–f. The high-resolution XPS spectra of C 1 s show four deconvoluted peaks at 283.48, 284.78, 286.01, and 287.92 eV, which are assigned to the (C–B), (C–C/C = C/C–Se), (C–N/C–O), and (C = O/N–C = O), respectively (Fig. S12b). The XPS spectra of the N 1 s exhibited three peaks at 398.54, 399.96, and 401.2 eV, which are responsible for the pyridinic-N, pyrrolic-N, and graphitic-N, respectively (Fig. S12c). The XPS spectra of the O 1 s demonstrate four distinct peaks attributed to the (B–O), (C–O), (C–OH), and (C = O) moieties at 530.2, 531.63, 532.73, and 534.05 eV, respectively (Fig. S12d). The appearance of (C = O), (N–H), and (–OH) moieties from the XPS spectra also suggests that the synthesized β -CD-SeQDs-APBA was formed due to the amide (O = C–N–H) bond existence by the EDC/NHS conjugation [53]. The XPS spectrum of B 1 s revealed three peaks at 190.13, 191.94, and 193.76 eV, which are attributed to the (B–N), (B–C), and (B–O) functional groups, respectively (Fig. S12e) [58]. The high-resolution XPS spectrum of Se 3d show a typical deconvoluted peak at 54.03 eV (Fig. S12f).

Furthermore, the valence states of the different elements were investigated for the as-functionalized β -CD-SeQDs-APBA@MWCNTs via XPS analysis. The total survey spectrum of β -CD-SeQDs-APBA@MWCNTs revealed multiple chemical species such as Se 3d, B 1 s, C 1 s, N 1 s, O 1 s, and Na 1 s at 54.15, 189.66, 284.88, 531.61, and 1070.26 eV, respectively (Fig. 3a). The individual high-resolution XPS spectra for the β -CD-SeQDs-APBA@MWCNTs are shown in Fig. 3b–f. The high-resolution XPS spectra of C 1 s show four deconvoluted peaks at 283.6, 284.76, 286.35, and 288.14 eV, which are assigned to the (C–B), (C–C/C = C), (C–N/C–O), and (C = O), respectively (Fig. 3b) [59]. The XPS spectra of the O 1 s demonstrate three peaks responsible for the (B–O), (C–OH), and (C = O) functional groups at 530.3, 531.79, and 535.1 eV, respectively (Fig. 3c). The XPS spectra of the N 1 s exhibited two peaks at 399.16 and 401.64 eV, which are responsible for the pyrrolic-N and graphitic-N, respectively (Fig. 3d). The XPS spectrum of B 1 s revealed three peaks at 188.28, 189.44, and 191.27 eV, which are accredited to the (B–C), oxidized (B–C), and (B–O) moieties, respectively (Fig. 3e) [60]. The high-resolution XPS spectrum of Se 3d show a very weaker signal at the binding energy region range of 52–58 eV in contrast to the same of β -CD-SeQDs-APBA (Fig. 3f). This is significantly attributed to the prevalent domination of oxidized moieties of (B–C) and (B–O) groups rather than the Se-related components on the surfaces of MWCNTs during the formation of final nanocomposite.

3.2. Electrochemical behavior of β -CD-SeQDs-APBA@MWCNTs

Fig. 4a shows the electrochemical behavior of pristine SeQDs, β -CD-SeQDs, and β -CD-SeQDs-APBA@MWCNTs. The peak current intensity of SeQDs-GCE (23.88 μA) is minimally higher than that of bare GCE (22.83 μA) implying that the minute conductive capacity of pristine SeQDs. In

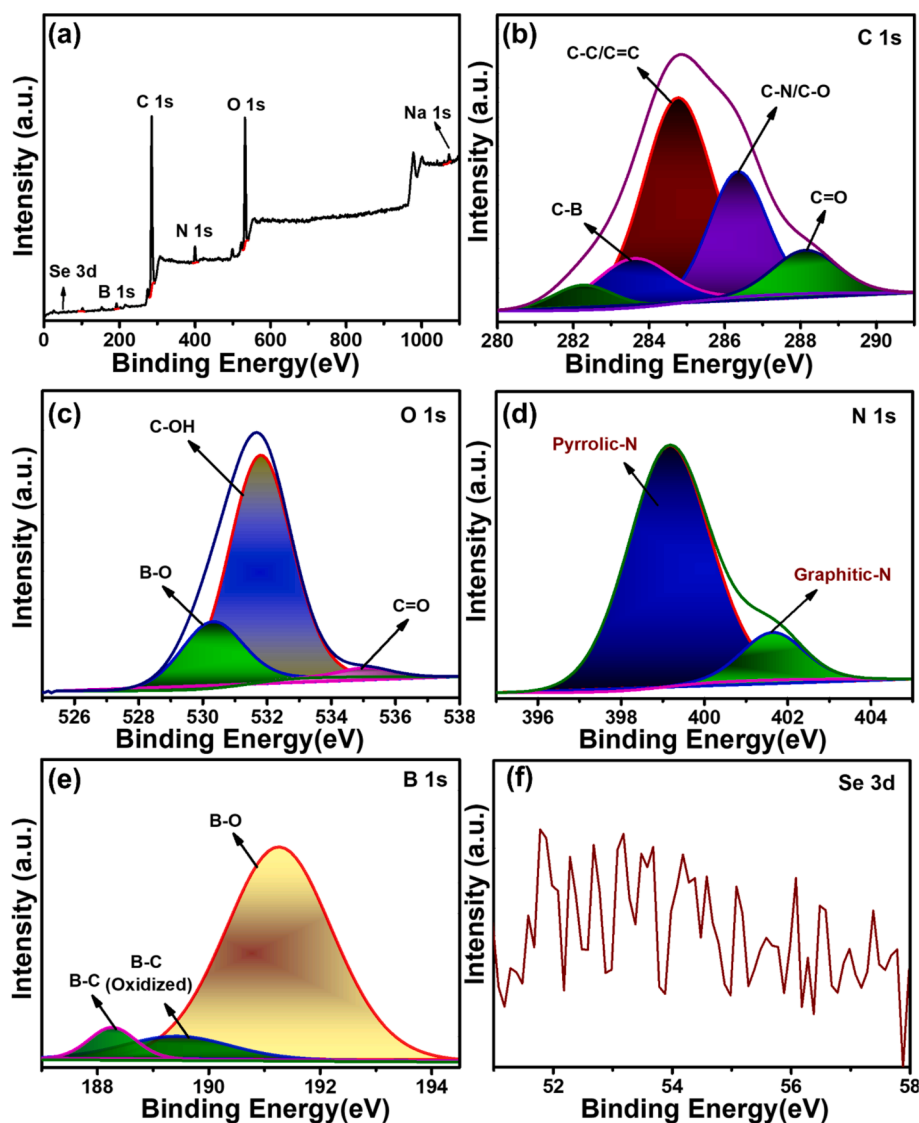


Fig. 3. (a) XPS total survey spectra of β -CD-SeQDs-APBA@MWCNTs, (b-f) high-resolution individual XPS spectra of C 1 s, O 1 s, N 1 s, B 1 s, and Se 3d.

the case of β -CD-SeQDs-GCE, the increase in the current intensity (25.73 μ A) was distinguishable, which is due to the presence of multiple hydroxyl groups and oxygen atoms, which in turn can enhance the electron transfer and surface hydrophilicity. Interestingly, the peak current intensity of the final nanocomposite i.e., β -CD-SeQDs-APBA@MWCNTs-GCE was much improved (33.01 μ A) in contrast to the β -CD-SeQDs-GCE, which is mainly attributed to the synergic effect of the final nanocomposite that enable sufficient electron transfer between β -CD-SeQDs-APBA and β -CD-SeQDs-APBA@MWCNTs-GCE [17]. Following the modification of pristine SeQDs to the final nanocomposite (β -CD-SeQDs-APBA@MWCNTs), the electrical conductivity was increased. Furthermore, the redox behavior of the β -CD-SeQDs-APBA@MWCNTs was investigated using 1 μ M DA by altering the voltage in the range of 10–500 mV/s, as shown in Fig. 4b. The difference in the high scan rate results in an induced peak current response, which demonstrating the typical redox reaction response of DA towards the final nanocomposite. However, the linear current response was observed with regards to the scan rate of 10–500 mV/s ($R^2 = 0.995$) (Fig. S13a). The relationship between the logarithm of the peak current and the logarithm of the scan rate yields a slope of 0.68, indicating that the electrochemical sensing of DA at the modified GCE is primarily governed by a diffusion-controlled mechanism (Fig. 4c). However, the slope deviates from the ideal value of 0.5, which is characteristic of purely diffusion-controlled processes,

suggesting a secondary contribution from adsorption effects. This implies that while DA molecules predominantly diffuse to the electrode surface for oxidation, a portion of them also adsorb onto the modified electrode's surface during the electrochemical reaction. The modified electrode's surface properties, such as enhanced conductivity and active sites provided by the incorporated materials, likely facilitate this partial adsorption. Consequently, the sensing mechanism involves a combination of diffusion-dominated mass transport and adsorption-influenced behavior, resulting in improved sensitivity and selectivity for DA detection [11].

The influence of the pH (1 μ M DA) on the current response of the β -CD-SeQDs-APBA@MWCNTs-GCE was investigated in acidic and alkaline environments (Fig. 4d and Fig. S13b). Due to the protonation effect, the rise in the peak current intensities were observed in acidic pH values ranging from 5.475 to 6.84. The high proportions of protonated nitrogen available in the DA quinone can sufficiently interact with the surfaces of the β -CD-SeQDs-APBA@MWCNTs-GCE and improves the current response. Meanwhile, a distinguishable decline and a slight shift was observed in the peak current intensities at neutral pH values of 7.215 and 7.4. This response is believed to be the deprotonation effect that led to the less availability of protons and for the oxidation of DA to DA quinone requires high electrode potential and shifting the current as well as redox potential to negative values [10].

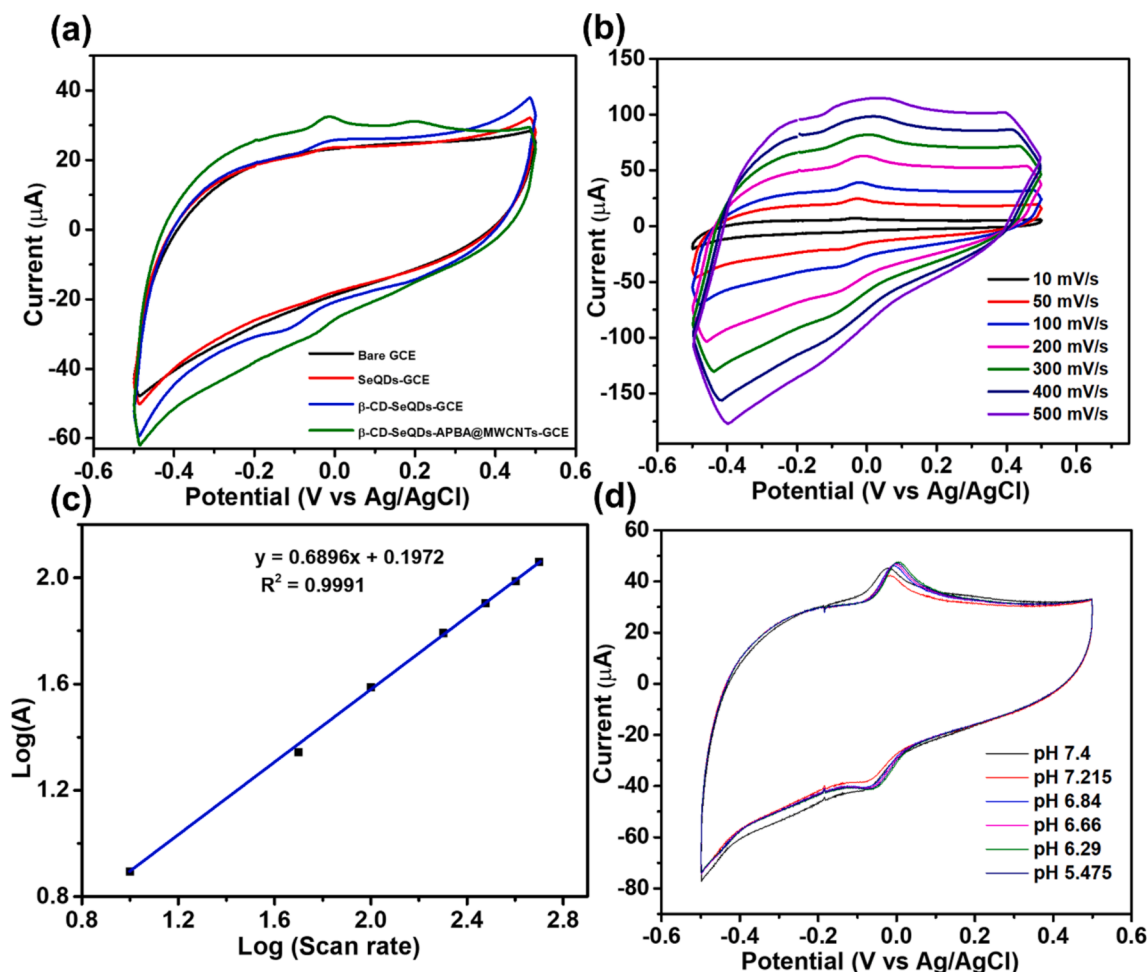


Fig. 4. (a) CV curves for the bare GCE, SeQDs-GCE, β -CD-SeQDs-GCE, and β -CD-SeQDs-APBA@MWCNTs-GCE in 1000 nM DA. (b) CV curves for the β -CD-SeQDs-APBA@MWCNTs-GCE regarding peak current vs. scan rate from 10–500 mV/s in 1000 nM DA. (c) The Log (scan rate) vs. Log(A) for 1000 nM DA. (d) pH response of β -CD-SeQDs-APBA@MWCNTs-GCE in 1000 nM DA by CV curves.

Furthermore, the redox behavior of the β -CD-SeQDs-APBA@MWCNTs-SPE was investigated using 5 μ M DA by varying the voltage in the range of 50–500 mV/s (Fig. S14a). By increasing the scan rate, an increased peak current response was observed, which revealing the characteristic redox reaction behavior of DA for the prepared final nanocomposite. Also, the linear current response was remarkable from the scan rate of 50–500 mV/s ($R^2 = 0.9956$) (Fig. S15). The similar behavior was observed in the β -CD-SeQDs-APBA@MWCNTs-SPE with a remarkable shift in the peaks of anodic current at higher scan rates, which is responsible for the formation of diffusion layer by the β -CD-SeQDs-APBA@MWCNTs-SPE. Thus, it is typically signified that the redox behavior is based on the diffusion-controlled mechanism [11]. The Nyquist plot demonstrates that β -CD-SeQDs-APBA@MWCNTs-SPE had a lower charge transfer resistance (R_{ct}) value than bare SPE (Fig. S14b). The R_{ct} values for the bare SPE, SeQDs-SPE, β -CD-SeQDs-SPE, β -CD-SeQDs-APBA-SPE, and β -CD-SeQDs-APBA@MWCNTs-SPE were calculated to be 731.11, 783.38, 183.56, 182.94, and 179.82 Ω , respectively. The lower R_{ct} value for β -CD-SeQDs-APBA@MWCNTs-SPE signify that the sufficient electron transfer occurs between the final nanocomposite and electrolyte, which is attributed to its desired conductivity [11,17].

3.3. DA sensing using β -CD-SeQDs-APBA@MWCNTs

The redox process of DA using β -CD-SeQDs-APBA@MWCNTs-GCE was investigated by employing CV and DPV techniques. Fig. 5 shows the

CV plot for DA sensing and linear regression plot of DA concentration vs current. The peak current was observed around -0.0213 V, and the current was linearly increased by increasing DA concentration from 0 to 1000 nM (Fig. 5a). The plot showed a good linear regression coefficient of $R^2 = 0.9933$ within the linear range of 200–1000 nM with a limit of detection (LOD) of 70.9 nM (Fig. 5b). The desired current response for the final nanocomposite during the DA oxidation is attributed to the favorable features those include rapid electron transfer, high adsorbing efficiency for DA, and increased surface area.

Meanwhile, the DPV plot was drawn for DA sensing and a linear relationship plot of DA concentration vs current. The peak current was observed around -0.084 V, and the current was linearly increased by increasing DA concentration from 0 to 1000 nM (Fig. 5c). The plot showed a good linear regression coefficient of $R^2 = 0.983$ within the linear range of 200–1000 nM with a LOD of 113.38 nM (Fig. 5d). The increased sensitivity of the final nanocomposite, while DQ formation can be attributed a wide-variety of superior features such as lower charge transfer resistance, fast electron transfer, host–guest interaction, and improved surface area. Altogether, the DA oxidation in DPV method involves a combined processes of diffusion and adsorption [10,11]. Table 1 summarizes the comparison of the sensing performance of the prepared final nanocomposite i.e., β -CD-SeQDs-APBA@MWCNTs-GCE with previously modified electrode materials [9,10,14,17,18,41,61–63]. Formerly, divergent 0D to 3D nanomaterial-based composites have already been designed for DA sensing, most of them are suffered from low sensitivity with a micromolar level detection. In the case of

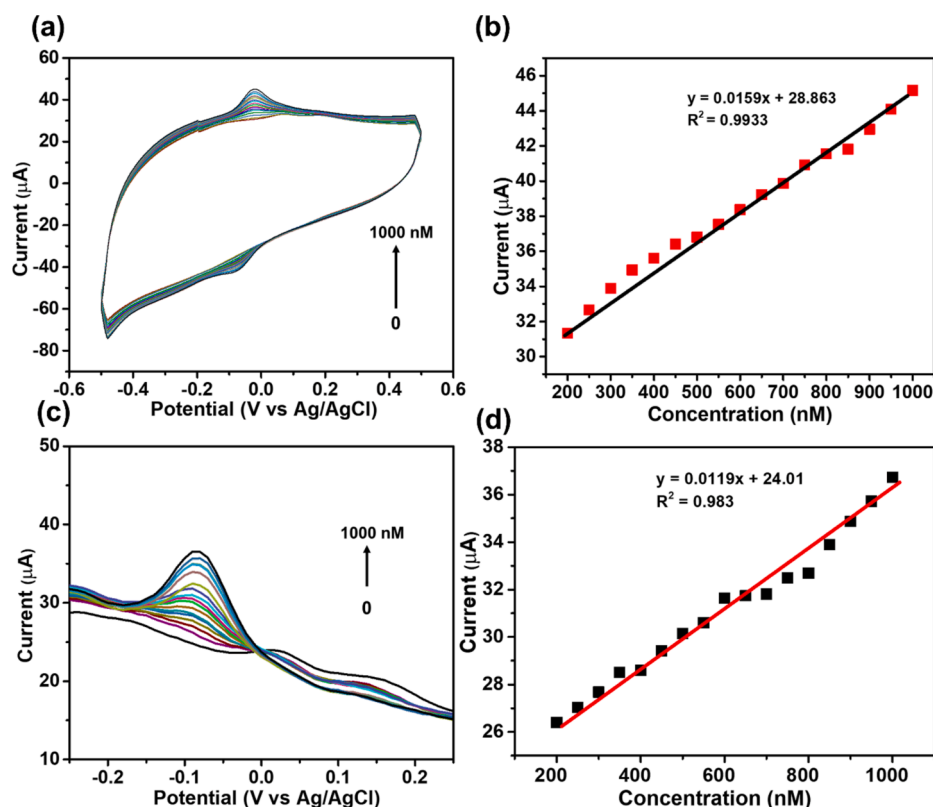


Fig. 5. (a) CV curves of β -CD-SeQDs-APBA@MWCNTs after the addition of DA (0–1000 nM). (b) linear regression plot of current vs. DA concentration (200–1000 nM). (c) DPV curves of β -CD-SeQDs-APBA@MWCNTs after the addition of DA (0–1000 nM). (d) linear regression plot of current vs. DA concentration (200–1000 nM).

Table 1

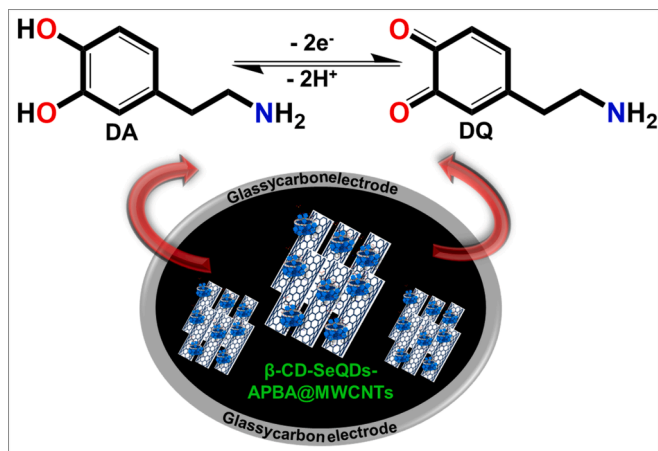
Comparison of the sensing performance for the prepared β -CD-SeQDs-APBA@MWCNTs-GCE with other modified electrode materials.

Electrode materials	Target Analyte	Linear range	Detection limit	Detection method	Ref
I ₂ -CMP-CNT-4	DA	0.8–20 and 0.75–20 μM	1.0 and 1.7 μM	CV and DPV	[9]
MOF-Ti ₃ C ₂ /GCE	DA	90–130 nM	110 nM	DPV	[10]
β -CD/Ni-MOF/GCE	DA	0.7–310.2 μM	0.227 μM	DPV	[14]
β -CD/CQDs/GCE	DA	4–220 μM	0.14 μM	DPV	[17]
β -CD/MWCNT/GCE	DA	0.04–0.08 mM	37 μM	CV	[18]
Ni/NiC _x -N- MWCNTs/GCE	DA	1–80 μM	0.19 μM	SWV	[41]
PtNCs-MWCNTs-GNPs/GCE	DA	2–50 μM	0.5 μM	DPV	[61]
CNP/GCE	DA	10–480 μM	0.86 μM	DPV	[62]
3D-KSC/C ₆₀ BP	DA	14.1 μM–0.1 mM	4.6 μM	DPV	[63]
β -CD-SeQDs-APBA@MWCNTs-GCE	DA	200 nM–1000 nM	70.9 nM and 113.38 nM	CV and DPV	This work

preparation of few nanocomposites, still challenges are need to be rectified, which include high-cost burden, need of sophisticated post-synthetic modification, and uplifting of poor stability [10,11,61]. Though, different β -CD-modified nanocomposites have been designed for DA sensing, their low sensitivity and minimal linear DA concentration windows are the major limitations to be emerged as potential sensors [14,17,18]. Based on the above-discussions, it is signified that the our β -CD-SeQDs-APBA@MWCNTs-GCE sensor is superior in terms of facile synthesis, cost-effectiveness, and sensitivity. The achieved desired electrochemical sensitivity is mainly attributed to the enhanced electroactive surface area (EASA) by the incorporation of SeQDs and its synergistic effect through the integration of MWCNTs. Significantly, the β -CD-SeQDs-APBA provide reasonable electrical conductivity to the electrode surface by the abundant negatively charged (–OH) moieties, electrostatic interactions, and π - π stacking with MWCNTs [14,17,18,39,64]. Further, the possible electrochemical sensing

mechanism for the proposed β -CD-SeQDs-APBA@MWCNTs-GCE sensor was explained (Scheme 2). Furthermore, the schematic depiction for the DA sensing mechanism using the β -CD-SeQDs-APBA-MWCNTs from its molecular interactions between the different components of the final nanocomposite and the substrate i.e., DA is illustrated in Scheme 3. The boronic acid group in the final nanocomposite facilitates the deprotonation of the catechol ring, resulting in the oxidation of DA to form DQ. This process releases protons, which trigger charge transfer within the β -CD compound. Furthermore, the quantum confinement effect of the SeQDs amplifies this charge transfer, allowing for the precise detection of DA in the PBS.

Furthermore, the redox behavior of DA was studied for the β -CD-SeQDs-APBA@MWCNTs-SPE using SPE as the main electrode platform by employing CV and DPV techniques. Fig. S16 shows the CV plot for DA sensing and linear regression plot of DA concentration vs current. The peak current was observed around + 0.0025 V, and the current was

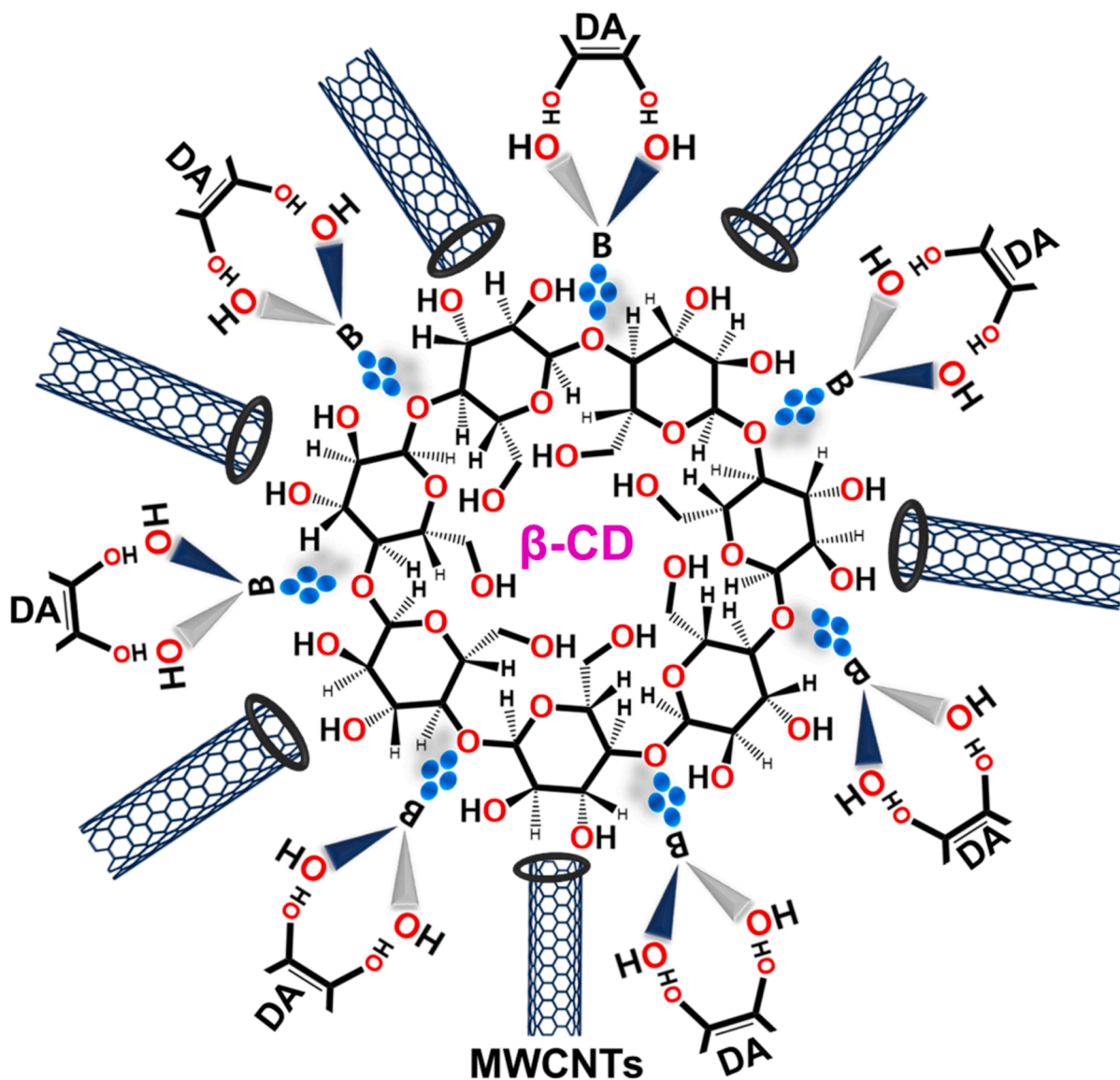


Scheme 2. Schematic representation for the electrochemical sensing of DA using the $\beta\text{-CD-SeQDs-APBA-MWCNTs}$ nanocomposite.

linearly increased by increasing DA concentration in the concentration range of 0–5 μM (Fig. S16a). The linear relationship plot showed a linear regression coefficient of $R^2 = 0.9755$ from DA range of 0–5 μM and found the LOD of 0.76 μM (Fig. S16b). The DPV plot was drawn for DA sensing and a linear regression plot of DA concentration vs current. The peak current was observed around -0.055 V , and the current was linearly increased by increasing DA concentration in the range of 0–5 μM (Fig. S16c). The plot showed a suitable linear regression coefficient of ($R^2 = 0.9719$) within the linear range of 0–5 μM with the LOD of 0.82 μM (Fig. S16d). These results are highlighting that the prepared nanocomposite possess effective sensing abilities in both kinds of electrode systems namely GCE and SPE. Especially, for the determination of DA concentrations via SPE electrode platform is highly encouraging that the prepared nanocomposite is indispensably portable and can be precisely opted in health care settings [12].

3.4. Interference study

The interference studies were investigated for the final nanocomposite using divergent neurotransmitters, biomolecules, cations, and anions against DA via CV and DPV techniques. No response in the



Scheme 3. Schematic depiction for the DA sensing using the $\beta\text{-CD-SeQDs-APBA-MWCNTs}$ nanocomposite from its molecular interactions between the components of the probe and the substrate.

peak current intensity was observed in the β -CD-SeQDs-APBA@MWCNTs-GCE, which suggested that the prepared final nanocomposite is desirably sensitive and selective for DA among other potential interferents (Fig. S17-S20). Moreover, the interference study for the nanocomposite is highly necessary to distinguish the extent of selectivity towards DA as the less sensitivity of the nanocomposite was observed in the SPE. In this context, selectivity of the nanocomposite was investigated for DA sensing (5 μ M) against divergent neurotransmitter analogues (5 μ M) including EP, NE, AA, GL, GABA, and Cys. There was no response in the peak current intensity was observed in the β -CD-SeQDs-APBA@MWCNTs-SPE, when using different interferents, except for DA (Fig. S21a-g). Based on these results, it is implied that the prepared β -CD-SeQDs-APBA@MWCNTs-SPE is reasonably sensitive and selective for DA.

3.5. Reproducibility and stability studies

The reproducibility and stability studies were investigated to explore the practicality and validity of the final nanocomposite. The reproducibility of β -CD-SeQDs-APBA@MWCNTs was studied by treating with the GCE consecutively four times and measured its CV response for DA (1000 nM) (Fig. 6a). The similar peak current intensities were observed

from the CV plot, which confirms the reproducibility of the prepared nanocomposite i.e., β -CD-SeQDs-APBA@MWCNTs. From this study, we calculated the average and RSD% values as 42.56 and 1.324, respectively (inset; Fig. 6a). Moreover, stability of the β -CD-SeQDs-APBA@MWCNTs was studied by repeating the CV experiment at a fixed concentration of DA (1000 nM) (Fig. 6b). From these results, there was no much difference in the current intensities was observed, which suggest the good stability of the β -CD-SeQDs-APBA@MWCNTs. Also, we found the average and RSD% values as 40.98 and 0.49, respectively ($n = 10$) (inset, Fig. 6b). The storage stability of the β -CD-SeQDs-APBA@MWCNTs was investigated at different time intervals starting from day 1 to day 30 (Fig. 6c). The identical peak current intensities were observed with the average and RSD% values around 41.36 and 0.64 respectively (inset; Fig. 6c). Furthermore, the reproducibility and stability studies were investigated in detail for the β -CD-SeQDs-APBA@MWCNTs-GCE using CV and chronoamperometry techniques (Fig. S22 and S23). From the reproducibility studies, the similar peak current intensities were observed after the treatment of β -CD-SeQDs-APBA@MWCNTs-GCE consecutively with seven times with the average and RSD% values around 110.22 and 0.69. Further, stability of the β -CD-SeQDs-APBA@MWCNTs-GCE was confirmed by detecting DA using the chronoamperometry technique in dynamic condition. The consistency

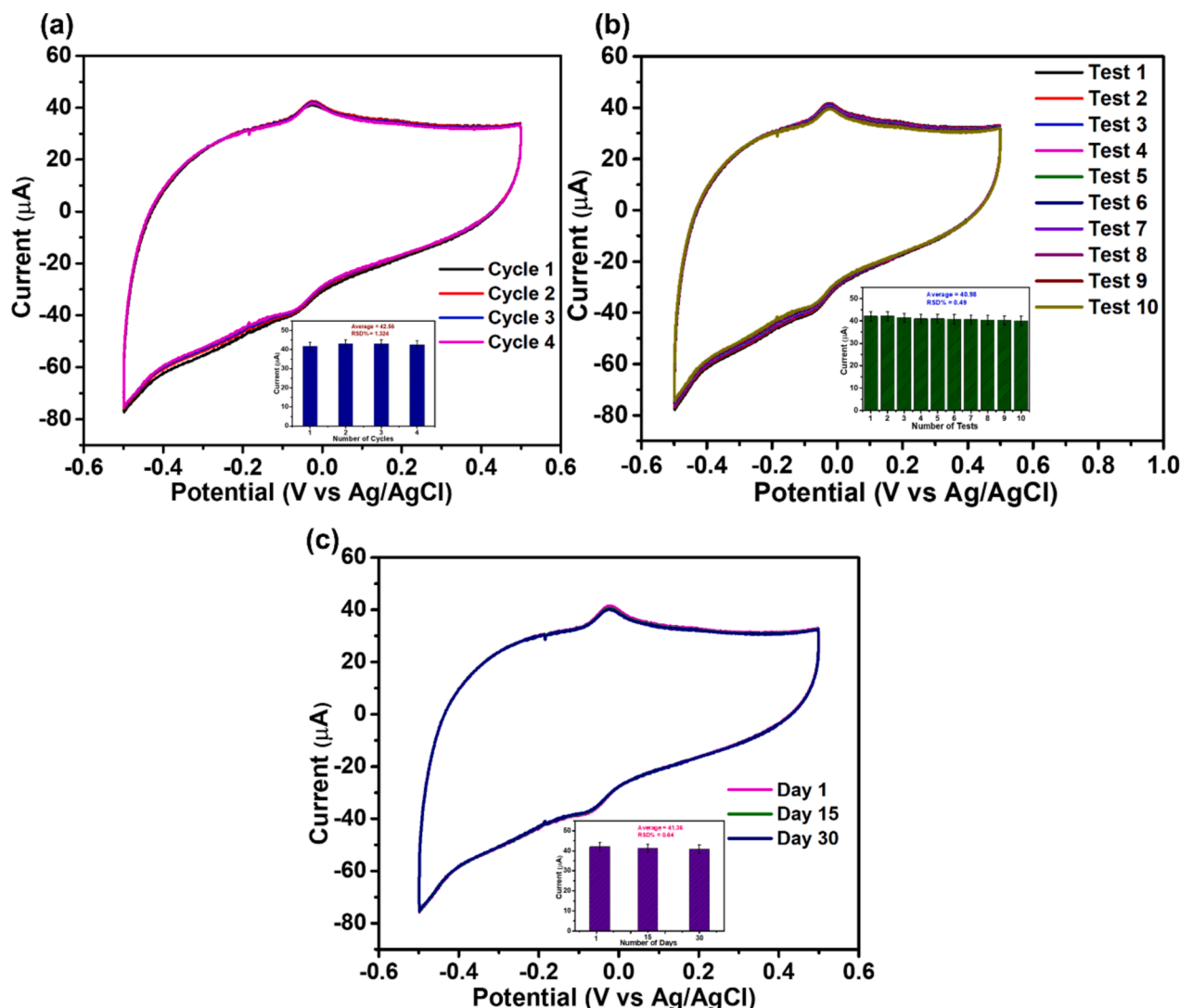


Fig. 6. (a) CV curves for the reproducibility of β -CD-SeQDs-APBA@MWCNTs (Number of cycles: 4) and the inset showing the bar diagram. (b) CV curves for the stability of β -CD-SeQDs-APBA@MWCNTs (Number of Tests: 10) and the inset illustrating the bar diagram. (c) CV curves for the storage stability of β -CD-SeQDs-APBA@MWCNTs (Number of days: 1, 15, and 30) and the inset illustrating the bar diagram.

in the peak current was observed with an current intensity of 8.48 μA during the time period of 200 sec after the treatment of 1000 nM of DA with $\beta\text{-CD-SeQDs-APBA@MWCNTs-GCE}$.

Moreover, the reproducibility and stability studies were studied for the $\beta\text{-CD-SeQDs-APBA@MWCNTs-SPE}$. The stability of the $\beta\text{-CD-SeQDs-APBA@MWCNTs-SPE}$ was investigated by repeating CV experiment ten times, which demonstrated very similar peak current intensities (Fig. S24a). The average and RSD% values were found to be 18.624 and 0.59, respectively ($n = 10$) (inset, Fig. S24a). The storage stability of the $\beta\text{-CD-SeQDs-APBA@MWCNTs-SPE}$ was investigated at different time periods, which showed identical peak current intensities with an average value of 18.695 (Fig. S24b). The reproducibility of the $\beta\text{-CD-SeQDs-APBA@MWCNTs-SPE}$ was studied thrice, which demonstrated identical peak current intensities and the average and RSD% values were found to be 18.60 and 0.76, respectively ($n = 3$) (inset, Fig. S24c). These results are suggesting that the prepared $\beta\text{-CD-SeQDs-APBA@MWCNTs}$ are convenient to use in both GCE and SPE electrode platforms. The GCE and SPE electrode systems in the present studies were presented in the supplementary information (Fig. S25a, b).

3.6. Real sample analysis

The CV response of the final nanocomposite i.e., $\beta\text{-CD-SeQDs-APBA@MWCNTs-GCE}$ was investigated in the real sample analysis i.e., human serum by spiking with DA at different concentrations. The $\beta\text{-CD-SeQDs-APBA@MWCNTs-GCE}$ exhibited a good response to DA in the concentration range of 0–3 μM (Fig. S26). A good linear relationship was observed from the concentration range of 0.4–3 μM with a R^2 value of 0.9964. Further, a good linear response in the peak current intensities was observed from the nanocomposite, which was attributed to the presence of multiple dissolved ions in the serum [11]. Furthermore, to validate the sensing performance of the $\beta\text{-CD-SeQDs-APBA@MWCNTs-GCE}$ in the real biological sample i.e., human serum, the interference studies were conducted using various contemporary neurotransmitters, biomolecules, cations, and anions against DA under the visualization of CV and DPV techniques. However, no distinguishable response in the peak current intensity was found and thereby suggested that the prepared final nanocomposite is desirably convenient in terms of sensitivity and selectivity for DA sensing in the real biological sample matrix (Fig. S27–S32).

4. Conclusion

In this study, electrochemical sensor was developed based on a $\beta\text{-CD-SeQDs-APBA-MWCNTs}$ nanocomposite-modified electrodes for DA sensing. The integration of functionalized $\beta\text{-CD-SeQDs-APBA}$ with the MWCNTs facilitated the convenient electrochemical response. As the $\beta\text{-CD-SeQDs-APBA-MWCNTs}$ acts as a host material and the selective analyte act as guest molecule and its electrochemical interactions lead to the improved sensitivity and selectivity for DA sensing. To the best of our knowledge, the novel $\beta\text{-CD-SeQDs-APBA-MWCNTs}$ nanocomposite was selectively detected DA in both GCE (70.9 nM and 113.38 nM) and SPE (0.76 μM and 0.82 μM) electrodes in the PBS buffer via CV and DPV techniques, respectively. The nanocomposite has delivered DA sensing in both nano and micromolar linear ranges of 0–1000 nM and 0–5 μM , respectively. Furthermore, the good stability, reproducibility, and high selectivity are the ideal parameters for the prepared nanocomposite. More importantly, the validation of nanocomposite for DA sensing has been applied to real samples like human serum. In future, the electrochemical response of the prepared nanocomposite can be studied extensively for the monitoring of DA levels in live cells and neuronal cells.

CRediT authorship contribution statement

Roopkumar Sangubotla: Writing – review & editing, Writing –

original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jose Paul:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Jongsung Kim:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgements

This research was support by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education (2021R1A6A1A03038996) and by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2022R1A2C1009968). We thank the Smart Materials Research Center for IoT at Gachon University for their technical support with instruments (FT-IR and SEM).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2024.162275>.

Data availability

Data will be made available on request.

References

- [1] R. Sangubotla, J. Kim, Recent trends in analytical approaches for detecting neurotransmitters in Alzheimer's disease, *TrAC - T Trends Anal. Chem.* 105 (2018) 240–250, <https://doi.org/10.1016/j.trac.2018.05.014>.
- [2] R. Sangubotla, J. Kim, Fiber-optic biosensor based on the laccase immobilization on silica-functionalized fluorescent carbon dots for the detection of dopamine and multi-color imaging applications in neuroblastoma cells, *Mater. Sci. Eng. C* 122 (2021) 111916, <https://doi.org/10.1016/j.msec.2021.111916>.
- [3] R. Mochizuki, Y. Ogra, Determination of intracellular dopamine by liquid chromatography–fluorescence detection with post-column derivatization using the König reaction, *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 1232 (2024) 123956, <https://doi.org/10.1016/j.jchromb.2023.123956>.
- [4] A. Roychoudhury, K.A. Francis, J. Patel, S.K. Jha, S. Basu, A decoupler-free simple paper microchip capillary electrophoresis device for simultaneous detection of dopamine, epinephrine and serotonin, *RSC Adv.* 10 (2020) 25487–25495, <https://doi.org/10.1039/d0ra03526b>.
- [5] H. Abdolmohammad-Zadeh, M. Zamani-Kalajahi, A novel chemiluminescent-based nano-probe for ultra-trace quantification of dopamine in human plasma samples, *Microchem. J.* 155 (2020) 104704, <https://doi.org/10.1016/j.microc.2020.104704>.
- [6] V. Sliesarenko, U. Bren, A. Lobnik, Fluorescence based dopamine detection, *Sens. Actuators Rep.* 7 (2024) 100199, <https://doi.org/10.1016/j.snr.2024.100199>.
- [7] P. Sun, M. Shang, R. Xie, Y. Gao, M. Tian, Q. Dai, F. Zhang, F. Chai, Dual-mode fluorimetric and colorimetric sensors based on iron and nitrogen co-doped carbon dots for the detection of dopamine, *Food Chem.* 445 (2024) 138794, <https://doi.org/10.1016/j.foodchem.2024.138794>.
- [8] Y. Choi, C.S. Jeon, K.B. Kim, H.J. Kim, S.H. Pyun, Y.M. Park, Quantitative detection of dopamine in human serum with surface-enhanced Raman scattering (SERS) of constrained vibrational mode, *Talanta* 260 (2023) 124590, <https://doi.org/10.1016/j.talanta.2023.124590>.
- [9] J. Paul, M. Moniruzzaman, J. Kim, Framing of poly(arylene-ethynylene) around carbon nanotubes and iodine doping for the electrochemical detection of dopamine, *Biosensors* 13 (2023), <https://doi.org/10.3390/bios13030308>.
- [10] J. Paul, J. Kim, Reticular synthesis of a conductive composite derived from metal-organic framework and Mxene for the electrochemical detection of dopamine, *Appl. Surf. Sci.* 613 (2023) 156103, <https://doi.org/10.1016/j.apsusc.2022.156103>.
- [11] J. Paul, R. Sangubotla, J. Kim, Competitive adsorption and selective sensing of dopamine over epinephrine and norepinephrine on MOF copper seed composite-based probe, *Electrochim. Acta* 479 (2024) 143885, <https://doi.org/10.1016/j.electacta.2024.143885>.
- [12] J. Paul, J. Kim, Selective sensing of dopamine using copper hollow tube-integrated conjugated poly(arylene-ethynylene)-4 in the presence of epinephrine and norepinephrine, *J. Ind. Eng. Chem.* (2024), <https://doi.org/10.1016/j.jiec.2024.09.023>.
- [13] X. Chen, N. Li, Y. Rong, Y. Hou, Y. Huang, W. Liang, β -Cyclodextrin functionalized 3D reduced graphene oxide composite-based electrochemical sensor for the

- sensitive detection of dopamine, RSC Adv. 11 (2021) 28052–28060, <https://doi.org/10.1039/d1ra02313f>.
- [14] C. Chen, J. Ren, P. Zhao, J. Zhang, Y. Hu, J. Fei, A novel dopamine electrochemical sensor based on a β -cyclodextrin/Ni-MOF/glassy carbon electrode, Microchem. J. 194 (2023) 109328, <https://doi.org/10.1016/j.microc.2023.109328>.
 - [15] R. Huang, F. Sun, G. Huang, X. Yang, Z. Yan, L. Xu, Y. Liu, A simple ultrasensitive electrochemical biosensor for simultaneous determination of dopamine, uric acid and ascorbic acid based on β -cyclodextrin/selenium doped carbon quantum dots modified glassy carbon electrode, Int. J. Electrochem. Sci. 15 (2020) 9888–9901, <https://doi.org/10.20964/2020.10.47>.
 - [16] S. Rong, P. Zhang, L. Zou, Y. Tian, M. Miao, D. Jia, R. Qiu, F. Qi, H. Ma, H. Pan, Electrochemical determination of dopamine at nafion and β -cyclodextrin-functionalized multi-walled carbon nanotubes composite modified glassy carbon electrode, IEEE Sens. J. 22 (2022) 5540–5547, <https://doi.org/10.1109/JSEN.2022.3149270>.
 - [17] J. Chen, P. He, H. Bai, S. He, T. Zhang, X. Zhang, F. Dong, Poly(B-cyclodextrin)/carbon quantum dots modified glassy carbon electrode: Preparation, characterization and simultaneous electrochemical determination of dopamine, uric acid and tryptophan, Sens. Actuators, B Chem. 252 (2017) 9–16, <https://doi.org/10.1016/j.snb.2017.05.096>.
 - [18] G. Alarcón-Angeles, B. Pérez-López, M. Palomar-Pardave, M.T. Ramírez-Silva, S. Alegret, A. Merkoçi, Enhanced host-guest electrochemical recognition of dopamine using cyclodextrin in the presence of carbon nanotubes, Carbon N. Y. 46 (2008) 898–906, <https://doi.org/10.1016/j.carbon.2008.02.025>.
 - [19] N.F. Atta, A. Galal, D.M. El-Said, Novel design of a layered electrochemical dopamine sensor in real samples based on gold nanoparticles/ β -cyclodextrin/nafion-modified gold electrode, ACS Omega 4 (2019) 17947–17955, <https://doi.org/10.1021/acsomega.9b01222>.
 - [20] R. Sangubotla, J. Kim, Ultra-sensitive turn-on fluorescent sensor based on β -cyclodextrin-stabilized melamine-derived carbon dots for the highly selective dual-detection of dopamine, Ceram. Int. 49 (2023) 16272–16282, <https://doi.org/10.1016/j.ceramint.2023.01.225>.
 - [21] D. Zhou, H. Huang, Y. Wang, J. Yu, Z. Hu, Functionalized selenium-doped carbon quantum dots for targeting detection of reactive oxygen species in live cells, in: IOP Conference Series: Earth and Environmental Science, Vol. 692, No. 3, IOP Publishing, 2021, p. 032066, <https://doi.org/10.1088/1755-1315/692/3/032066>.
 - [22] S. Tajik, Z. Dourandish, F. Garkani Nejad, H. Beitollahi, P.M. Jahani, A. Di Bartolomeo, Transition metal dichalcogenides: synthesis and use in the development of electrochemical sensors and biosensors, Biosens. Bioelectron. 216 (2022) 114674, <https://doi.org/10.1016/j.bios.2022.114674>.
 - [23] W. Luo, Y. Wang, F. Lin, Y. Liu, R. Gu, W. Liu, C. Xiao, Selenium-doped carbon quantum dots efficiently ameliorate secondary spinal cord injury via scavenging reactive oxygen species, Int. J. Nanomedicine 15 (2020) 10113–10125, <https://doi.org/10.2147/IJN.S282985>.
 - [24] Q. Xu, X. Liu, Y. Jiang, P. Wang, A highly sensitive and selective probe for the colorimetric detection of Mn(II) based on the antioxidative selenium and nitrogen co-doped carbon quantum dots and ABTS^{•+}, Front. Chem. 9 (2021) 1–11, <https://doi.org/10.3389/fchem.2021.658105>.
 - [25] Z.T. Rosenkrans, T. Sun, D. Jiang, W. Chen, T.E. Barnhart, Z. Zhang, C.A. Ferreira, X. Wang, J.W. Engle, P. Huang, W. Cai, Selenium-doped carbon quantum dots act as broad-spectrum antioxidants for acute kidney injury management, Adv. Sci. 7 (2020) 1–11, <https://doi.org/10.1002/advs.202000420>.
 - [26] S. Yang, J. Sun, P. He, X. Deng, Z. Wang, C. Hu, G. Ding, X. Xie, Selenium doped graphene quantum dots as an ultrasensitive redox fluorescent switch, Chem. Mater. 27 (2015) 2004–2011, <https://doi.org/10.1021/acs.chemmater.5b00112>.
 - [27] J. Shi, Y. Pu, J.X. Wang, D. Wang, J.F. Chen, Synthesis of ultrasmall and monodisperse selenium-doped carbon dots from amino acids for free radical scavenging Rina Su, Ind. Eng. Chem. Res. 59 (2020) 16876–16883, <https://doi.org/10.1021/acs.iecr.0c03402>.
 - [28] L. Yang, H. Huang, T. Wang, D. Zhou, Q. Chen, D. Li, S. Chen, P. Lin, Endoplasmic reticulum-targetable selenium-doped carbon nanodots with redox-responsive fluorescence for in situ free-radical scavenging in cells and mice, Arab. J. Chem. 16 (2023) 105036, <https://doi.org/10.1016/j.arabjc.2023.105036>.
 - [29] C. Wu, Y. Zhang, M. Han, R. Zhang, H. Li, F. Wu, A. Wu, X. Wang, Selenium-based nanozyme as a fluorescence-enhanced probe and imaging for chlortetracycline in living cells and foods, Food Chem. 432 (2024) 137147, <https://doi.org/10.1016/j.foodchem.2023.137147>.
 - [30] F. Li, T. Li, C. Sun, J. Xia, Y. Jiao, H. Xu, Selenium-doped carbon quantum dots for free-radical scavenging, Angew. Chemie - Int. Ed. 56 (2017) 9910–9914, <https://doi.org/10.1002/anie.201705989>.
 - [31] K. Anupama, T. Paul, K.A. Ann Mary, Solid-state fluorescent selenium quantum dots by a solvothermal-assisted sol-gel route for curcumin sensing, ACS Omega 6 (2021) 21525–21533, <https://doi.org/10.1021/acsomega.1c02441>.
 - [32] G. Huang, Y. Lin, L. Zhang, Z. Yan, Y. Wang, Y. Liu, Synthesis of sulfur-selenium doped carbon quantum dots for biological imaging and scavenging reactive oxygen species, Sci. Rep. 9 (2019) 1–9, <https://doi.org/10.1038/s41598-019-55996-w>.
 - [33] J. Masud, W.P.R. Liyanage, X. Cao, A. Saxena, M. Nath, Copper selenides as high-efficiency electrocatalysts for oxygen evolution reaction, ACS Appl. Energy Mater. 1 (2018) 4075–4083, <https://doi.org/10.1021/acsaem.8b00746>.
 - [34] S. Umaphathi, J. Masud, H. Coleman, M. Nath, Electrochemical sensor based on CuSe for determination of dopamine, Microchim. Acta 187 (2020), <https://doi.org/10.1007/s00604-020-04405-5>.
 - [35] R. Suresh, M. Pandiaraj, M. Sankaralingam, K. Giribabu, Graphene-metal chalcogenide modified electrochemical sensors, in: Graphene-based electrochemical sensors for biomolecules, Elsevier, 2019, pp. 139–153, <https://doi.org/10.1016/B978-0-12-815394-9.00006-6>.
 - [36] S.R. Ali, R.R. Parajuli, Y. Balogun, Y. Ma, H. He, A nnoxidative electrochemical sensor based on a self-doped polyaniline/carbon nanotube composite for sensitive and selective detection of the neurotransmitter dopamine: a review, Sensors 8 (2008) 8423–8452, <https://doi.org/10.3390/s8128423>.
 - [37] Y.Z. Keteklahijani, F. Sharif, E.P.L. Roberts, U. Sundararaj, Enhanced sensitivity of dopamine biosensors: an electrochemical approach based on nanocomposite electrodes comprising polyaniline, nitrogen-doped graphene, and DNA-functionalized carbon nanotubes, J. Electrochem. Soc. 166 (2019) B1415–B1425, <https://doi.org/10.1149/2.0361915jes>.
 - [38] R. Sangubotla, J. Kim, Fluorometric biosensor based on boronic acid-functionalized ZnO-derived nanostructures for the detection of N-acetylneuraminic acid and its in vivo bio-imaging studies, J. Taiwan Inst. Chem. Eng. 138 (2022) 104477, <https://doi.org/10.1016/j.jtice.2022.104477>.
 - [39] S.K. Arumugasamy, S. Govindaraju, K. Yun, Electrochemical sensor for detecting dopamine using graphene quantum dots incorporated with multiwall carbon nanotubes, Appl. Surf. Sci. 508 (2020) 145294, <https://doi.org/10.1016/j.apsusc.2020.145294>.
 - [40] M. Saleh Mohammadnia, H. Roghani-Mamaqani, M. Ghalkhani, S. Hemmati, A modified electrochemical sensor based on N,S-doped carbon dots/carbon nanotube-poly(Amidoamine) dendrimer hybrids for imatinib mesylate determination, Biosensors 13 (2023), <https://doi.org/10.3390/bios13050547>.
 - [41] G. Lv, M. Yang, Y. Pan, Y. Fan, J. Zuo, X. Liu, J. Chen, S. Zhang, High-sensitive electrochemical sensor based on Ni/NiCx-integrated functional carbon nanotubes for simultaneous determination of acetaminophen and dopamine, Colloids Surfaces A Physicochem. Eng. Asp. 703 (2024) 135428, <https://doi.org/10.1016/j.colsurfa.2024.135428>.
 - [42] X. Liao, X. Luo, Y. Li, Y. Zhou, Q. Liang, K. Feng, M.B. Camarada, J. Xiong, An antifouling electrochemical sensor based on multiwalled carbon nanotubes functionalized black phosphorus for highly sensitive detection of carbendazim and corresponding response mechanisms analyses, Microchem. J. 190 (2023), <https://doi.org/10.1016/j.microc.2023.108671>.
 - [43] Z. Huang, M. Luisa Cerón, K. Feng, D. Wang, M. Belén Camarada, X. Liao, Anchoring black phosphorus quantum dots over carboxylated multiwalled carbon nanotubes: A stable 0D/1D nanohybrid with high sensing performance to Ochrotoxin a, Appl. Surf. Sci. 583 (2022), <https://doi.org/10.1016/j.apsusc.2022.152429>.
 - [44] D.D. Chronopoulos, H. Saini, I. Tantis, R. Zboril, K. Jayaramulu, M. Otyepka, Carbon nanotube based metal-organic framework hybrids from fundamentals toward applications, Small 18 (2022), <https://doi.org/10.1002/sml.202104628>.
 - [45] X. Li, S. Zuo, W. Liu, Y. He, Z. Xiao, C. Zhu, Field emission properties of the dendritic carbon nanotubes film embedded with ZnO quantum dots, J. Nanomater. 2011 (2011), <https://doi.org/10.1155/2011/382068>.
 - [46] S. Żarska, R. Szukiewicz, S. Coseri, V. Pavlyuk, D. Krasowska, W. Ciesielski, Synthesis and structural studies of new selenium derivatives based on covalent functionalization of MWCNTs, Int. J. Mol. Sci. 24 (2023), <https://doi.org/10.3390/ijms24043299>.
 - [47] N. Rajamohan, S. Bosu, M. Rajasimman, S. Varjani, Environmental remediation of selenium using surface modified carbon nano tubes - characterization, influence of variables, equilibrium and kinetic analysis, Environ. Res. 216 (2023) 114629, <https://doi.org/10.1016/j.envres.2022.114629>.
 - [48] X. Jiang, W. Huang, R. Wang, H. Li, X. Xia, X. Zhao, L. Hu, T. Chen, Y. Tang, H. Zhang, Photocarrier relaxation pathways in selenium quantum dots and their application in UV-Vis photodetection, Nanoscale 12 (2020) 11232–11241, <https://doi.org/10.1039/c9nr10235c>.
 - [49] N. Sharma, I. Sharma, M.K. Bera, Microwave-assisted green synthesis of carbon quantum dots derived from calotropis gigantea as a fluorescent probe for bioimaging, J. Fluoresc. 32 (2022) 1039–1049, <https://doi.org/10.1007/s10895-022-02923-4>.
 - [50] R. Gopinath, P. Billigraham, T.P. Sathishkumar, Physico-chemical, mechanical and thermal properties of novel cellulosic fiber extracted from the bark of Tithonia Diversifolia, J. Nat. Fibers 20 (2023), <https://doi.org/10.1080/15440478.2023.2170944>.
 - [51] R.K. Das, S. Mohapatra, Highly luminescent, heteroatom-doped carbon quantum dots for ultrasensitive sensing of glucosamine and targeted imaging of liver cancer cells, J. Mater. Chem. B 5 (2017) 2190–2197, <https://doi.org/10.1039/c6tb03141b>.
 - [52] R. Sangubotla, J. Kim, Tripeptide and phenylboronic acid-functionalized eco-friendly carbon dots for dual sensing of dopamine and their bioimaging applications in SH-SY5Y cells, Dye. Pigment. 191 (2021) 109364, <https://doi.org/10.1016/j.dyepig.2021.109364>.
 - [53] R. Sangubotla, S. Won, J. Kim, Boronic acid-modified fluorescent sensor using coffee biowaste-based carbon dots for the detection of dopamine, J. Photochem. Photobiol. A Chem. 438 (2023) 114542, <https://doi.org/10.1016/j.jphotochem.2023.114542>.
 - [54] Y. Huang, G. Lu, L. Zhou, A mini review on selenium quantum dots: synthesis and biomedical applications, Front. Bioeng. Biotechnol. 11 (2023) 1–7, <https://doi.org/10.3389/fbioe.2023.1332993>.
 - [55] H.K. Jeong, E. Echeverria, P. Chakraborti, H.T. Le, P.A. Dowben, Electronic structure of cyclodextrin-carbon nanotube composite films, RSC Adv. 7 (2017) 10968–10972, <https://doi.org/10.1039/c6ra26900a>.
 - [56] T. Skaltsas, A. Stergiou, D.D. Chronopoulos, S. Zhao, H. Shinohara, N. Tagmatarchis, All-carbon nanosized hybrid materials: fluorescent carbon dots conjugated to Multiwalled carbon nanotubes, J. Phys. Chem. C 120 (2016) 8550–8558, <https://doi.org/10.1021/acs.jpcc.6b02267>.
 - [57] W. Kiciński, B. Budner, M. Norek, M. Szala, M. Polański, S. Dyjak, Origin of microporosity in chalcogen-doped carbon materials: the case of selenium-doped

- carbogels, *Microporous Mesoporous Mater.* 272 (2018) 260–264, <https://doi.org/10.1016/j.micromeso.2018.06.047>.
- [58] L.J. Mohammed, K.M. Omer, Dual functional highly luminescence B, N Co-doped carbon nanodots as nanothermometer and Fe³⁺/Fe²⁺ sensor, *Sci. Rep.* 10 (2020) 1–12, <https://doi.org/10.1038/s41598-020-59958-5>.
- [59] X. Chen, X. Wang, D. Fang, A review on C1s XPS-spectra for some kinds of carbon materials, *Fullerenes Nanotub. Carbon Nanostruct.* (2020) 1048–1058, <https://doi.org/10.1080/1536383X.2020.1794851>.
- [60] J.P. Victoria Tafoya, S. Doszczeczko, M.M. Titirici, A.B. Jorge Sobrido, Enhancement of the electrocatalytic activity for the oxygen reduction reaction of boron-doped reduced graphene oxide via ultrasonic treatment, *Int. J. Hydrogen Energy* 47 (2022) 5462–5473, <https://doi.org/10.1016/j.ijhydene.2021.11.127>.
- [61] Z.N. Huang, J. Jiao Zou, Q. Teng, M.M. Liu, F.P. Yuan, X.Y. Jiao, J.G.Y. Jiang, A novel electrochemical sensor based on self-assembled platinum nanochains - multi-walled carbon nanotubes-graphene nanoparticles composite for simultaneous determination of dopamine and ascorbic acid, *Ecotoxicol. Environ. Saf.* 172 (2019) 167–175, <https://doi.org/10.1016/j.ecoenv.2019.01.091>.
- [62] Y. Huang, Y. Zang, S. Ruan, Y. Zhang, P. Gao, W. Yin, C. Hou, D. Huo, M. Yang, H. B. Fa, A high efficiency N, P doped porous carbon nanoparticles derived from lotus leaves for simultaneous electrochemical determination of ascorbic acid, dopamine, and uric acid, *Microchem. J.* 165 (2021), <https://doi.org/10.1016/j.microc.2021.106152>.
- [63] X. Peng, Y. Xie, Y. Du, Y. Song, S. Chen, Simultaneous detection of ascorbic acid, dopamine and uric acid based on vertical N-doped carbon nanosheets/three-dimensional porous carbon, *J. Electroanal. Chem.* 904 (2022) 115850, <https://doi.org/10.1016/j.jelechem.2021.115850>.
- [64] Y. Zhou, Y. Fang, R.P. Ramasamy, Non-covalent functionalization of carbon nanotubes for electrochemical biosensor development, *Sens. (Switzerland)* 19 (2019), <https://doi.org/10.3390/s19020392>.