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ARTICLE TYPE

A highly sensitive persulfate sensor based on hybrid nanocomposite with silicomolybdate doping poly(3,4-ethylenedioxythiophene) on multi-walled carbon nanotubes

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A novel hybrid nanocomposite has been successfully fabricated for persulfate ($S_2O_8^{2-}$) detection. It can be easily prepared by grafting silicomolybdate (SiMO) and poly(3,4-ethylenedioxythiophene) (PEDOT) on multi-walled carbon nanotubes (MWCNT) to form the SiMO-PEDOT/MWCNT hybrid composite. The SiMO-PEDOT film formation is initiated through the electropolymerization of EDOT monomers. The monomers are firstly electropolymerized to form the positive PEDOT and then the positive polymers are attractive to the negative SiMO, resulting in the electrocodeposition on electrode surface. It shows three significant redox couples and the redox peak currents can be enhanced by using a MWCNT-modified electrode. Morphological features were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The electrode shows good activity towards $S_2O_8^{2-}$ reduction with low overpotential ($E_{pc} = 0$ V). Amperometric response provides linear range of 1–3333 μ M with sensitivity of 2928.9 μ A $mM^{-1} cm^{-2}$, detection limit of 1×10^{-6} M ($S/N = 3$), and response time of 2.3 s. The SiMO-PEDOT/MWCNT electrode can effectively analyse $S_2O_8^{2-}$ due to its low overpotential, high sensitivity, good stability, fast response, and low cost.

1. Introduction

Persulfate ($S_2O_8^{2-}$) is a strong oxidant and has been used for many applications such as water and soil decontaminants,¹ circuit board fabrication,² cosmetics,³ and polymerization.⁴ It has been reported that $S_2O_8^{2-}$ may either cause or intensify diseases such as asthma⁵ and skin reactions.⁶ Because of a gradual increase in application of $S_2O_8^{2-}$ finding a simple and convenient measurement of $S_2O_8^{2-}$ in water is desired. Therefore, many studies have been performed for the quantitative determination of $S_2O_8^{2-}$ in the recent years.^{7,8} Some of these methods such as reductometric,^{9,10} polarographic,^{11–13} and spectrophotometric^{14,15} have been criticized for time consumption, sample pre-treatment, and complicated procedure. Electrochemical methods^{16–20} are types of methods valuable to be used for further investigation because of advantages such as functional simplicity, fast and selective response, and low cost.

The modification of electrode surfaces with inorganic or organic coatings often avoids some drawbacks and represents a rapid and versatile resource for the preparation of stable and selective new electrochemical sensors.^{21–23} Recently, Salimi et al. have reported their works for electrochemical detection of sulphur oxoanions²⁴ and immobilization of flavin adenine dinucleotide onto nickel oxide nanostructures for fabrication of a highly sensitive $S_2O_8^{2-}$ sensor.⁸ Razmi and Heidari have reported a novel lead pentacyanonitrosylferrate modified electrode can be used as an amperometric sensor for the determination of peroxydisulfate.⁷ Savari et al. also have reported the fabrication of $S_2O_8^{2-}$ sensors for a highly sensitive amperometric and voltammetric of $S_2O_8^{2-}$ sensor with neutral red/nickel oxide

nanowires modified carbon paste electrodes.²⁵ Roushani and Karami have reported a nanocomposite containing nano-ruthenium oxide/thionine and nano-ruthenium oxide/celestine blue for electrochemical detection of $S_2O_8^{2-}$.²⁶ The applicability of graphene quantum dots/riboflavin nanocomposite modified electrode as amperometric sensor for $S_2O_8^{2-}$ detection was investigated for the detection of $S_2O_8^{2-}$.²⁷ However, some of them are not eco-friendly such as those using lead or dye composites.

Some researches have been noticed on the electropolymerization of some aromatic compounds on a GCE surface, e.g. some authors devoted in electrochemical glutathione sensor based on electrochemically deposited poly-m-aminophenol and poly(brilliant cresyl blue).^{28,29} Among the conducting polymers, poly(3,4-ethylenedioxythiophene), PEDOT, is a very attractive material due to its low band gap, high conductivity and stability, and transparency in the doped state.^{30–32} PEDOT has been proposed as an alternative to traditional polymers as the electroactive component in biosensors.^{23,33,34} Various superior properties of PEDOT can be expected to keep further researching for determination of $S_2O_8^{2-}$.

Silicomolybdate (SiMO) polyoxometalate, $SiMo_{12}O_{40}^{4-}$, form nanometer-sized polyoxometalate clusters that are of interest in bioanalysis, material science, catalysis, magnetism, surface chemistry and medicine. The polyoxometalate anion is a mixed-valence species and polyoxometalate modified electrodes and their electrocatalytic properties are very important and are the subject of intensive research.³⁵ Recently, a simple procedure is also proposed for immobilization of copper complex $[Cu(bpy)_2]Br_2$ with SiMO and single-walled carbon nanotubes, presenting a very low detection limit for H_2O_2 .³⁶ The negatively charged SiMO might provide a good chance to be coimmobilized

with other positively charged and electroactive materials such as PEDOT.

Since the discovery of carbon nanotubes (CNTs),³⁷ research on CNTs have improved speedily and have become one of the most attractive parts of nanotechnology in the world.^{38,39} They are known to possess interesting chemical and physical properties such as electric conductivity, chemical stability, mechanical and tensile strength.^{40,41} Multi-walled carbon nanotubes (MWCNT) incorporated with naphthol green B was used to determine $\text{S}_2\text{O}_8^{2-}$.⁴² Good electrocatalytic activities of CNTs are expected so that CNTs hybrid composites with organic or inorganic compounds are worthy to study in the electrochemical sensors.

In the present study, we present a simple and facile method to immobilize SiMO and PEDOT on a MWCNT-modified electrode for $\text{S}_2\text{O}_8^{2-}$ sensor. The SiMO-PEDOT/MWCNT hybrid nanocomposite is prepared by the codeposition of PEDOT and SiMO on a MWCNT-modified electrode. The negatively charged SiMO could be easily induced to codeposit on electrode surface by the positively charged PEDOT after the electropolymerization of the EDOT monomers. The SiMO-PEDOT/MWCNT hybrid nanocomposite was characterized and studied with the electrocatalytic property for $\text{S}_2\text{O}_8^{2-}$ reduction. All test results are also analyzed regarding to sensitivity, linear range and selectivity toward $\text{S}_2\text{O}_8^{2-}$ detection.

2. Experimental

2.1 Materials and apparatus

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), 3,4-ethylenedioxythiophene (EDOT), and silicomolybdate (SiMO) were purchased from Sigma-Aldrich (USA) and used as received. All other chemicals (Merck) used were of analytical grade (99%). Double-distilled deionized water ($> 18.1 \text{ M}\Omega \text{ cm}^{-1}$) was used to prepare all the solutions. All other reagents were of analytical grade and used without further purification.

The SiMO-PEDOT/MWCNT hybrid composite was characterised by cyclic voltammetry, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The electrochemical experiments were conducted using a CHI 1205a electrochemical workstation (CH Instruments, USA) with a conventional three-electrode setup using the SiMO-PEDOT/MWCNT/GCE as the working electrode, an Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode. A BAS (Bioanalytical Systems, Inc., USA) glassy carbon electrode (GCE) with a diameter of 0.3 cm was used for all electrochemical experiments. All potentials reported in this paper were referred to an Ag/AgCl electrode. The buffer solution was completely deaerated using a nitrogen gas atmosphere. The composite was analysed by its morphology was characterised by SEM and AFM. Indium tin oxide (ITO) was used as the substrate for various films in the SEM and AFM analyses.

2.2 Fabrication of the PEDOT, SiMO, MWCNT, and SiMO-PEDOT/MWCNT modified electrodes

GCE and ITO substrates were coated with different modifiers, including PEDOT, SiMO, MWCNT, and SiMO-PEDOT/MWCNT, for study in this work.

The PEDOT modified electrodes were individually prepared in a sulphuric solution (pH 1.5) containing 0.01 M EDOT using a bare electrode. By consecutive cyclic voltammetry, they were

controlled in the potential range of -0.2–1.1 V with a scan rate of 0.1 Vs^{-1} and 12 scan cycles.

The SiMO modified electrodes were prepared by drop-casting. $10 \mu\text{l}$ of a sulphuric solution (pH 1.5) containing $1 \times 10^{-4} \text{ M}$ SiMO was directly dropped on a bare electrode. The electrodes were further dried out in an oven at 40°C .

The MWCNT modified electrodes were prepared by drop-casting. In order to have hydrophilic property for well dispersion in aqueous solution, pristine MWCNT was taken with acidic treatment.²³ $10 \mu\text{l}$ of MWCNT solution (1 mg ml^{-1} , pH 1.5) was directly dropped on a bare electrode. The electrodes were further dried out in an oven at 40°C .

The electrocodeposition of PEDOT and SiMO was easily carried out in a sulphuric solution (pH 1.5) containing $1 \times 10^{-4} \text{ M}$ SiMO and 0.01 M EDOT using a bare or a MWCNT modified electrode to prepare the SiMO-PEDOT or SiMO-PEDOT/MWCNT modified electrode. By consecutive cyclic voltammetry, it was controlled in the potential range of -0.2–1.1 V with a scan rate of 0.1 Vs^{-1} and 12 scan cycles.

The PEDOT, SiMO, MWCNT, and SiMO-PEDOT/MWCNT modified electrodes were individually prepared as aforementioned processes and they were stored at room temperature before use.

3. Results and discussion

3.1 Preparation and characterisation of the SiMO-PEDOT/MWCNT hybrid composite

Conducting polymers including polypyrroles, polyanilines and polythiophenes (e.g., PEDOT) are prepared by oxidizing corresponding monomers. They have positive charges every three to five monomeric units along polymeric backbone.⁴³ This information provides the chance to utilize PEDOT co-immobilize some negatively charged species (e.g., SiMO) on electrode surface. Therefore, the SiMO and PEDOT immobilized on a MWCNT-electrode is expected to perform through the EDOT electropolymerization with suitable potential control.^{23,43}

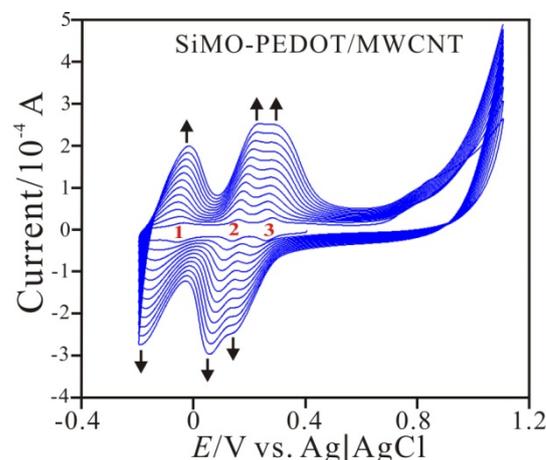


Fig. 1 Consecutive cyclic voltammograms of a MWCNT/GCE examined in sulphuric solution (pH 1.5) containing $1 \times 10^{-4} \text{ M}$ silicomolybdate and 0.01 M EDOT. Scan rate = 0.1 Vs^{-1} .

Fig. 1 shows the voltammograms of a MWCNT-modified GCE electrode examined in pH 1.5 sulphuric solution containing 1×10^{-4}

⁴ M SiMO and 0.01 M EDOT. In the first scan cycle, there are three redox couples (redox couple 1, 2, and 3) revealing to $\text{H}_4\text{SiMo}_{12}\text{O}_{40}/\text{H}_6\text{SiMo}_{12}\text{O}_{40}$, $\text{H}_6\text{SiMo}_{12}\text{O}_{40}/\text{H}_8\text{SiMo}_{12}\text{O}_{40}$, and $\text{H}_8\text{SiMo}_{12}\text{O}_{40}/\text{H}_{10}\text{SiMo}_{12}\text{O}_{40}$ redox processes.³⁵ It can be seen that redox peak currents increase with the increase of scan cycle. In the formation process, the negatively charged SiMO is attracted to positively PEDOT to form the SiMO-PEDOT hybrid composite and deposit on MWCNT-electrode surface.

Different materials modified electrodes were prepared and studied by cyclic voltammetry. Fig. 2 shows the voltammograms of (a) PEDOT, (b) MWCNT, (c) SiMO, and (d) SiMO-PEDOT/MWCNT modified electrodes. Both PEDOT and MWCNT modified electrodes (curve (a) and (b)) show no any obvious redox couples. In contrast, the SiMO modified electrode shows three significant redox couples with formal potential of $E^{\circ}_1 = -0.057$ V, $E^{\circ}_2 = +0.137$ V, $E^{\circ}_3 = +0.257$ V for redox processes of $\text{H}_4\text{SiMo}_{12}\text{O}_{40}/\text{H}_6\text{SiMo}_{12}\text{O}_{40}$, $\text{H}_6\text{SiMo}_{12}\text{O}_{40}/\text{H}_8\text{SiMo}_{12}\text{O}_{40}$, and $\text{H}_8\text{SiMo}_{12}\text{O}_{40}/\text{H}_{10}\text{SiMo}_{12}\text{O}_{40}$, respectively. Furthermore, the SiMO-PEDOT/MWCNT shows the redox couples with formal potential of $E^{\circ}_1 = -0.087$ V, $E^{\circ}_2 = +0.126$ V, $E^{\circ}_3 = +0.225$ V, similar to those of SiMO modified electrode. This result indicates that the SiMO-PEDOT/MWCNT hybrid composite can maintain the electrochemical properties of single PEDOT, SiMO, and MWCNT. Particularly, the hybrid composite shows the redox peak current responses much higher than that of single PEDOT, SiMO, and MWCNT modified electrodes. One can conclude that these active materials can be stably immobilized on the electrode surface and exhibit strong electrochemical characteristic with synergetic effect.

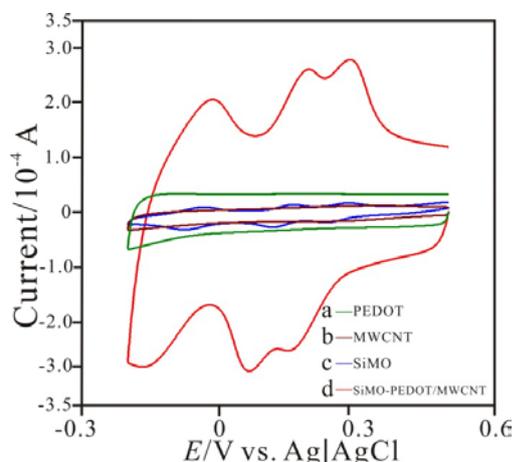


Fig. 2 Cyclic voltammograms of a modified GCE examined in pH 1.5 sulphuric solution with different modifiers including (a) PEDOT, (b) MWCNT, (c) SiMO, and (d) SiMO-PEDOT/MWCNT, respectively. Scan rate = 0.1 Vs⁻¹.

Fig. 3 shows the SEM images for (A) PEDOT, (B) SiMO, (C) MWCNT, and (D) SiMO-PEDOT/MWCNT, respectively. Fig. 3A-C exhibit clusters, big clusters, and dendritic structures for (A) PEDOT, (B) SiMO, and (C) MWCNT, respectively. Particularly, the SiMO-PEDOT/MWCNT shows the specific cauliflower image different from the PEDOT (Fig. 3A), SiMO (Fig. 3B), and MWCNT (Fig. 3C). This result indicates that the SiMO-PEDOT/MWCNT can be successfully immobilized on electrode

surface due to the hybrid formation of PEDOT and SiMO on MWCNT.

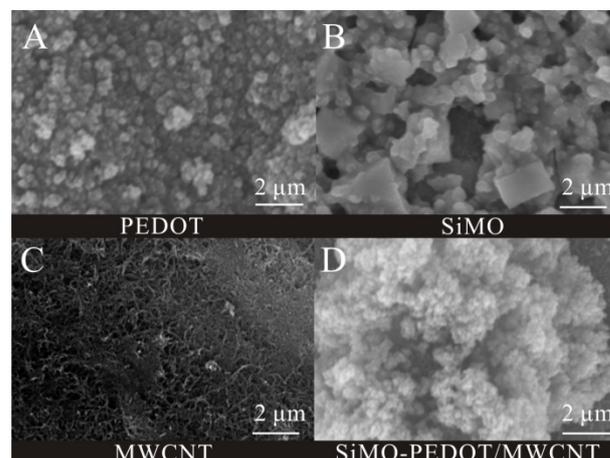


Fig. 3 SEM images of (A) PEDOT, (B) SiMO, (C) MWCNT, and (D) SiMO-PEDOT/MWCNT coated ITO electrodes.

Fig. 4 shows the AFM images for (A) PEDOT, (B) SiMO, and (C) MWCNT, and (D) SiMO-PEDOT/MWCNT, respectively. The AFM images of these modifiers show average diameter of 138.8 nm, 56.2 nm, 16.6 nm, and 120.9 nm for PEDOT, SiMO, MWCNT, and SiMO-PEDOT/MWCNT, respectively. They show the average height of 8.3 nm, 15.0 nm, 17.4 nm, and 31.0 nm, respectively. Although the SiMO-PEDOT/MWCNT shows high average diameter, it exhibits the average height in nano-scale. The SiMO-PEDOT/MWCNT hybrid composite has higher average height might prove that the electroactive specific SiMO and PEDOT successfully immobilized on MWCNT resulted in specific stacking structure. Further considering the roughness, they are estimated in 6.0 nm, 11.9 nm, 11.6 nm, and 26.4 nm, respectively. The result indicates that the different materials can be successfully overlapped in nano-scale by our method. One can conclude that the hybrid nanocomposite (SiMO-PEDOT/MWCNT) can be easily prepared by the simple method.

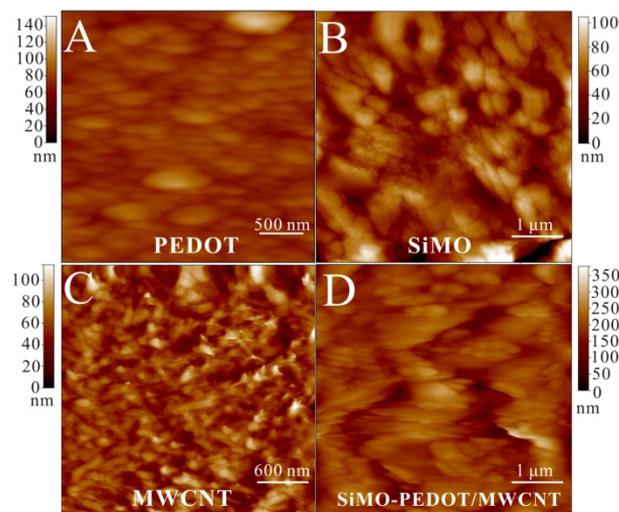


Fig. 4 AFM images of (A) PEDOT, (B) SiMO, (C) MWCNT, and (D) SiMO-PEDOT/MWCNT coated ITO electrodes.

Further considering the morphology of the SiMO-PEDOT/MWCNT hybrid composite, the related materials (SiMO, PEDOT, and MWCNT) were also examined by TEM. As shown in Fig. S1, the SiMO-PEDOT/MWCNT displays the stacking structure. The result has extreme agreement with those tested by SEM and AFM. As the above results, one can conclude that the SiMO and PEDOT can be successfully immobilized on MWCNT resulted in compact and specific stacking structure.

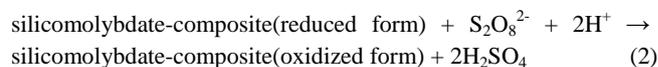
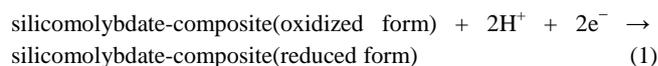
3.2 Electrocatalytic reduction of persulfate at the SiMO-PEDOT/MWCNT electrode

Different modifiers were investigated for electrocatalytic reduction of $S_2O_8^{2-}$. Fig. S2 shows the voltammograms of different modifiers including (A) SiMO, (B) PEDOT, (C) MWCNT, (D) SiMO/MWCNT, (E) SiMO-PEDOT, and (F) SiMO-PEDOT/MWCNT modified GCEs examined in the absence/presence of 1×10^{-3} M $S_2O_8^{2-}$. For single modifier except of SiMO, both PEDOT and MWCNT individually contributed net current of 102.9 μ A and 9.7 μ A at +0.2 V. For binary modifier, the SiMO-PEDOT shows current increase at three cathodic peaks ($E_{pc1} = -0.13$ V, $E_{pc2} = +0.08$ V, $E_{pc3} = +0.18$ V) with net current of 18.8 μ A, 47.0 μ A, and 32.6 μ A, respectively. For tertiary modifier, the SiMO-PEDOT/MWCNT also shows current increase at three cathodic peaks ($E_{pc1} = -0.15$ V, $E_{pc2} = +0.06$ V, $E_{pc3} = +0.16$ V) with net current of 9.8 μ A, 57.9 μ A, and 81.8 μ A, respectively. Both SiMO and SiMO/MWCNT do not provide current increase for $S_2O_8^{2-}$, this phenomenon might indicate that the immobilization is weak because only adsorption method is used to immobilize SiMO on bare electrode or MWCNT-electrode. Once PEDOT was applied to immobilize SiMO, they can show good electrocatalytic property for reduction of $S_2O_8^{2-}$ such as SiMO-PEDOT and SiMO-PEDOT/MWCNT. One can conclude that the SiMO can be well immobilized by the electrocodeposition of SiMO and PEDOT on bare electrode or MWCNT-electrode, providing ability for electrocatalytic reduction of $S_2O_8^{2-}$. Furthermore, SiMO can be successfully immobilized on electrode surface by PEDOT and the hybrid composite can show high current response for electrocatalytic reduction of persulfate.

Considering about optimization, the SiMO-PEDOT/MWCNT was examined with different pH condition for electrocatalytic reduction of $S_2O_8^{2-}$. Fig. 5A–C shows the voltammograms of the SiMO-PEDOT/MWCNT examined in the absence/presence of 1×10^{-3} M $S_2O_8^{2-}$ with pH 1.5, pH 7, and pH 13, respectively. It might indicate that modifier is electroactive so that one small cathodic peak is still present even in the blank solution. It presents obvious redox peaks in pH 1–7. When the electrode was tested in the alkaline solution (Fig. 5C), the redox peaks are not obvious with low current in the absence and presence of $S_2O_8^{2-}$. It indicates that the SiMO-PEDOT/MWCNT hybrid composite prefers to acidic condition. The results are similar to their single materials (PEDOT and SiMO). One can conclude that the hybrid composite can show well electrocatalytic reduction of $S_2O_8^{2-}$ in acidic condition.

Particularly, Fig. 5A shows high current response to $S_2O_8^{2-}$ concentration. By the comparison between curve (a) and (b), the cathodic peak current increases with the increase of $S_2O_8^{2-}$

concentration. The electrocatalytic cathodic peaks can be found at -0.154 V, +0.063 V, and +0.163 V. It shows lower overpotential and higher current response to $S_2O_8^{2-}$ when compared to that of bare electrode. The reduction potential is corresponding to the redox process for $H_4SiMo_{12}O_{40}/H_6SiMo_{12}O_{40}$, $H_6SiMo_{12}O_{40}/H_8SiMo_{12}O_{40}$, and $H_8SiMo_{12}O_{40}/H_{10}SiMo_{12}O_{40}$, respectively.³⁵ As indicated in the literature, the reduction of $S_2O_8^{2-}$ was catalysed by the silicomolybdate redox processes according to the following reactions:



Although PEDOT does not have obvious redox couple in the voltammogram, the function of PEDOT in hybrid during the persulfate sensing process cannot be neglected. The reduction of $S_2O_8^{2-}$ catalysed by the PEDOT redox processes can be expressed as the following reactions:

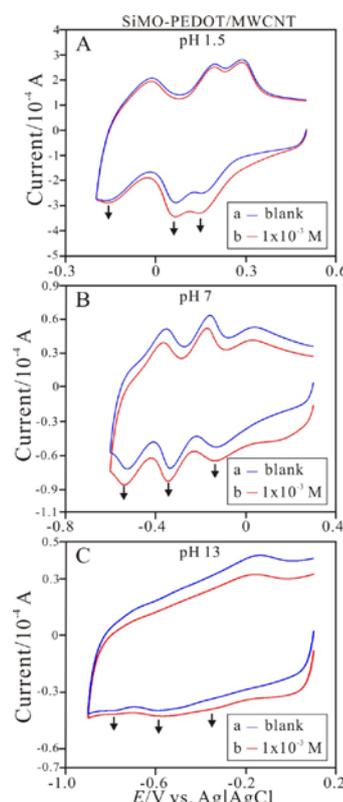
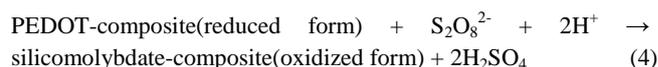
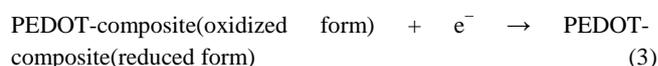


Fig. 5 Cyclic voltammograms of SiMO-PEDOT/MWCNT/GCE examined in (A) pH 1.5, (B) pH 7, and (C) pH 13 containing $[Na_2S_2O_8] =$ (a) blank and (b) 1×10^{-3} M, respectively. Scan rate = 0.1 Vs^{-1} .

3.3 Amperometric response of persulfate at the SiMO-PEDOT/MWCNT electrode

Fig. 6 shows the amperometric response of the SiMO-PEDOT/MWCNT electrode examined with several additions of $\text{S}_2\text{O}_8^{2-}$ spiked into pH 1.5 sulphuric solutions. The response curve turns downward with increasing concentration because an increasing amount of intermediate species is adsorbed onto the electrode surface, prolonging the reaction time. Inset (a) of Fig. 6 shows fast response time of 2.3 s and detection limit of $1 \mu\text{M}$ ($1 \times 10^{-6} \text{ M}$) based on signal/noise = 3. The calibration curve for $\text{S}_2\text{O}_8^{2-}$ sensor is shown in the inset (b) of Fig. 6, which provides the regression equation, $I_{\text{pc}}(\mu\text{A}) = 207.1C_{\text{S}_2\text{O}_8}(\text{mM}) + 9.4$, with correlation coefficient of $R^2 = 0.9971$. The electrode shows a linear concentration range of $1\text{--}3333 \mu\text{M}$ and a very high sensitivity of $2928.9 \mu\text{A mM}^{-1} \text{ cm}^{-2}$. Particularly, it also provides another linear concentration range of $9.3 \times 10^{-3}\text{--}4.4 \times 10^{-2} \text{ M}$ and sensitivity of $131.5 \mu\text{A mM}^{-1} \text{ cm}^{-2}$. One can conclude that the hybrid composite can be a candidate due to fast response, low overpotential, and high sensitivity.

The SiMO-PEDOT/MWCNT sensor was compared with various $\text{S}_2\text{O}_8^{2-}$ sensors in Table 1. It shows competitive performance among these modifiers. Particularly, the SiMO-PEDOT/MWCNT modified electrode shows low overpotential and high sensitivity towards $\text{S}_2\text{O}_8^{2-}$. It is more eco-friendly compared with those using lead and dye. Excellent performance is clearly disclosed due to the specific SiMO-PEDOT/MWCNT composite. The hybrid composite significantly increases the electrocatalytic current response and promotes electron transfer in the reduction of $\text{S}_2\text{O}_8^{2-}$. The SiMO-PEDOT/MWCNT hybrid composite can be an ideal electrocatalyst in the literature for $\text{S}_2\text{O}_8^{2-}$ sensors based on low overpotential and high sensitivity.

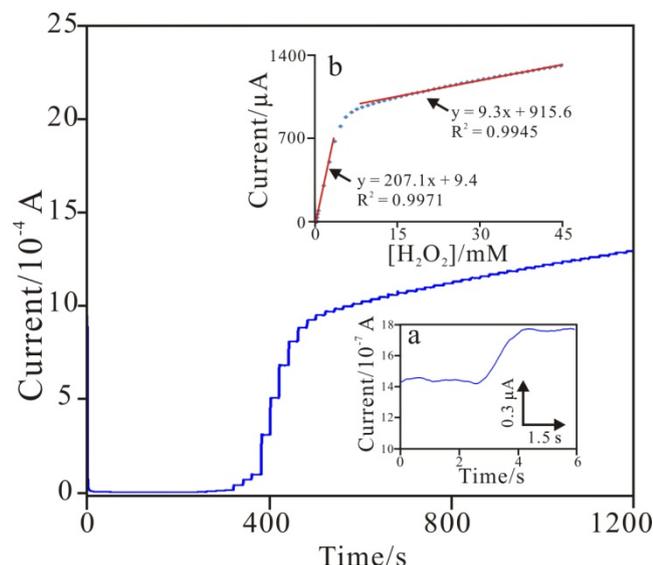


Fig. 6 Amperograms of SiMO-PEDOT/MWCNT/GCE examined in sulphuric solution (pH 1.5) with several additions of $\text{Na}_2\text{S}_2\text{O}_8$. Electrode rotation speed = 5000 rpm. $E_{\text{app}} = 0 \text{ V}$. Insets: (a) the scale-up amperogram in the presence of $1 \times 10^{-6} \text{ M}$ $\text{Na}_2\text{S}_2\text{O}_8$ and (b) the calibration curve.

Table 1 Performance comparison of various $\text{S}_2\text{O}_8^{2-}$ sensors.

Modified electrode	E_{app} ^a (V vs. Ag/AgCl)	Sensitivity ($\mu\text{A mM}^{-1} \text{ cm}^{-2}$)	LOD ^b (μM)	Linear range (μM)	Ref.
Lead pentacyano-nitrosylferrate/Carbon ceramic	0.05	527.7	1.58	5–50	7
FAD/NiOx/GCE	-0.2	528.7	0.38	3–1500	8
Neutral red/Nickel oxide nanowires/Carbon paste	-0.2	647.3	0.03	0.1–12000	25
Graphene quantum dots/riboflavin/GCE	-0.1	149.7	0.2	1–1000	27
Poly(brilliant cresyl blue)/MWCNTs/GCE	-0.03	124.5	1	10–100	29
Naphthol green B/MWCNT	-0.3	301.9	6.9	15.9–7100	42
SiMO-PEDOT/MWCNT/GCE	0	2928.9	1	1–3333	This work

^a E_{app} = Applied potential.

^bLOD = Limit of detection.

3.4 Reproducibility, stability, and anti-interference property of the SiMO-PEDOT/MWCNT electrode

The reproducibility and stability of the sensor were evaluated. Five SiMO-PEDOT/MWCNT electrodes were investigated by amperometry ($E_{\text{app}} = 0 \text{ V}$). The amperometric responses of the SiMO-PEDOT/MWCNT were obtained in pH 1.5 with sequential additions of $1 \times 10^{-3} \text{ M}$ $\text{S}_2\text{O}_8^{2-}$. Test result was shown in Table S1. The relative standard deviation (R.S.D.) was 3.9%, confirming the high reproducibility of the preparation method. Ten successive measurements of $\text{S}_2\text{O}_8^{2-}$ at one SiMO-PEDOT/MWCNT electrode yielded an R.S.D. of 4.3% (Table S2), indicating that the sensor was stable. The long-term stability of the sensor was also evaluated by measuring its current response to $\text{S}_2\text{O}_8^{2-}$ within a 7-day period. The sensor was exposed to air, and its sensitivity was tested every day. The current response of the SiMO-PEDOT/MWCNT electrode was approximately 94% of its original counterpart, which can be mainly attributed to the chemical stability of SiMO-PEDOT/MWCNT in acidic solution. Based on these results, the SiMO-PEDOT/MWCNT electrode shows a nearly constant peak current towards $\text{S}_2\text{O}_8^{2-}$ reduction, indicating that the electrode is very stable in the determination of $\text{S}_2\text{O}_8^{2-}$.

Fig. 7 shows the amperometric response of SiMO-PEDOT/MWCNT examined in pH 7 PBS with sequential additions of $\text{S}_2\text{O}_8^{2-}$ and potential interferences including sodium sulphite, sodium sulphate, cobalt(II) chloride, and nickel(II) chloride ($1 \times 10^{-3} \text{ M}$ for each addition). A well-defined $\text{S}_2\text{O}_8^{2-}$ response was obtained, and insignificant responses were observed for interfering species. As the results, the SiMO-PEDOT/MWCNT electrode shows good selectivity for $\text{S}_2\text{O}_8^{2-}$ detection.

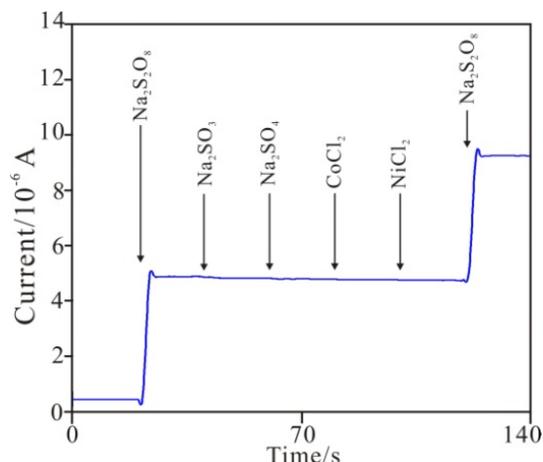


Fig. 7 Amperograms of SiMO-PEDOT/MWCNT/GCE examined in sulphuric solution (pH 1.5) with 1×10^{-5} M $\text{Na}_2\text{S}_2\text{O}_8$ and potential interferences (each for 1×10^{-3} M). Electrode rotation speed = 5000 rpm. $E_{\text{app}} = 0$ V.

4. Conclusions

The SiMO-PEDOT/MWCNT hybrid nanocomposite can be successfully prepared on electrode surface by a simple method. It shows competitive performance for effective determination of $\text{S}_2\text{O}_8^{2-}$. The novel $\text{S}_2\text{O}_8^{2-}$ sensor presents attractive features, such as low overpotential, high sensitivity, high selectivity, simple method, low cost, and eco-friendly.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- P. F. Killian, C. J. Bruell, C. J. Liang and M. C. Marley, *Soil Sediment Contam.*, 2007, **16**, 523.
- J. Branson, J. Naber and G. Edelen, *IEEE T. Educ.*, 2000, **43**, 257.
- T. Mensing, W. Marek, M. Raulf-Heimsoth and X. Baur, *Eur. Respir. J.*, 1998, **12**, 1371.
- H. R. Lin, *Eur. Polym. J.*, 2001, **37**, 1507.
- X. Munoz, M. J. Cruz, R. Orriols, C. Bravo, M. Espuga and F. Morell, *Chest*, 2003, **123**, 2124.
- A. A. Fisher and A. Doomsgoossens, *Arch. Dermatol.*, 1976, **112**, 1407.
- H. Razmi and H. Heidari, *Electroanalysis*, 2008, **20**, 2370.
- A. Salimi, A. Noorbakhsh and A. Semnani, *J. Solid State Electrochem.*, 2011, **15**, 2041.
- I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, New York: Interscience (2nd ed.), 1947.
- I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, 1953, **25**, 298.
- I. M. Kolthoff and R. J. Woods, *J. Am. Chem. Soc.*, 1966, **88**, 1371.
- D. Amin, *Analyst*, 1981, **106**, 1217.
- D. Amin and A. K. Hareez, *Analyst*, 1981, **106**, 1221.
- P. M. Shuiundu, A. P. Wade and S. B. Jonnalagadda, *Can. J. Chem.*, 1990, **68**, 1750.

- K. C. Huang, R. A. Couttenye and G. E. Hoag, *Chemosphere*, 2002, **49**, 413.
- P. A. Dimovasilis and M. I. Prodromidis, *Sens. Actuators B*, 2011, **156**, 689.
- X. Xing, S. Liu, J. Yu, W. Lian and J. Huang, *Biosens. Bioelectron.*, 2012, **31**, 277.
- S. Pakapongpan, R. Palangsantikul and W. Surareungchai, *Electrochim. Acta*, 2011, **56**, 6831.
- J. Li, H. Xie and L. Chen, *Sens. Actuators B*, 2011, **153**, 239.
- L. Yuan, J. Zhang, P. Zhou, J. Chen, R. Wang, T. Wen, Y. Li, X. Zhou and H. Jiang, *Biosens. Bioelectron.*, 2011, **29**, 29.
- S. M. Chen, C. H. Wang and K. C. Lin, *Int. J. Electrochem. Sci.*, 2012, **7**, 405.
- K. C. Lin, C. Y. Yin and S. M. Chen, *Int. J. Electrochem. Sci.*, 2011, **6**, 3951.
- K. C. Lin, T. H. Tsai and S. M. Chen, *Biosens. Bioelectron.*, 2010, **26**, 608.
- A. Salimi, M. Roushani and R. Hallaj, *Electrochim. Acta*, 2006, **51**, 1952.
- Z. Savari, S. Soltanian, A. Noorbakhsh, A. Salimi, M. Najafi and P. Servati, *Sens. Actuators B*, 2013, **176**, 335.
- M. Roushani and E. Karami, *Electroanalysis*, 2014, **26**, 1761.
- M. Roushani and Z. Abdi, *Sens. Actuators B*, 2014, **201**, 503.
- Y. Oztekin, A. Ramanaviciene and A. Ramanavicius, *Electroanalysis*, 2011, **23**, 701.
- K. C. Lin, J. Y. Huang and S. M. Chen, *Int. J. Electrochem. Sci.*, 2012, **7**, 9161.
- J. Ouyang, C. W. Chu, F. C. Chen, Q. Xu and Y. Yang, *Adv. Funct. Mater.*, 2005, **15**, 203.
- L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.
- G. Heywang and F. Jonas, *Adv. Mater.*, 1992, **4**, 116.
- A. Kros, S. W. F. M. Van-Hovell, N. A. J. M. Sommerdijk and R. J. M. Nolte, *Adv. Mater.*, 2001, **13**, 1555.
- A. Kros, N. A. J. M. Sommerdijk and R. J. M. Nolte, *Sens. Actuators B*, 2005, **106**, 289.
- Y. T. Chang, K. C. Lin and S. M. Chen, *Electrochim. Acta*, 2005, **51**, 450.
- A. Salimi, A. Korani, R. Hallaj, R. Khoshnavazi and H. Hadadzadeh, *Anal. Chim. Acta*, 2009, **635**, 63.
- S. Iijima, *Nature*, 1991, **354**, 56.
- Y. R. Wang, P. Hu, Q. L. Liang, G. A. Luo and Y. M. Wang, *Chin. J. Anal. Chem.*, 2008, **36**, 1011.
- D. S. Bag, R. Dubey, N. Zhang, J. Xie, V. K. Varadan, D. Lal and G. N. Mathur, *Smart. Mater. Struct.*, 2004, **13**, 1263.
- M. Valcarcel, B. M. Simonet, S. Cardenas and B. Zuzarek, *J. Anal. bioanal. Chem.*, 2005, **382**, 1783.
- A. S. Adekunle, B. O. Agloola, J. Pillay and K. I. Ozoemena, *Sens. Actuators B*, 2010, **148**, 93.
- Y. Umasankar, S. H. Wang and S. M. Chen, *Anal. Methods*, 2011, **3**, 2604.
- H. S. Park, S. J. Ko, J. S. Park, J. Y. Kim and H. K. Song, *Sci. Rep.*, 2013, **3**, 2454