Enhancing visible-light-enhanced photoelectrochemical activity of BiOI microspheres for 4-chlorophenol detection by promoting with Bi surface plasmon resonance (SPR) and multi-walled carbon nanotubes

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Received: 27 March 2020 / Accepted: 9 June 2020 / Published online: 15 June 2020
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Abstract

This work interprets Bi surface plasmon resonance (SPR) and Multi-walled carbon nanotubes, which promote BiOI microspheres (MWCNT/Bi-BiOI) and put into synthesis in virtue of one-stage solvothermal method. The measurement of the combination structure with morphology is achieved in virtue of a range of physical characteristics. Moreover, as the photoelectrochemical (PEC) tests indicate, MWCNT/Bi-BiOI features higher PEC properties compared to those of pure BiOI for the reason of the active SPR influence of Bi nanoparticles as well as the excellent electrical conductivity of MWCNT. Besides, MWCNT/Bi-BiOI is characterized by superior absorption of visible light together with a lower-electron recombination ratio. Thereby, MWCNT/Bi-BiOI-based PEC sensors have been made up to detect 4-chlorophenol (4-CP). They display wide linear within the range of 1–12,800 ng mL⁻¹, based on the high sensing 4-CP stability. As a result, the PEC sensor harbors an excellent potential application in the detection of 4-CP.

Keywords Surface plasmon resonance · Multi-walled carbon nanotubes · Photoelectrochemical · Detection · 4-Chlorophenol

1 Introduction

4-Chlorophenol (4-CP) is an organochlorine widely used in chemical and pharmaceutical, coking, steelmaking and construction [1–3]. However, 4-CP is highly toxic and can harm human health and life [3]. Accordingly, an urgent demand is existing for the monitoring the water condition of 4-CP concentrations.

Therefore, developing rapid and sensitive detection methods for 4-CP can promote the ability to launch preventive for this environmental issue in a timely manner. There are several methods to detect 4-CP, such as gas

chromatography [4], high-performance liquid chromatography [5], electrochemical detection [6]. Every strategy has distinct advantages for detection of 4-CP, yet suffers significantly from time-consuming preparation, toxic solvents, and high equipment cost. Therefore, accurate, ultra-sensitive, easy to use, and low-cost detection methods still of critical urgency for tracking 4-CP pollution.

At present, Photoelectrochemical (PEC) detection has been successfully used to detect multiple drugs as a reliable and rapidly evolving technology [7] since the excitation source and the electrochemical detection signal are completely separated, background noise can be reduced and

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-3027-2>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2020) 2:1214 | <https://doi.org/10.1007/s42452-020-3027-2>

sensitivity can be improved [8, 9]. The measurement of the PEC method is based on the optical and electrical properties of semiconductor materials [10, 11]. Therefore, the development of semiconductor materials that are easy to synthesize and have a broad optical response is essential for manufacturing ultrasensitive PEC methods.

Bismuth-system oxides, which is composed of 6 s Bi orbital with 2p oxygen orbital, displays strong optical activity and excellent electrical properties [12, 13]. The reason accounting for why BiOX (X = Cl, I, Br) has attracted widely attention in PEC field is because of its abundance, low toxicity and inexpensiveness [14–16]. Among them, BiOI have the narrowest band gap (~ 1.8 eV), and it is a semiconductor of p type equipped with a large visible light-absorption capacity [17, 18]. In addition, BiOI harbors has superior photocatalytic activity due to the unique layered structure [19]. However, BiOI belongs to the narrow band gap semiconductor, which results the sped-up recombination of photogenerated electrons as well as holes [20, 21]. The combination of some else semiconductor-based materials and BiOI accelerates electron–hole pair division in virtue of improving electron transfer efficiency to increase energy conversion efficiency [22–25].

Metal bismuth (Bi), which is characterized by some low-expense and broad-source advantages is a kind of semi-metal, with narrow-band gap and small-carrier-effective mass, as well as high anisotropic Fermi surface with low carrier density [26, 27]. Moreover, being the precious metals, Bi takes on the same features of surface plasmon resonance (SPR), enhanced utilization of electron–hole pairs as it is often employed as the combined electron performer with conductor [28]. Multi-walled carbon nanotubes (MWCNTs) are attracting attention due to their special structure and unique electrical properties [29]. In addition, multi-walled carbon nanotubes have higher electron conductivity. It acts as an efficient electron acceptor to improve the photo-induced charge transfer that enhances the PEC performance [30]. Therefore, they have potential application prospects in the field of PEC.

In this manuscript, it reports the PEC sensor of the 4-CP based on MWCNT/Bi-BiOI. The PEC experiments show that 20-MWCNT/Bi-BiOI-0.5 harbors wonderful PEC performance, meanwhile exhibiting a broad linear range, low detection limit (0.65 ng mL^{-1} , $S/N=3$) as well as superior selectivity of 4-CP detection. According to the results, the sensor on the basis of 20-MWCNT/Bi-BiOI-0.5 holds superior application prospects within practically useful 4-CP detection.

2 Experiment section

2.1 Correspondence reagent

All the reagents were of analysis-based grade free of further purification. Sinopharm Chemical Reagent Co., Ltd (www.sinoreagent.com) was the supplier for Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), potassiumiodide (KI), MWCNTs (diameters < 8 nm and 0.5–2 μm length), ethylene glycol (EG), glucose, acetone and ethanol.

2.2 Prepared-item for the MWCNT/Bi-BiOI heterojunction

The MWCNT/Bi-BiOI heterojunction was given the preparations from one-stage hydrothermal approach: proper KI and glucose used as individual addition into the solution of 40 ml EG. Next, some proper $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, glucose and MWCNT got added to KI solution and continuous with 30-min stirring. The mixed solution was put into 24 h heat at 160 °C in Teflon-lined autoclave (100 mL). At last, after the hydrothermal process, product were collected, washed with deionized water and ethanol several times and dried at 60 °C, these ready-made materials conforming that the material amount will be on show in Table S1.

2.3 Characterization

X-ray diffraction (XRD) patterns were committed to a Bruker D8 Advance diffractometer based on Cu K α radiation. X-ray photoelectron spectra were obtained by X-ray photoelectron spectroscope (XPS, ESCALAB 250Xi). The testament of diffuse reflection spectra (DRS) for materials was made by UV–Vis spectrophotometer by taking reference of BaSO_4 . The samples' morphology was featured with electron microscopy (SEM) and Transmission electron microscopy (TEM).

2.4 Photoelectrochemical experiments

Photocurrent tests were measured with the three-electrode system in an electrolytic cell (CHI 660E). Pt wire and SCE (saturated calomel electrode) acted as counter electrode and reference electrode, respectively. The working electrode referred to the indium tin oxide (ITO) glass. The light source referred to Xenon lamp (PLS-SXE 300, 100 mW cm^{-2} , $\lambda \geq 420 \text{ nm}$). From frequency (Hz) 1–1,000,000 in PBS (0.1 M, PH=7), we carried out the electrochemical impedance spectroscopy (EIS). Using water, acetone and ethanol, the indium tin oxide (ITO) glass (10 × 15 mm) were cleaned respectively for 5 min.

Subsequently, in mixed chitosan and ethanol liquid (0.5 mL), 3 mg catalyst powders were distributed for the formation of homogeneous suspension. Subsequently, ITO electrode (0.5 cm^2) was coated with $20 \mu\text{L}$ suspensions.

3 Results and discussions

3.1 Materials choice

The investigation on the phase of all the synthesized materials is made by XRD. Figure 1a reveals that as for all of the Bi-BiOI composites, all of diffraction peaks of BiOI (JCPDS 10-0445) are under clear observation. The three un-striking peaks respectively at around 27.16° , 37.95° and 39.62° were corresponded to the (012), (104), (110) of Bi (JCPDS44-1246). In Fig. 1b, for MWCNT/Bi-BiOI, after adding MWCNT, the characteristic peaks of BiPO_4 and BiOI did not change significantly. More than that, the featured peaks respectively at around 26.01° are corresponded to

the (002) of MWCNT. According to the results display, the synthesized materials can be classified as MWCNT/Bi-BiOI in a perfect way.

Further evaluate the PEC properties of all synthetic materials through photocurrent reaction experiments (Fig. 1c, d), which was redone 4 times at the frequency of the every regular 20 s in 0.1 M PBS under the irradiation of visible light. All materials' photocurrents are enhanced with the irradiation of visible light. The photocurrent value of Bi-BiOI-0.5 is significantly higher compared to these of BiOI, Bi-BiOI-0.2 and Bi-BiOI-0.7 (Fig. 1c). Furthermore, 20-MWCNT/Bi-BiOI-0.5 has higher photocurrent than 10-MWCNT/Bi-BiOI-0.5 and 30-MWCNT/Bi-BiOI-0.5 in Fig. 1d. Consequently, compared to other materials, the photocurrent of 20-MWCNT/BPI-5% is higher.

Electrochemical impedance spectra (EIS) were utilized for further evaluation on the electron transfer kinetics harbored by the whole composites (Figure S1A–B). The EIS is made up of a pressed semicircle part as well as a linear part. The electron transfer resistance (R_{ct}) is

Fig. 1 XRD spectrum of the MWCNT/Bi-BiOI (a, b) composites, photocurrent responses (c, d) of the all materials in 0.1 M PBS

quantified with the help of the semicircle diameter [13]. And it can be ranked as: BiOI > Bi-BiOI-0.2 > Bi-BiOI-0.7 > Bi-BiOI-0.5 > 10-MWCNT/Bi-BiOI-0.5 > 30-MWCNT/Bi-BiOI-0.5 > 20-MWCNT/Bi-BiOI-0.5. And 20-MWCNT/Bi-BiOI-0.5 shows the lowest impedance among composites. The result indicates that MWCNT and Bi provide rapid electron transfer capability and remarkable conductivity [27, 30]. Drawing from the above results, 20-MWCNT/Bi-BiOI-0.5 was selected to be further investigated.

3.2 The characterization of 20-MWCNT/Bi-BiOI-0.5

The detailed chemical composition of 20-MWCNT/Bi-BiOI-0.5 was investigated by the XPS spectra in Fig. 2a–d. The C1s XPS is shown in Fig. 2b. The four peaks located at 284.12 eV, 284.6 eV, 285.69 eV and 288.48 eV, which are ascribed to C–O, C–C=C, C=O and O–C=O, respectively [30]. As Fig. 2c shows, the peaks harbored by 158.8 eV and 164.2 eV are distributed toward Bi 4f_{7/2} as well as Bi 4f_{5/2} in the standard Bi³⁺ [31]. The peak of 156.3 eV and 161.7 eV result from zero valence state of metallic Bi [32]. Two peaks about 630.2 eV and 618.5 eV are ascribed to 3d_{3/2} and 3d_{5/2} of BiOI, which correspond to I[−] (Fig. 2d) [33]. Figure 2e shows a broadened characteristic peak at 530.8 eV, assigning to the O section of the heterojunction in the O 1s spectrum [34]. In Figure S2, the Raman spectrum of 20-MWCNT/Bi-BiOI-0.5 and Bi-BiOI-0.5 also indicates that MWCNT is successfully introduced into 20-MWCNT/Bi-BiOI-0.5. All the findings are indicating that the composite is coexisted with MWCNT, Bi and BiOI.

The morphology of Bi-BiOI-0.5 and 20-MWCNT/Bi-BiOI-0.5 composites were characterized by SEM. Figure 3a offers a clearly expression that Bi-BiOI is composed of uniform interpretation made up of a microsphere structure. These microstructures featured by 20-MWCNT/Bi-BiOI-0.5 are shown in Fig. 3b. It is obvious that MWCNT belong to the Bi-BiOI-0.5 microspheres. Figure 3c displays the TEM image of 20-MWCNT/Bi-BiOI-0.5. The HRTEM examination displays three lattices spacing of 0.267 nm, 0.285 nm and 0.301 nm, which conforms to Bi (110), MWCNT (002) and BiOI (102) in Fig. 3d. All of the findings reveal that the MWCNT/Bi-BiOI was given successful preparation.

The absorption attributes harbored by BiOI, Bi-BiOI-0.5 and 20-MWCNT/Bi-BiOI-0.5 was put under analysis by UV–Vis DRS of Fig. 4a. BiOI interpreted an absorption edge nearly 600 nm in the seen region. Additionally, it could be observed clearly that Bi-BiOI and 20-MWCNT/Bi-BiOI-0.5 are featured by higher-level absorption compared to BiOI within the range of visible light of 400–600 nm. Besides, 20-MWCNT/Bi-BiOI-0.5 is featured by dramatically higher than visible light absorption capacity than BiOI. Based on

the fundamental electronegativity conception [35], the band gap energy is calculated in virtue of Eq. (1).

$$\alpha h\nu = A(\nu h - E_g)n/2 \quad (1)$$

In the situation that h is Planck's constant, ν refers to incident light frequency, A means constant, and n stands for the sort of optical transition, BiOI refers to a direct semi-conducting part, so n reaches 1 [36]. As Fig. 4b shows, E_g of BiOI is about 1.71 eV. Subsequently, Fig. 4c further studies the ability of synthetic materials, aiming to isolate the electrons and holes by PL spectra. 20-MWCNT/Bi-BiOI-0.5 is characterized by lower intensity than BiOI, which suggests 20-MWCNT/Bi-BiOI-0.5 having low electron recombination rate. Figure 4d further reveals the charge carrier transfer properties in virtue of the time-resolved PL spectrum [37]. They reveal that 20-MWCNT/Bi-BiOI-0.5 has wonderful charge carrier transfer attributes, 0.91, 1.01 and 1.92 ns represented the lifetime of BiOI, Bi-BiOI-0.5 and 20-MWCNT/Bi-BiOI-0.5. In accordance with the discussion above 20-MWCNT/Bi-BiOI-0.5 possesses best PEC performance.

3.3 Photoelectrochemical sensor

Figure 5 explains the photocurrent performance of BiOI, Bi-BiOI-0.5 as well as 20-MWCNT/Bi-BiOI-0.5 with the addition of 200 ng mL^{−1} 4-CP under visible light excitation in 0.1 M PBS at 0 V versus SCE. The photocurrent of all materials is increased correspondingly after adding 4-CP. Meanwhile, 20-MWCNT/Bi-BiOI-0.5 photocurrent value is much higher than other materials, attributing to that the SPR of metal Bi and the excellent electrical conductivity of MWCNT significantly enhanced the PEC efficiency for 4-CP [27, 30].

To evaluate the PEC performance given by the 20-MWCNT/Bi-BiOI-0.5 for 4-CP, photocurrent tests were carried out on different concentrations of 4-CP. After adding different concentrations of 4-CP, it can be seen in Fig. 6a that the photocurrent rises sharply, and Fig. 6b plots the linear relationship of the photocurrent with different concentrations. Figure 6b displays two linear connections of the sensor on the basis of 20-MWCNT/Bi-BiOI-0.5 for 4-CP. From 1 to 200 ng mL^{−1}, the linear regressing equation means $\Delta I = 0.6591 + 0.0131c$ ($R^2 = 0.9970$), and within the scope of 400–12,800 ng mL^{−1}, the linear relationship is $\Delta I = 5.6146 + 9.914 \times 10^{-4}c$ ($R^2 = 0.9933$). 0.65 ng mL^{−1} ($S/N = 3$) stands for the detection limit of the sensor. Moreover, Table 1 interprets a comparison of 20-MWCNT/Bi-BiOI-0.5 with other 4-CP sensors in the literature reports. For electrochemical, the PEC sensor of 20-MWCNT/Bi-BiOI-0.5 have the low detection limit, for other PEC sensor, we have wide linear range. Evidently, our sensor is better than other 4-CP sensors in terms of some aspect.

Fig. 2 XPS spectrum of **a** 20-MWCNT/Bi-BiOI-0.5 composites: **b** C 1s, **c** Bi 4f, **d** I 3d, **e** O 1s

Fig. 3 SEM images of Bi-BiOI (a), 20-MWCNT/Bi-BiOI-0.5 (b); c TEM and d HR-TEM images of 20-MWCNT/Bi-BiOI-0.5

The stability harbored by 20-MWCNT/Bi-BiOI-0.5 was put under examination in virtue of monitoring the photocurrent of repeatedly made photoexcitation above 900 s (Fig. 6c). And the reaction photocurrent of 20-MWCNT/Bi-BiOI-0.5 remained 95.7% of its initial value towards 200 ng mL⁻¹ 4-CP within 21 days (Fig. 6d). The reproducibility featured by 20-MWCNT/Bi-BiOI-0.5 was tested through detecting 200 ng mL⁻¹ 4-CP by five parallel electrodes (Fig. 6e), as well as the photocurrents shows no evident changes, which indicates its satisfying reproducibility. The photocurrent reactions of 20-MWCNT/Bi-BiOI-0.5 towards 200 ng mL⁻¹ 4-CP and interfering substance were expressed in Fig. 6f, the photocurrent responses of interferences are of negligibility. The holes of 20-MWCNT/Bi-BiOI-0.5 can reduce 4-CP, which can electrode can accelerate the charge separation and suppress the electron-hole recombination, leading to the increment of photocurrent intensity. According to this mechanism, the 20-MWCNT/Bi-BiOI-0.5 PEC sensor has an acceptable anti-interference capacity for 4-CP detection [39, 40].

To validate the practical reliability harbored by the ready-made 4-CP sensor, the combination of tap water with lake water which contain 4-CP were employed as an authentic I sample. The findings are demonstrated in Table 2, the RSD are lower than 4.7%, the recoveries discovered as 99.82–100.60%. Those findings demonstrate that the sensor, which is based upon 20-MWCNT/Bi-BiOI-0.5, is of reliability for the detection of 4-CP in authentic samples.

3.4 Mechanism of PEC sensing 4-CP

In terms of investigation on mechanism of PEC sensor of 4-CP according to MWCNT-M, E_{VB} and E_{CB} of and BiOI are explored with the assistance of the following equation [42]:

$$E_{VB} = X - E_e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

Fig. 4 UV-Vis diffuse reflectance spectrum (a); plots of $(Ah\nu)^{1/2}$ versus photon energy ($h\nu$) for BiOI (b); PL spectrum (c) and the time-resolved PL spectrum (d) of materials

Fig. 5 Photocurrent responses of the materials in the absence and presence 200 ng mL⁻¹ 4-CP determination in 0.1 M PBS at 0 V versus SCE with visible light excitation

E_e reaches nearly 4.5 eV, indicating the energy powered by free electrons at the hydrogen level. X indicates semiconductor's electronegativity, and the X value of BiOI reached 6.49 eV. The CB edge potentials of BiOI reached 0.62 eV. Besides, we found the VB edge potentials attached to BiOI as +2.30 eV. Accordingly, PEC system of MWCNT/Bi-BiOI is schematically portrayed as the Fig. 7 show. While the compound is on illumination, electrons are able to be triggered from the E_{VB} of BiOI to generating photo-induced electron-hole pairs. When the Bi nanoparticles with MWCNT got connected to BiOI microspheres, the metal-semiconductor junction, along with heterojunction was taken into formation in the interfaces of Bi-BiOI and MWCNT/BiOI separately. What was worth mentioning is that Bi nanoparticles on BiOI microspheres could serve as light collectors in the compound. After irradiation of the visible light, electron-hole pairs were set up in the Bi nanoparticles as well as a result of the active SPR influence. Next, the hot electron was to transport to the E_{CB} of BiOI. In terms of high charge carrier mobility, MWCNT undertakes

Fig. 6 Photocurrent responses of 20-MWCNT/Bi-BiOI-0.5 toward 4-CP under increasing concentrations (a), the corresponding calibration plots of the 4-CP concentration (b), stable photocurrent response of 20-MWCNT/Bi-BiOI-0.5 in the presence of 200 ng mL⁻¹ 4-CP (c), stable photocurrent response of 20-MWCNT/Bi-BiOI-0.5

in the presence of 200 ng mL⁻¹ 4-CP (d), the current responses of five-parallel (e), Influence of interferences on 200 ng mL⁻¹ 4-CP determination in 0.1 M PBS at 0 V versus SCE with visible light excitation (f)

Table 1 Comparison of different sensors for 4-CP assay

Detection method	Linear range (ng/mL)	Detection limit (ng/mL)	References
Electrochemical detection	103–12,900	38.6	[38]
Electrochemical detection	1280–38,500	474	[6]
Amperometric detection	321–5140	50.1	[39]
	8040–15,100		
Voltammetric	38.57–51,424	14.14	[40]
Photoelectrochemical detection	129–1930	10.3	[41]
Photoelectrochemical detection	20–33,800	0.00678	[42]
Photoelectrochemical detection	1–200	0.65	This work
	400–12,800		

Table 2 PEC detection characterized by 4-CP in lake water samples

Sample	Supplied	Discovered	Recovery (%)	RSD (%)	HPLC
1	1.00	1.06	100.60	2.7	1.00
2	50.00	49.91	99.82	2.5	50.03
3	200.00	200.06	100.03	4.1	199.97
4	1000.00	999.82	99.98	3.6	1000.11
5	8000.00	8003.12	100.04	4.7	8000.08

to be an electron acceptor as well as a transporter to effectively stop the reintegration occurring to the photo-generated electron-hole pairs. Thereby, the lifespan of

photo-generated charge carriers could be dramatically promoted in the duration of the process, thus bringing about a vastly upgraded photocatalytic effect amidst the irradiation of visible light, as the comparison with pure BiOI. When 4-CP introduction occurs, the holes within the BiOI valence band (VB) could be defeated by 4-CP, which can electrode can accelerate the charge separation and suppress the electron-hole recombination, leading to the increment of photocurrent intensity. This kind of synergy effect in the MWCNT/Bi-BiOI electrode is able to speed up the charge separation by suppressing the electron-hole reintegration that contributes to the growth of photocurrent intensity.

Fig. 7 PEC mechanism of MWCNT/Bi-BiOI for the detection of 4-CP

4 Conclusions

In summary, the PEC method based on MWCNT/Bi-BiOI was developed to detect exhibit 4-CP, introducing metal Bi and MWCNT is a well-functioning approach to improving the assaying properties. The findings expressed better photoelectrocatalytic active due to metal Bi and MWCNT strengthened the degree of light absorption as well as reducing the reintegration ratio of the electron holes. The study demonstrated the potential application of MWCNT/Bi-BiOI to 4-CP photoelectrochemical detection.

Acknowledgements This work is supported by the Applied Basic Research Youth Science and Technology Foundation of Shanxi Province of China (No. 201901D211433), the Natural Science Foundation of Shanxi Province of China (No. 201801D121073), the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi Province (No. 2019L0737), the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi Province (No. 2019L0749), 2019 Open Research Fund of Shanxi Province Research Center for Innovative Application of New Mesoporous Materials (No. MMIA2019106), The Key projects of science and technology research in Hebei higher education institutions (ZD2018311), Xingtai young science and Technology Talents Project (2019ZZ023), Xingtai science and technology program (2019ZC007, 2018ZC031, 2018ZC227).

Compliance with ethical standards

Conflict of interest The authors have no conflicts of interest to declare.

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