

Fabrication of alizarin red S/multi-walled carbon nanotube nanocomposites and their application in hydrogen peroxide detection

Haitao Han · Xuran Wu · Shijie Wu ·
Qing Zhang · Wenjing Lu · Haiyun Zhang ·
Dawei Pan

Received: 22 October 2012 / Accepted: 28 December 2012 / Published online: 15 January 2013
© Springer Science+Business Media New York 2013

Abstract In this work, an easy and effective method to synthesize alizarin red S/multi-walled carbon nanotube (ARS/MWCNT) nanocomposites based on the π - π stacking non-covalent interactions between ARS and MWCNTs was introduced. The characters of ARS/MWCNT nanocomposites were investigated by Fourier transformation infrared spectroscopy, UV-Vis spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscope, and electrochemical techniques. ARS tightly coating on MWCNTs surface makes the nanocomposites good dispersibility in water and excellent electrochemical activity. Because of the combination of the excellent electroactivity of ARS and the unique properties of MWCNTs, ARS/MWCNT nanocomposites-modified glassy carbon electrode exhibits a good response to the reduction of hydrogen peroxide and takes on a promising prospect of the practical application in electrochemical sensors field.

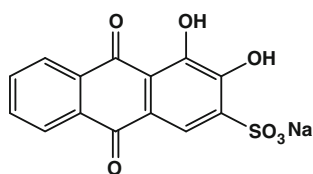
Introduction

It is well known that carbon nanotubes (CNTs), no matter with single or multiple walls, have been paid more and more attention in the fields of material science and chemistry since they were found in 1991 [1]. CNTs possess a series of advanced mechanical, electrical, and electrochemical properties which make them in a wide scope of applications. For example, they can compete with copper in electrical conductivity and promote electron transfer in electrochemical reactions because of their high effective surface areas [2, 3]. Their promising applications in nanodevices, nanoprobe, bioelectronics, and sensors are fascinating [4]. Many composites containing carbon nanotubes also possess series of wonderful properties such as electrical conductivity and shielding effectiveness [5]. In electrochemical field, CNTs have become a wonderful material and been widely used as chemically modified electrodes owing to their super properties of low resistivity, large surface area, and chemical stability [6, 7]. The electrodes modified with CNTs or their composites have been applied widely for the detection of analytes like dopamine [6, 8], kojic acid [9], ascorbic acid [10], uric acid [11], NADH [12] and so on. CNTs are also used as Pt and Pt Ru supports in polymer electrolyte membrane fuel cells [13]. However, owing to their large mass, it is very difficult to disperse them well in aqueous solution, which significantly limits their manipulation and applications [14]. To improve the dispersibility of CNTs in aqueous media, various approaches have been reported [15–17]. This problem has been solved partly through pretreatment of the CNTs including expose the CNTs to sulfuric acid, nitric acid, hydrochloric acid, or the mixture of these acids at room temperature with refluxing or sonication for different times [18–21]. Chemical modification of CNTs with other functional molecules is an efficient way to change the chemical

H. Han · X. Wu (✉)
School of Chemistry and Chemical Engineering, Yantai
University, Yantai 264005, Shandong, China
e-mail: ytdxwxr@126.com

H. Han · S. Wu · Q. Zhang · W. Lu · H. Zhang · D. Pan (✉)
Key Laboratory of Coastal Zone Environmental Processes,
Yantai Institute of Coastal Zone Research(YIC), Chinese
Academy of Sciences(CAS), Shandong Provincial Key
Laboratory of Coastal Zone Environmental Processes, YICCAS,
Yantai 264003, Shandong, China
e-mail: dwpan@yic.ac.cn

S. Wu · Q. Zhang
The Key Lab in Molecular and Nano-materials Probes of the
Ministry of Education of China, College of Chemistry, Chemical
Engineering and Materials Science, Shandong Normal
University, Jinan 250014, Shandong, China



Scheme 1 Structure of ARS

properties of CNTs through the formation of a new property profile. It has been discovered that only when the functional molecules are introduced to the sidewalls, not on the tip, of the CNTs, can be largely change their properties. The functionalized CNTs can be got through the formation of covalent bonds or non-covalent bonds such as π - π stacking and van der Waals interactions between the CNTs and functional groups. Many dyes can interact with CNTs through non-covalent interactions to functionalize and improve CNTs dispersibility in water [17]. Quinones and their derivatives have been widely used as modified electrode since they can play an important role in natural electron transfer systems.

On the other hand, alizarin red S (1, 2-dihydroxy-9, 10-anthraquinone-3-sulfonate, ARS), is a widely used water-soluble anthraquinone dye. Its structure is shown in Scheme 1. ARS has vicinal diols and anthraquinone part and is broadly used as chelating agent in the determination of Th, Zn, V, Al, Zr, Cu, B [22–28]. Owing to the existence of anthraquinone which can be used as electron mediator, ARS is also employed for the electrochemical detection of dopamine, polysaccharides, and proteins [8, 29, 30]. It is also extensively used in textile industry and histochemical staining field. However, almost all the works were focused on either the electrochemical properties of ARS in solution or the electro-polymerization of ARS.

In this work, ARS was attached on the sidewalls of MWCNTs to synthesize the novel ARS/MWCNT nanocomposites. ARS/MWCNT nanocomposites were characterized with various optical and electrical methods like Fourier transformation infrared spectroscopy (FTIR), UV-Vis spectroscopy (UV-Vis), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and cyclic voltammetry (CV). The proposed ARS/MWCNT nanocomposites-modified electrode can be used for electrochemical determination of hydrogen peroxide and shows wide linear range and high sensitivity.

Experimental

Reagents and apparatus

Alizarin red S (ARS, $C_{14}H_7NaO_7S$) was purchased from Sigma. Carboxylic MWCNTs treated with nitric acid (about 20–40 nm in diameter and less than 5 μ m in length)

were supplied by Shenzhen NanoTech Port Co. Ltd, China. Standard potassium permanganate solution was purchased from National information center for certified reference materials, China. All other chemicals were analytical reagents and used without further purification. All experiments were carried out at room temperature. Deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout. Disinfectants from different companies of China as real samples were purchased from local supermarket (Yantai).

SEM images were taken on a Hitachi S-4800 microscope (Japan). FTIR spectra were recorded with a Nicolet iS 10 infrared spectrometer. UV-Vis spectra were obtained by a DU 800 ultraviolet and visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Kratos Amicus spectrometer with a monochromatized Mg K α X-ray source at pass energy of 75 eV. All the electrochemical experiments were performed on a LK 2006 Electrochemical Workstation (Tianjin Lanlike Chemical Electronic High Technology Co. Ltd, China). A conventional three-electrode system consisting of a glassy carbon working electrode (GC), a platinum wire auxiliary electrode, and an Ag/AgCl (with saturated KCl) reference electrode was employed. All the potentials in this paper were with respect to Ag/AgCl reference electrode.

Synthesis of ARS/MWCNT nanocomposites

20 mg MWCNTs were added into 342.26 mg mL⁻¹ ARS aqueous solution with ultrasonication for 2 h and the mixture was left for one night to make MWCNTs interact with ARS thoroughly. Then, the mixed liquor was experienced filter fully to dislodge the ARS which was not immobilized onto MWCNTs. The resulting mixture was centrifuged, washed with water and dried.

Fabrication of ARS/MWCNT nanocomposites-modified electrode

ARS/MWCNT powder 5 mg were dispersed in 5-mL deionized water to obtain 1 mg mL⁻¹ suspension. Then the mixture was ultrasonicated for 10 min. The glassy carbon (GC) electrode was firstly mechanically polished over a micro-cloth with 0.05- μ m alumina slurry and then was rinsed and ultrasonicated by deionized water. The ARS/MWCNT suspension 10 μ L was added on the surface of GC electrode and dried under an infrared lamp to obtain the ARS/MWCNT/GC electrode.

Electrochemical analysis procedure

Electrochemical characterization of the ARS/MWCNT nanocomposites was investigated by cyclic voltammetry.

The ARS/MWCNT-modified glass carbon (ARS/MWCNT/GC) electrode was placed in voltammetric cell with 10 ml 0.5 M H_2SO_4 solution. The voltammetric experiments were carried out in the potential range from -0.8 to 1.2 V at a scan rate of 100 mV s^{-1} . As compared, the bare GC and MWCNTs-modified (MWCNTs/GC) electrode were performed under the same conditions. Amperometric detections of hydrogen peroxide at ARS/MWCNT/GC electrode were carried in ammonia buffer solution ($\text{pH} = 7.4$) at -0.6 V.

Results and discussion

MWCNTs can combine with ARS molecules owing to their large specific surface areas. Because the carbon atoms of CNTs are mainly sp^2 hybridized hybridization, CNTs contain many π electrons which make them the ability to combine with other π electrons via π – π stacking [2]. Besides, van der waals interactions are also existent between the MWCNTs and ARS molecules. It is the existence of these non-covalent interactions between MWCNTs and ARS that the ARS/MWCNT nanocomposites can be successfully synthesized.

Dispersibility of ARS/MWCNT nanocomposites in aqueous solution

ARS is an anthraquinone dye with a plane big ring which is full of π electrons. Due to its special molecular structure, ARS can be covered on the sidewalls of MWCNTs through the non-covalent interactions with MWCNTs to obtain the novel ARS/MWCNT nanocomposites. One of the outstanding physical properties of ARS is that it can dissolve well in water. Similarly, the dispersibility of ARS/MWCNT in aqueous solution is very good. Compared with the MWCNTs suspension precipitated in a short time, there was no precipitation in the ARS/MWCNT suspension even after 3 months under the same conditions.

UV–Vis spectrum of the ARS/MWCNT nanocomposites

Figure 1 shows the UV–Vis spectrum of the ARS/MWCNT nanocomposites. ARS has its own typical UV–Vis absorbance because of the existence of anthracene ring and carbonyl group, both of which are good chromophore groups. Compared with the UV–Vis spectrum of the ARS (Fig. 1a), the intensity of the absorbance peak at 260 nm yielded by the anthracene ring decreases significantly. The characteristic absorbance peak of carbonyl groups at 335 nm is distorted and shifted to lower wavelength obviously. The absorbance peak at 544 nm shifts toward

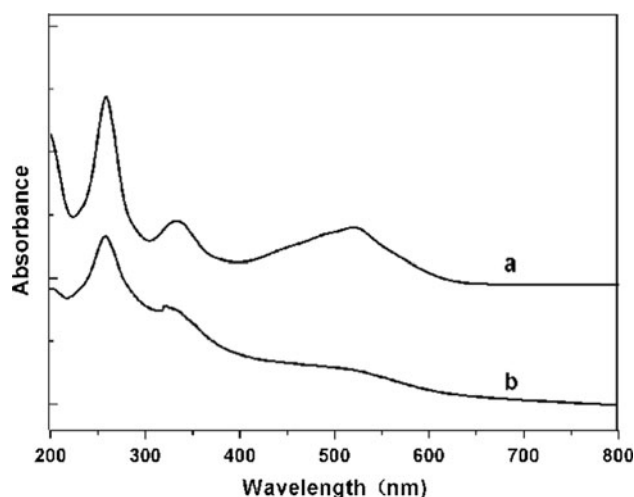


Fig. 1 UV–Vis spectra of the ARS (a) and ARS/MWCNT (b)

longer wavelength. All these phenomenonons are similar to that reported in the literature [2] and indicate the inter-molecular interactions between MWCNTs and ARS.

FTIR spectrum of the ARS/MWCNT nanocomposites

To clarify the mechanism about how ARS attached on the MWCNTs surface, FTIR measurements for ARS, MWCNTs and ARS/MWCNT were carried out and the corresponding results are shown in Fig. 2. Compared with the spectra of MWCNTs (Fig. 2a) and ARS (Fig. 2b), the peak in the band of 1628 cm^{-1} which may due to the $\text{C}=\text{O}$ group decreases significantly and a band of 1590 cm^{-1} with a strong intensity appears in the spectrum of ARS/MWCNT (Fig. 2c). According to the literature [17], peak at 1590 cm^{-1} is assigned to $\text{C}=\text{C}$ stretch of benzene. Considering the diminution of the absorption band for carbonyl functionalities, the formation of $\text{C}_{\text{MWCNTs}}-\text{O}-\text{C}_{\text{ARS}}$ bond between the MWCNTs and ARS may be a reasonable explanation. This result is in accordance with that derived from the UV–Vis spectra discussed above. The presence of adsorbed ARS on MWCNTs is evident from the FTIR spectrum because that both the typical bands of MWCNTs and ARS (the bands of 1628 and 1590 cm^{-1}) can be observed on the nanocomposites (Fig. 2c).

XPS spectrum of the ARS/MWCNT nanocomposites

To further confirm the immobilization of ARS onto the nanocomposites, X-ray photoelectron spectroscopy (XPS) experiments were undertaken. Figure 3a shows the wide XPS of MWCNTs and ARS/MWCNT nanocomposites. It can be seen that $\text{C}1\text{s}$ and $\text{O}1\text{s}$ peaks are present in both MWCNTs and ARS/MWCNT nanocomposites. However, in contrast to MWCNTs, the $\text{S}2\text{p}$ XPS spectrum (Fig. 3b)

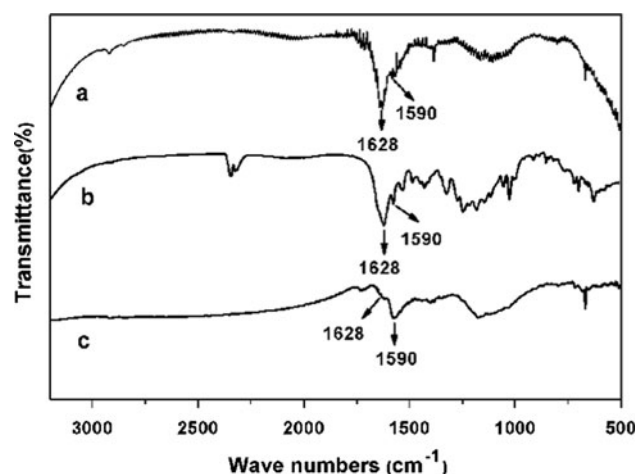


Fig. 2 FTIR spectra of the MWCNTs (a), ARS (b) and ARS/MWCNT (c)

of ARS/MWCNT nanocomposites appears a peak of sulfur functionality at 168.39 eV (the S in SO_3^-). This forcefully proves the attachment of ARS onto MWCNTs. There is no doubt that the XPS spectrum provides essential and useful information for the immobilization of ARS onto the nanocomposites.

SEM image of ARS/MWCNT nanocomposites

In present work, to describe the morphology of ARS/MWCNT nanocomposites, SEM was employed. Figure 4 illustrates the typical SEM photographs of MWCNTs (Fig. 4a) and ARS/MWCNT (Fig. 4b). It can be observed from Fig. 4a that MWCNTs exhibit random coiled and curved features due to the intrinsic Van der Waals attractions between the individual nanotubes as well as large surface area. The diameter of MWCNTs is almost 25–40 nm. However, the SEM picture of ARS/MWCNT shows significant differences. ARS is distributed in the MWCNTs matrix and covered on the surface of CNTs to form a membraneous structure. Compared with MWCNTs, the diameter of ARS/MWCNT is obviously larger (about 50–65 nm). It can also be seen that the length of nanotubes in ARS/MWCNT nanocomposites is not obviously changed. This implies there was no “cutting” of the nanotubes in the procedure of synthesizing the nanocomposites. The SEM proves that ARS molecules are attached on the surface of MWCNTs.

Electrochemical behaviors of ARS/MWCNT nanocomposites

Cyclic voltammograms of the GC, MWCNTs/GC, and ARS/MWCNT/GC electrodes in 0.5 M H_2SO_4 solution from -0.8 to 1.2 V with the scan rate of 100 mV s^{-1} are

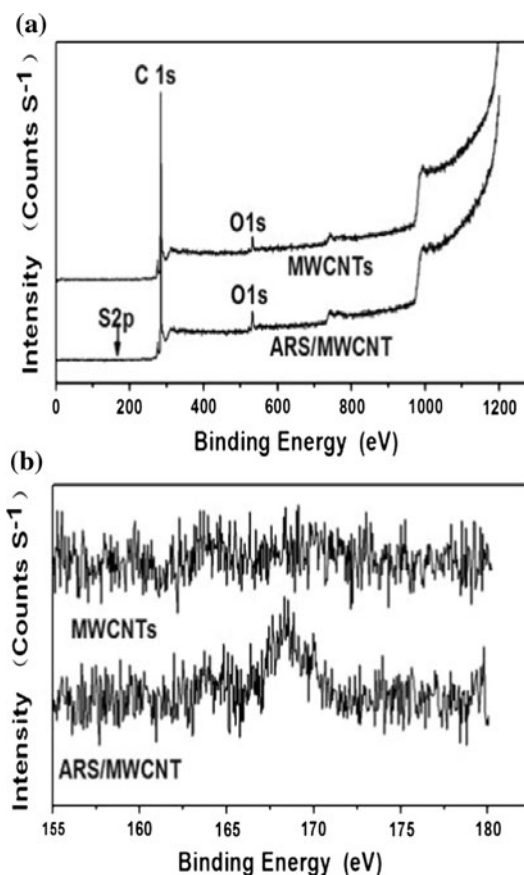


Fig. 3 Wide (a) and S2p (b) XPS of MWCNTs and ARS/MWCNT

presented in Fig. 5. Obviously, there was no redox peak that can be observed at the bare GC electrode (Fig. 5a) in the scan ranges. There appears a pair of redox peak at about 0.4 V which may be caused by the MWCNTs at the MWCNTs/GC electrode (Fig. 5b). However, at the ARS/MWCNT/GC electrode (Fig. 5c), it can be seen that there are three pairs of redox peaks and a single reductive peak, while the pair of redox peak at about 0.4 V is almost to be disappeared. Voltammetric behavior of the ARS/MWCNT/GC electrode is in accordance with that of the glass carbon electrode adsorbed with ARS [31]. Moreover, if the ARS is polymerized on the surface of electrode modified with MWCNTs, only the redox peak at about 0.8 V is left while the other peaks are disappeared [32]. This proves that the dyes modified on MWCNTs are alizarin red S molecules but not poly (alizarin red S) or other forms.

Amperometric detection of hydrogen peroxide at the ARS/MWCNT-modified glass carbon electrode

From all above results, it can be proved that ARS/MWCNT nanocomposites were fabricated successfully and exhibit unique electrochemical property. The application of ARS/MWCNT nanocomposites in electrochemical detection of

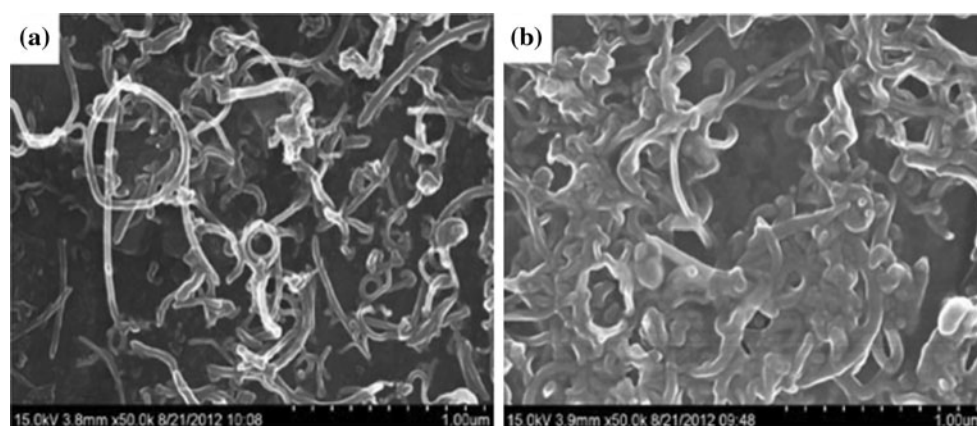


Fig. 4 SEM images of MWCNTs (a) and ARS/MWCNT (b)

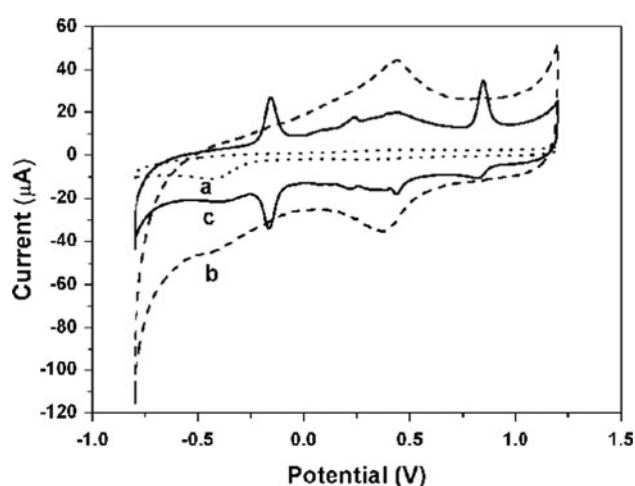
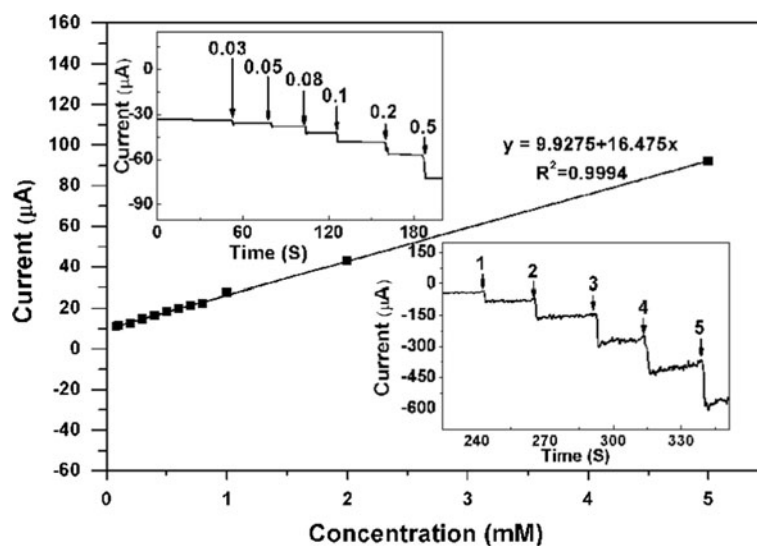


Fig. 5 Cyclic voltammograms of GC (a), MWCNTs/GC (b) and ARS/MWCNT/GC (c) electrodes in 0.5 M H_2SO_4 (scan rate of 100 mV s^{-1} , scan range from -0.8 to 1.2 V)

Fig. 6 Amperometric response curves of hydrogen peroxide at the ARS/MWCNT/GC electrode with successive additions of different concentrations of H_2O_2 (from 0.03 to 5 mM) in ammonia buffer ($\text{pH} = 7.4$) at the operational potential of -0.6 V and calibration curve covering the concentration of H_2O_2 range from 0.03 to 5 mM



hydrogen peroxide is explored. It was discovered that ARS/MWCNT/GC electrode exhibits rapid response to the reduction of hydrogen peroxide (H_2O_2). Amperometric detection of H_2O_2 at ARS/MWCNT/GC electrode was carried out in ammonia buffer solution ($\text{pH} = 7.4$) at the applied potential of -0.6 V . The amperometric responses at the ARS/MWCNT/GC electrode with different concentrations of H_2O_2 successively injected were exhibited as Fig. 6. A proportional and linear relationship between Δi (the change of peak current when a certain concentration of H_2O_2 was injected) and the concentration of H_2O_2 with the equation of $\Delta i = 9.93 + 16.48 C$ ($R^2 = 0.9994$, $\Delta i \mu\text{A}^{-1}$, $C \text{ mM}^{-1}$) is observed. At the ARS/MWCNTs/GC electrode, the linear range spans the concentration of H_2O_2 from 0.03 to 5 mM, which is wider than that at graphene/prussian blue-modified glassy carbon electrode [33]. The sensitivity is $16.5 \mu\text{A mM}^{-1}$, which is superior to the previously reported PB-SWNTs/chitosan/GC

Table 1 Comparison of the results of H₂O₂ detection in disinfectant solutions (diluted 2000-fold) by the proposed and permanganate titration method ($n = 3$)

Disinfectants	Detected by proposed method (mM)	Detected by titration method (mM)
Sample 1	0.478 ± 0.015	0.470 ± 0.004
Sample 2	0.509 ± 0.020	0.498 ± 0.002
Sample 3	0.499 ± 0.016	0.485 ± 0.002

electrode [34]. The detection limit is 1.2 μM, which is also better than that at graphene/prussian blue-modified glassy carbon electrode [33]. Due to its outstanding performance, the ARS/MWCNT-modified electrode would take on promising prospects of the application in chemo/bio sensors.

Real samples analysis

To assess the accuracy and feasibility of this proposed method for practical application, various disinfectants as real samples were comparatively analyzed using the ARS/MWCNT/GC electrode and the classical potassium permanganate titration method [35]. These samples were diluted with ammonia buffer (deionized water in potassium permanganate titration method). All of the detected H₂O₂ concentrations were in the linear response range. The results are provided in Table 1. As can be seen from it, the results obtained from this proposed method are in good agreement with those from potassium permanganate titration method. The real samples analysis was proven the accuracy and feasibility of this proposed method for practical application.

Conclusions

The novel nanocomposites of ARS/MWCNT nanocomposites were synthesized by a facile method based on the π – π stacking non-covalent interactions between ARS and MWCNTs. Fourier transformation infrared spectrometry (FTIR), UV–Vis spectroscopy (UV–Vis), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and cyclic voltammetry (CV) were used to characterize the nanocomposites. The spectrographic studies reveal that the ARS/MWCNT nanocomposites exhibit a good stability in aqueous solution. Furthermore, the ARS/MWCNT/GC electrode exhibits a sensitive response to the reduction of hydrogen peroxide. Owing to its outstanding performance, the ARS/MWCNT nanocomposites would take on a promising prospect of the practical application in electroanalytical chemistry field (such as electrochemical sensors).

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (21007087, 41276093), the Chinese Academy of Sciences (KZCX2-YW-JS208), the Natural Science Foundation of Shandong Province (BS2010HZ030), the Taishan Scholar Program of Shandong Province, and the Youth Innovation Promotion Association of CAS.

References

- Iijima S (1991) *Nature* 354:56
- Wu K, Hu S (2004) *Carbon* 42:3237
- Liu G, Riechers SL, Mellen MC, Lin Y (2005) *Electrochem Commun* 7:1163
- Jin E, Bian X, Lu X, Wang C (2012) *J Mater Sci* 47:4326. doi: [10.1007/s10853-012-6283-8](https://doi.org/10.1007/s10853-012-6283-8)
- Gupta A, Choudhary V (2011) *J Mater Sci* 46:6416. doi: [10.1007/s10853-011-5591-8](https://doi.org/10.1007/s10853-011-5591-8)
- Zhang M, Gong K, Zhang H, Mao L (2005) *Biosens Bioelectron* 20:1270
- Merkoçi A (2006) *Microchim Acta* 152:157
- Şen M, Tamer U, Pekmez NÖ (2011) *J Solid State Electrochem* 16:457
- Liu J, Zhou D, Liu X, Wu K, Wan C (2009) *Colloids Surf B Biointerfaces* 70:20
- Zuo X, Li N, Zhang H (2011) *J Mater Sci* 47:2731. doi: [10.1007/s10853-011-6099-y](https://doi.org/10.1007/s10853-011-6099-y)
- Wang J, Musameh M, Lin Y (2003) *J Am Chem Soc* 125:2408
- Liu J, Tian S, Knoll W (2005) *Langmuir* 21:5596
- Brandão L, Passeira C, Mirabile Gattia D, Mendes A (2010) *J Mater Sci* 46:7198. doi: [10.1007/s10853-010-4638-6](https://doi.org/10.1007/s10853-010-4638-6)
- Furtado C, Kim U, Gutierrez H, Pan L, Dickey E, Eklund PC (2004) *J Am Chem Soc* 126:6095
- Sun Y, Wilson SR, Schuster DI (2001) *J Am Chem Soc* 123:5348
- Wu K, Fei J, Hu S (2003) *Anal Biochem* 318:100
- Zhang W, Silva SR (2010) *Spectrochim Acta A Mol Biomol Spectrosc* 77:175
- Musameh M, Wang J, Merkoçi A, Lin Y (2002) *Electrochem Commun* 4:743
- Salimi A, Banks CE, Compton RG (2004) *Analyst* 129:225
- Valentini F, Amine A, Orlanducci S, Terranova ML, Palleschi G (2003) *Anal Chem* 75:5413
- Guo M, Chen J, Liu D, Nie L, Yao S (2004) *Bioelectrochem* 62:29
- Li J, Yi F, Jiang Z, Fei J (2003) *Microchim Acta* 143:287
- Sai Sathish R, Ravi Kumar M, Nageswara Rao G, Anil Kumar K, Janardhana C (2007) *Spectrochim Acta A Mol Biomol Spectrosc* 66:457
- Deng P, Fei J, Zhang J, Li J (2008) *Electroanalysis* 20:1215
- Deng P, Fei J, Zhang J, Li J (2008) *Microchim Acta* 165:211
- Deng P, Zhang J, Liao S, Li J (2008) *Microchim Acta* 161:123
- Alghamdi AH (2010) *J Saudi Chem Soc* 14:1
- Sahin I, Nakiboglu N (2006) *Anal Chim Acta* 572:253
- Schumacher S, Nagel T, Scheller FW, Gajovic-Eichelmann N (2011) *Electrochim Acta* 56:6607
- Zhong H, Li N, Zhao F, Ka Li (2004) *Talanta* 62:37
- Dai HP, Shiu KK (1998) *Electrochim Acta* 43:2709
- Yue W, Zheng D, Hu C, Hu S (2010) *J Nanosci Nanotechnol* 10:6586
- Jin E, Lu X, Cui L, Chao D, Wang C (2010) *Electrochim Acta* 55:7230
- Zhang W, Wang L, Zhang N, Wang G, Fang B (2009) *Electroanalysis* 21:2325
- Klassen N, Marchington D, McGowan H (1994) *Anal Chem* 66:2921