Electrochemical sensor based on TiO₂/polyvinyl alcohol nanocomposite for detection of ciprofloxacin in rainwater

Junwei Zhao, Pengcheng Huang[*], Wei Jin

Power China Guiyang Engineering Corporation Limited, Guiyang 550081, China
[*]E-mail: Huang_pc666@126.com

This work was focused on evaluating the electrochemical properties of TiO₂/polyvinyl alcohol (PVA) nanocomposite to determine Antibiotics in rainwater using differential pulse voltammetry (DPV) technique. TiO₂/PVA nanocomposite was coated using a facile dip-coating technique on a glassy carbon electrode (GCE). The morphological and structural properties of TiO₂/PVA nanocomposites were studied by SEM and XRD measurements. The surface morphology of the prepared TiO₂/PVA-GCE nanocomposite indicated that the TiO₂ nanoparticles were uniformly distributed in the structure of the PVA. Cyclic voltammetry results indicated that TiO₂/PVA nanocomposites have a high repeatability response and stability for the detection of antibiotics. The low detection limit, high sensitivity and wide linear range for determination of ciprofloxacin as an antibiotic were obtained 0.04μM, 0.8165μA/μM, and 10μM-120μM, respectively. The high performance of ciprofloxacin determination by TiO₂/PVA-GCE sensor in rainwater as a real sample indicated that the proposed sensor can be an appropriate choice for practical detection of pollutions in water sources.

1. INTRODUCTION

Rainwater seems to be one of the most promising options for freshwater supply in the face of water scarcity and rising demand [1-3]. Rainwater harvesting may provide freshwater directly to households, including in rural and semi-urban areas where conventional technologies are not able to provide it [4-6]. Although rainwater is commonly considered clean and pure, the potential risk of public health related to the pathogenic microorganisms in rainwater cannot be ignored [7, 8]. Feces of mammals, insects, reptiles and wild birds that can access the roof could be washed away in the event of rain into the storage tank [9, 10]. As a result, contamination of rainwater harvested by including

fecal coliforms, intestinal bacteria, Enterococcus spp. and Escherichia coli, generally found in the intestines of warm-blooded animals has been reported [11-13].

Moreover, several types of research indicated that high levels of antibiotics have negative effects on the health of humans [14-16]. Therefore, the determination of antibiotic levels in food, pharmaceuticals, and water specimens is necessary and some researchers have been focused on the design, development, and optimization of antibiotic sensing methods [17, 18]. Ciprofloxacin is a group of drugs called fluoroquinolones [19, 20]. Fluoroquinolones cause more serious side effects than any other class of antibiotics [21, 22]. Complications include irreversible neurological problems, tendon problems, bleeding kidneys, kidney damage, and in some cases heart and liver problems. It is contraindicated before the age of 18 due to damage to the bone growth plates [23-25].

Antibiotic sensing techniques conclude molecular absorption spectrophotometry, quartz crystal microbalance, high-performance liquid chromatography, capillary electrophoresis, surface-enhanced Raman spectroscopy, and electrochemical methods [26-29]. Among these methods, electrochemical techniques have been done on friendly, rapid, accurate, and cost-effective operation systems to evaluate oxidation-reduction reaction and the detection of inorganic and organic analytes in water resources [30, 31].

Many electrochemical investigations were conducted based on different materials and structures, such as nanowires, nanoparticles, graphene, carbon nanotube, polymer and semiconductors to advance the analytical performance of antibiotic sensors [32, 33]. However, the application of semiconductors nanocomposites for the development of the antibiotic sensors showed enhancement in sensing properties, and research has not been studied for the analytical performance of Tio_2/polyvinyl alcohol (PVA)/GCE nanocomposite as an antibiotic electrochemical sensor. So far only a few electrochemical sensors were developed for the determination of ciprofloxacin. Santos suggested an electrochemical sensor based on a glassy carbon electrode modified by nickel oxide and graphene oxide [34]. The authors used square wave voltammetry for analytes determination in enriched biological specimens, including serum and urine. Another research was done by Kingsley et al. [35]. For the construction of the sensor, the authors modified a carbon paste electrode with copper-zinc ferrite nanoparticles. The developed technique was tested in the detection of ciprofloxacin in serum and urine specimens and pharmaceutical formulations by using adsorptive stripping voltammetry. Thus, the Tio_2/PVA/GCE sensor was prepared and applied for the detection of antibiotics using differential pulse voltammetry (DPV) and cyclic voltammetry (CV) measurements.

2. MATERIALS AND METHODS

The synthesis process is like to report one by Mondal et al [36]. Briefly, an aqueous solution of Titanium(III) chloride ($TiCl_3$) was prepared by addition of 1mL of it into 40mL of Sodium hydroxide (NaOH, 0.4 M). The homogeneous mixture of PVA solution (4gm in 100mL of DI water, heated to 80ºC) was blended into the NaOH solution under severe stirring. Then the as-obtained precipitates were collected using centrifugation and washed by DI water. At the next step, the achieved filtrate was moved in a steel autoclave, and then the total content was made 70mL by the addition of water. The

autoclave was holding for 6 hours at 180ºC. The samples were separated after several items of washing with water and ethanol via centrifugation, and then the powder samples were obtained after air drying at 40°C.

The surface of the glass carbon electrode (GCE) was polished with 0.1µm alumina suspension and washed with deionized water. The GCE electrode with the prepared nanocomposite is completed using the dip-coating technique. Usually bare GCE is first treated with 0.6M HCl, DI water, and then wiped with cotton. Then the prepared powder samples (1mg) were ultrasonically dispersed in DMSO (5ml) for 30 min. The cleaned pre-treated GCE was dipped in solution and finally rinsed with water to remove any weakly bound particles. The electrode is called TiO2/PVA-GCE.

In order to the morphological and structural analysis of prepared samples, X-ray powder diffraction (XRD) and scanning electron microscope (SEM) were used. Electrochemical analysis was performed in a conventional electrochemical cell which including three electrodes: a platinum wire as a counter electrode, Ag/AgCl/(sat KCl) as a reference electrode, and TiO2/PVA-GCE as a working electrode. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed with an Autolabpotentiostat (MetrohmAutolab B.V. the Netherlands). The electrolyte was contained 0.1M phosphate buffer solution (PBS) that prepared for NaH_2PO_4 (>99%) and H3PO4 (≥85%). The pH value of 7 for PBS was adjusted by NaOH and HCl solutions. Rainwater was collected in an urban area to prepare the real samples. Several Pyrex glasses were deployed immediately before a rainfall event. Prior to use glasses, they were cleaned and washed with dichloromethane, acetone, and methanol. Rainwaters were gathered by casting the contents of the glasses into wide-mouth amber bottles and then immediately chilled to 4°C.

3. RESULTS AND DISCUSSION
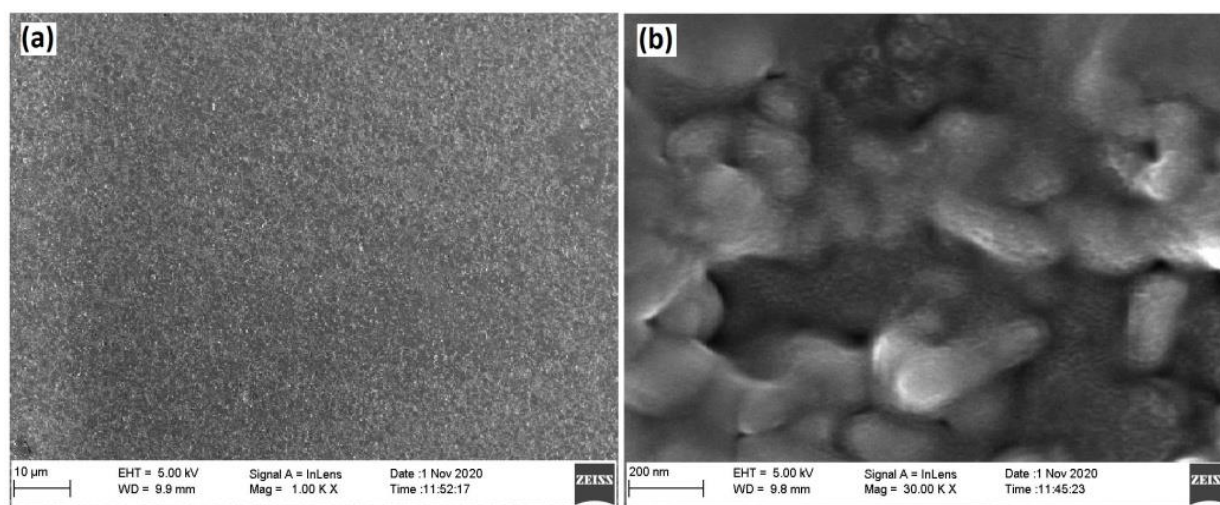
Figure 1. Surface morphology of prepared TiO2/PVA-GCE nanocomposite

Surface morphology of prepared TiO₂/PVA-GCE sample was indicated using the FESEM is presented in Figure 1. A wide distribution of spherical particles is observed, indicating that the Tio₂ nanoparticles were evenly distributed in the structure of the PVA.
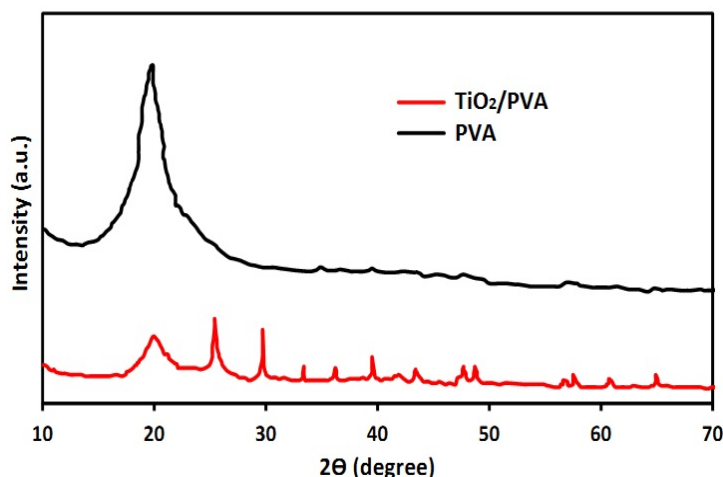

Figure 2. XRD patterns of PVA and TiO₂/PVA nanocomposites

Figure 2 indicates XRD patterns of PVA and TiO2/PVA nanocomposites. The comparison of the XRD patterns of the pure PVA thin film with that of TiO2/PVA nanocomposites clearly shows that the addition of the TiO2 nanoparticles in PVA decreases the intensity of the basic PVA peak causing an increase in the amorphous degree. Furthermore, the other peaks indicate the existence of TiO₂[37, 38]. All possible diffraction peaks were well-matched by the JCPDS card No.781510.
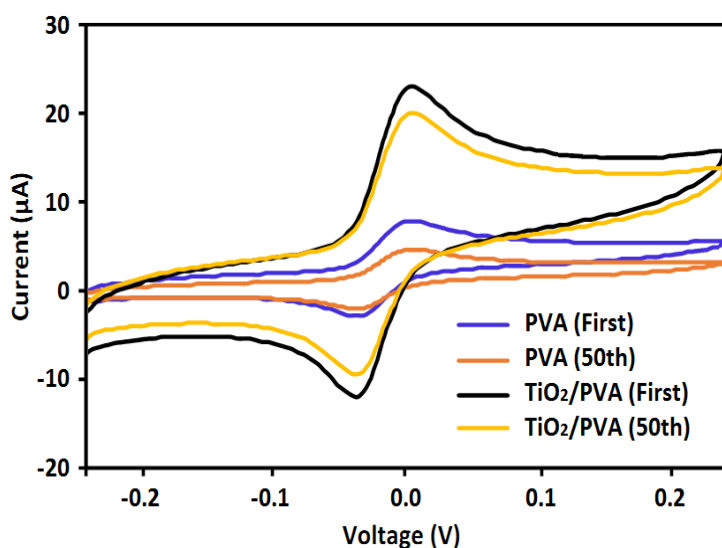
Figure 3. First and 50th recorded CVs of (a) PVA and (b) TiO₂/PVA-GCE electrode in potential ranging from -0.24V to 0.24V in 0.1M PBS containing 20μM ciprofloxacin.

Figure 3 indicates the first and 50th recorded CVs of PVA and TiO2/PVA-GCE electrodes in potential ranging from -0.24V to 0.24V in 0.1M PBS containing 20μM ciprofloxacin as an antibiotic. It may be observed anodic peaks at 0.01V for all CVs. The CV curve of TiO$_2$/PVA-GCE electrodes reveals higher and sharp anodic peaks current which can be attributed to the improvement of electrode conductivity by introducing TiO$_2$ nanostructures in PVA structures [39]. Moreover, the TiO$_2$nanoparticles can produce more active sites, exposed surface-area, and efficient electron transmission which may facilitate the electrochemical reactions [40]. In order to consider the stability of PVA and TiO$_2$/PVA-GCE electrode responses to the presence of ciprofloxacin in the electrochemical test, the 50th recorded CV of both electrodes is also shown in Fig. 3. As indicated, anodic peak current was decreased 70% and 15% for PVA and TiO$_2$/PVA-GCE electrodes, respectively, which revealed greater stability of TiO$_2$/PVA-GCE electrodes to the presence of ciprofloxacin. Therefore, the following electrochemical investigations are done on TiO$_2$/PVA-GCE electrodes.
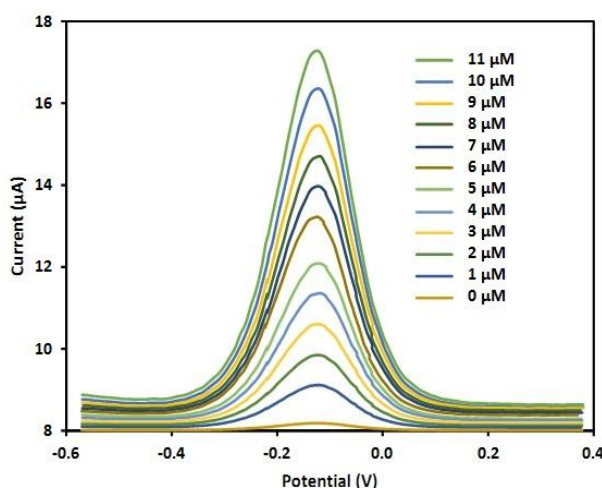
Figure 4. DPV responses of TiO$_2$/PVA-GCE in 0.1M PBS in successive addition of 1μM ciprofloxacin

The DPV method was used to study the detection limit, linear range, and sensitivity of TiO$_2$/PVA-GCE as a ciprofloxacin sensor. Figure 4 reveals the recorded DPV response of TiO$_2$/PVA-GCE by successive addition of 1μM ciprofloxacin in 0.1M PBS. The recorded DPVs indicate a noticeable cathodic peak in -0.14V which can show evidence of electrochemical activities of ciprofloxacin in the solution [41, 42].

Figure 5a exhibits the calibration curve as an electrocatalytic response to the content effect of ciprofloxacin. The sensitivity and detection limit in low-content of ciprofloxacin are obtained 0.8165μA/μM and 0.04μM, respectively. For obtaining a linear range of the ciprofloxacin sensor, the DPV study was repeated for the addition of 10μM ciprofloxacin in the electrochemical cells [43]. Thus, the obviously linear relationship from 10μM to 120μM (R^2=0.9986) is found in Figure 5c. Furthermore, sensitivity in high-content of ciprofloxacin was obtained to be 0.7286μA/μM.
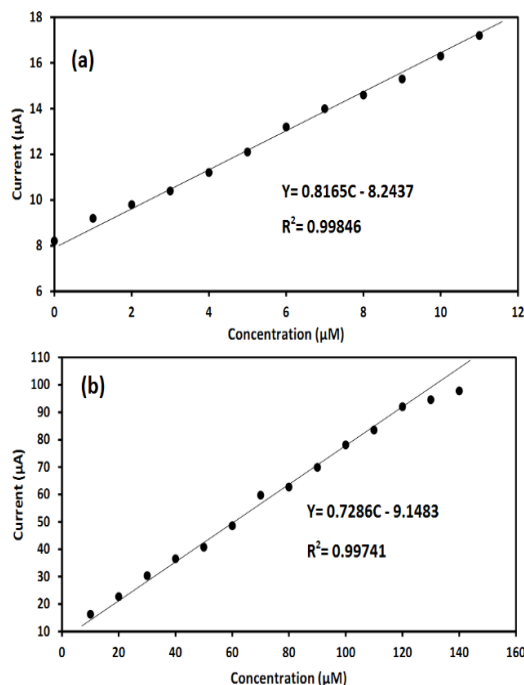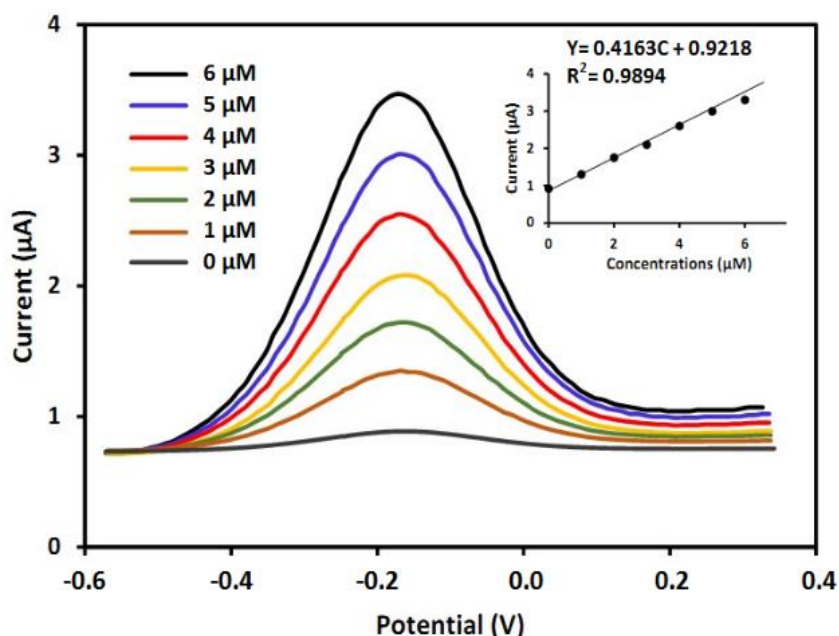
Figure 5. The calibration plots for successive addition of (a) 1µM and (b) 10µM ciprofloxacin

Table 1 indicates the comparison of linear range and detection limit values of the TiO_2/PVA-GCE with other antibiotic electrochemical sensors. Results show that GR-ZnO/GCE [44] and Graphene oxide decorated with Cu–Ag core-shell nanoparticles [45] exhibit wider linear ranges than the TiO_2/PVA-GCE. Furthermore, a comparison of the analytical parameters reveals that the performance of the proposed sensor is comparable or superior to the reported antibiotic electrochemical sensor. It must be noted that the TiO_2/PVA-GCE sensor is low cost, very stable and its ingredients are very eco-friendly. Appropriate electronic features of TiO_2 in the PVA structures provide the capability to promote charge-transfer reactions which improved the electrochemical activities of modified electrodes for ciprofloxacin detection.

Table 1. The comparison of linear range and detection limit values of the TiO_2/PVA-GCE with other antibiotic electrochemical sensors

Electrodes	Method	Detection limit(µM)	Linear range (µM)	Ref.
TiO_2/PVA-GCE	DPV	0.04	10-120	This work
Nanodiamond /GCE	Square-wave voltammetry	0.22	0.79–49	[46]
GR-ZnO/GCE	DPV	0.4	1–180	[44]
OLA-Fe_3O_4/MWCNTs/GCE	DPV	0.06	0.01–8.9	[47]
Graphene oxide decorated with Cu–Ag core–shell nanoparticles	CV	0.46	10–1000	[45]
Poly(methylene green)–Ethaline deep eutectic solvent/Fe_2O_3 NPs modified electrode	CV	0.33	0.5-20	[48]
GO/ZnO/GCE	CV	0.01	0.2-7.2	[49]

To investigate the practical possibility of the ciprofloxacin sensor, the performance of the proposed electrode was considered in rainwater as a real specimen [25, 50]. The standard additions of the ciprofloxacin were used to determine ciprofloxacin in the real specimens by the DPV method (Fig. 6). The calibration curve is shown in the inset of Figure 6. The calibration curve obtained the sensitivity of 0.4163, linearity range of 1-5 µM, and a detection limit of 0.05. Furthermore, a recovery was tested 98.65-100.3 for different concentrations of ciprofloxacin in the presence of rainwater samples revealing no interference from endogenous rainwater constituents. These results exhibited the reliability of the prepared sensor for the detection of ciprofloxacin in rainwater samples.

Figure 6. DPV responses of TiO$_2$/PVA-GCE in 0.1M PBS in successive additions of 1µM ciprofloxacin in rainwater; inset indicates the calibration plots for ciprofloxacin determination in rainwater.

Table 2. Analytical results of ciprofloxacin electrochemical determination in real samples using TiO$_2$/PVA-GCE (n = 4)

Real sample	Amount added(µM)	Found concentrations(µM)	Recovery(%)	Relative standard deviations(%)
Rainwater	1.00	0.87	89.0	3.21
	2.00	1.75	87.3	1.98
	4.00	3.76	92.6	1.92
	6.00	5.73	94.1	4.12

Table 2 indicates the analytical results. These results show that the recoveries values range was from 87.3% to 94.1% and relative standard deviations values were lower than 4.12% which indicated

the TiO₂/PVA-GCE with acceptable precision and accuracy can be used for the detection of ciprofloxacin in rainwater specimens.

4. CONCLUSIONS

Here, the TiO₂/PVA nanocomposite was coated on the GCE surface and its electrochemical properties to determine Antibiotic levels in rainwater were evaluated using the DPV technique. The morphological and structural properties of TiO₂/PVA nanocomposites were studied by SEM and XRD measurements. The surface morphology of the prepared TiO₂/PVA-GCE nanocomposite indicated that the TiO₂ nanoparticles were uniformly distributed in the structure of the PVA. CV results indicated that TiO₂/PVA nanocomposites have a high repeatability response and stability for the detection of antibiotics. The low detection limit, high sensitivity and wide linear range for determination of ciprofloxacin as an antibiotic were obtained 0.04µM, 0.8165µA/µM and 10µM-120µM, respectively. The high performance of ciprofloxacin determination by TiO₂/PVA-GCE sensor in rainwater as a real sample indicated that the proposed sensor can be an appropriate choice for practical detection of pollutions in water sources.

References

1.   D. Rey, I.P. Holman and J.W. Knox, *Regional environmental change*, 17(2017)1527.
2.   H. Guan, S. Huang, J. Ding, F. Tian, Q. Xu and J. Zhao, *Acta Materialia*, 187(2020)122.
3.   L. Zhang, M. Zhang, S. You, D. Ma, J. Zhao and Z. Chen, *Science of The Total Environment*, 780(2021)146505.
4.   V. Sheikh, *Sustainable Cities and Society*, 60(2020)102278.
5.   X. Xu and M. Nieto-Vesperinas, *Physical review letters*, 123(2019)233902.
6.   Y. Orooji, B. Tanhaei, A. Ayati, S.H. Tabrizi, M. Alizadeh, F.F. Bamoharram, F. Karimi, S. Salmanpour, J. Rouhi and S. Afshar, *Chemosphere*, 281(2021)
7.   M.A. Alim, A. Rahman, Z. Tao, B. Samali, M.M. Khan and S. Shirin, *Journal of Cleaner Production*, 248(2020)
8.   X. Xu, Y. Yang, L. Chen, X. Chen, T. Wu, Y. Li, X. Liu, Y. Zhang and B. Li, *Laser & Photonics Reviews*, 15(2021)2000546.
9.   J. Struk-Sokołowska, J. Gwoździej-Mazur, P. Jadwiszczak, A. Butarewicz, P. Ofman, M. Wdowikowski and B. Kaźmierczak, *Water*, 12(2020)252.
10.   W. Zhang, Y. Hu, J. Liu, H. Wang, J. Wei, P. Sun, L. Wu and H. Zheng, *Saudi Journal of Biological Sciences*, 27(2020)1667.
11.   M. Waso, S. Khan and W. Khan, *Environmental research*, 161(2018)446.
12.   J.K. Denissen, B. Reyneke, M. Waso, S. Khan and W. Khan, *Frontiers in microbiology*, 12(2021)1027.

13.   H. Karimi-Maleh, M.L. Yola, N. Atar, Y. Orooji, F. Karimi, P.S. Kumar, J. Rouhi and M. Baghayeri, *Journal of colloid and interface science*, 592(2021)174.
14.   R.S. Al-Farsi, M. Ahmed, A. Al-Busaidi and B. Choudri, *Emerging Contaminants*, 3(2017)132.
15.   Z.-L. Li, R. Cheng, F. Chen, X.-Q. Lin, X.-J. Yao, B. Liang, C. Huang, K. Sun and A.-J. Wang, *Journal of Hazardous Materials*, 405(2021)124366.
16.   L. Zhang, J. Zheng, S. Tian, H. Zhang, X. Guan, S. Zhu, X. Zhang, Y. Bai, P. Xu and J. Zhang, *Journal of Environmental Sciences*, 91(2020)212.
17.   U. Szymańska, M. Wiergowski, I. Sołtyszewski, J. Kuzemko, G. Wiergowska and M.K. Woźniak, *Microchemical Journal*, 147(2019)729.
18.   B. Zhang, D. Ji, D. Fang, S. Liang, Y. Fan and X. Chen, *IEEE Electron Device Letters*, 40(2019)780.
19.   M. Rusch, A. Spielmeyer, H. Zorn and G. Hamscher, *Applied microbiology and biotechnology*, 103(2019)6933.
20.   Z. Chen, H. Zhang, X. He, G. Fan, X. Li, Z. He, G. Wang and L. Zhang, *BioResources*, 16(2021)2644.
21.   Y. Han, Y. Ma, S. Yao, J. Zhang and C. Hu, *Environmental Pollution*, 277(2021)116779.
22.   Y. Yang, H. Chen, X. Zou, X.-L. Shi, W.-D. Liu, L. Feng, G. Suo, X. Hou, X. Ye and L. Zhang, *ACS applied materials & interfaces*, 12(2020)24845.
23.   T.T. Van, E. Minejima, C.A. Chiu and S.M. Butler-Wu, *Journal of clinical microbiology*, 57(2019)e02072.
24.   G. Bonaldo, L.A. Andriani, O. D'Annibali, D. Motola and A. Vaccheri, *Pharmacoepidemiology and drug safety*, 28(2019)1457.
25.   H. Karimi-Maleh, Y. Orooji, F. Karimi, M. Alizadeh, M. Baghayeri, J. Rouhi, S. Tajik, H. Beitollahi, S. Agarwal and V.K. Gupta, *Biosensors and Bioelectronics*, 184(2021)113252.
26.   Y. Wu, G. Li, Y. Hong, X. Zhao, P.I. Reyes and Y. Lu, *Journal of Microbiological Methods*, 178(2020)106071.
27.   X. Song, J. Xie, M. Zhang, Y. Zhang, J. Li, Q. Huang and L. He, *Journal of Chromatography B*, 1076(2018)103.
28.   R. Bosma, J. Devasagayam, A. Singh and C.M. Collier, *Scientific Reports*, 10(2020)1.
29.   H. Karimi-Maleh, M. Alizadeh, Y. Orooji, F. Karimi, M. Baghayeri, J. Rouhi, S. Tajik, H. Beitollahi, S. Agarwal and V.K. Gupta, *Industrial & Engineering Chemistry Research*, 60(2021)816.
30.   T. Maier, K. Kainz, I. Barišić and R. Hainberger, *International Journal of Electrochemical Science*, 10(2015)2026.
31.   Y. Pang, *International Journal of Electrochemical Science*, 15(2020)5232.
32.   P. Sundaresan, T.-W. Chen, S.-M. Chen, T.-W. Tseng and X. Liu, *International Journal of Electrochemical Science*, 13(2018)1441.
33.   M.M. Sahihazar, M.T. Ahmadi, M. Nouri and M. Rahmani, *Journal of Solid State Electrochemistry*, 23(2019)1641.
34.   A.M. Santos, A. Wong, A.A. Almeida and O. Fatibello-Filho, *Talanta*, 174(2017)610.
35.   M.P. Kingsley, P.K. Kalambate and A.K. Srivastava, *RSC advances*, 6(2016)15101.
36.   S. Mondal, R. Madhuri and P.K. Sharma, *Journal of Alloys and Compounds*, 646(2015)565.
37.   V. Kaler, U. Pandel and R. Duchaniya, *Materials Today: Proceedings*, 5(2018)6279.
38.   M. Zhang, L. Zhang, S. Tian, X. Zhang, J. Guo, X. Guan and P. Xu, *Chemosphere*, 253(2020)126638.
39.   T. Li, Y. Wu, Q. Wang, D. Zhang, A. Zhang and M. Miao, *Journal of Materials Science*, 52(2017)7733.
40.   Y. Ma, Q. Tang, W.-Y. Sun, Z.-Y. Yao, W. Zhu, T. Li and J. Wang, *Applied Catalysis B: Environmental*, 270(2020)118856.

41.   O. Hendrickson, E. Zvereva, I. Shanin, A. Zherdev, N. Tarannum and B. Dzantiev, *Applied Biochemistry and Microbiology*, 54(2018)670.
42.   X. Wang, Z. Feng, B. Xiao, J. Zhao, H. Ma, Y. Tian, H. Pang and L. Tan, *Green Chemistry*, 22(2020)6157.
43.   T.S.H. Pham, P.J. Mahon, G. Lai and A. Yu, *Electroanalysis*, 30(2018)2185.
44.   X. Yue, Z. Li and S. Zhao, *Microchemical Journal*, 159(2020)105440.
45.   A. Feizollahi, A.A. Rafati, P. Assari and R.A. Joghani, *Analytical Methods*, 13(2021)910.
46.   N.B. Simioni, T.A. Silva, G.G. Oliveira and O. Fatibello-Filho, *Sensors and Actuators B: Chemical*, 250(2017)315.
47.   D.R. Kumar, D. Manoj and J. Santhanalakshmi, *Journal of nanoscience and nanotechnology*, 14(2014)5059.
48.   W. da Silva, A.C. Queiroz and C.M. Brett, *Sensors and Actuators B: Chemical*, 325(2020)128747.
49.   N. Sebastian, W.-C. Yu and D. Balram, *Inorganic Chemistry Frontiers*, 6(2019)82.
50.   S.A. Lim and M.U. Ahmed, *Analytical Sciences*, 32(2016)687.