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Highly Effective Detection of 4-Nitrophenol by Tremella-like Indium Silver Sulfide Modified GCE

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A highly sensitive electrochemical sensor for 4-nitrophenol was established based on a tremella-like indium silver sulfide modified glassy carbon electrode (TLISS/GCE). Indium silver sulfide was facilely synthesized by co-precipitation. The morphology and phase of TLISS was investigated by scanning electron microscopy and X-ray diffraction. An electrochemical study was conducted by an electrochemical impedance spectroscopic technique, cyclic voltammetry and differential pulse voltammetry. The as-prepared sensor detected 4-nitrophenol with high accuracy, satisfactory reproducibility and good stability in wide range of 4-nitrophenol concentrations, and the determination limit (3S/m) was as low as 1.09 μM. In addition, tap and river waters were used to evaluate the practical application of the newly developed TLISS/GCE sensor, and high performance was also obtained. To the best of our knowledge, this is the first report regarding the 4-nitrophenol detection performance of indium silver sulfide. The method reported here is helpful for developing more highly effective 4-nitrophenol detection methods.

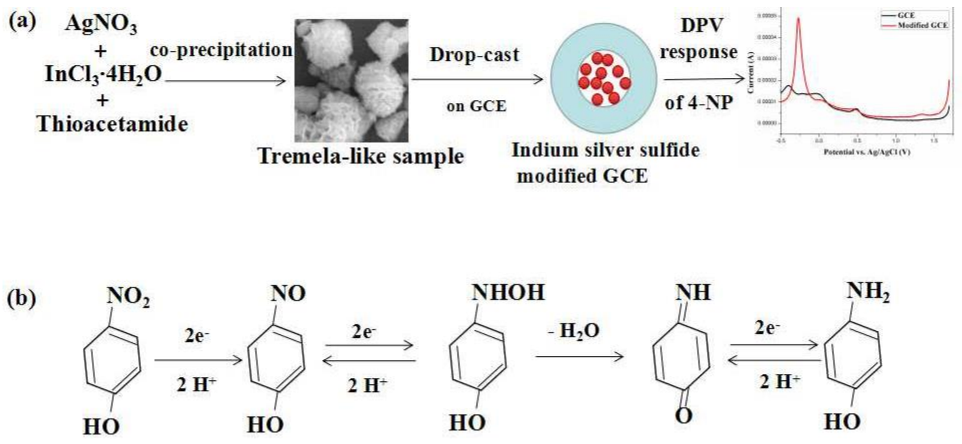
Keywords: Sensors; Indium silver sulfide; Modified GCE; 4-Nitrophenol

1. INTRODUCTION

Nitrophenol (NP) isomers have been used in many industrial sectors such as pharmaceutical, agrochemical, petroleum, textile and paper. Furthermore, nitrophenols have constituted reaction intermediates and side-products in the chemical industry and have also been produced from pesticide degradation. As a result, these isomers are widely distributed in environment, especially in surface water [1, 2]. 4-Nitrophenol (4-NP) is one kind of nitrophenols, which is highly hazardous and toxic due to its high damage to the central nervous system, kidneys, liver, and blood system in humans [3]. Because of their embryonic, mutagenic and carcinogenic toxicants, nitrophenols containing industrial effluents must be identified and dealt with before being discharged [4, 5]. Consequently, the development of methods to reliably detect phenols and substituted phenols in wastewater has attracted much attention [5]. To date, several methods, such as luminescence, high-performance liquid chromatography and UV-vis spectrophotometry [6-11], have been applied to detect 4-NP. Nevertheless, disadvantages including high cost and complicated operation still exist. Additional cheap, fast and simple detection methods are urgently needed. Electrochemical methods are excellent techniques to detect trace substrates due to their outstanding accuracy, sensitivity, reproducibility and stability. However, unfortunately, bare electrodes often exhibit low sensitivity and suffer from high interference and a high overpotential [12]. Consequently, modified electrodes receive special attention in electroanalysis due to their celerity, high sensitivity, low cost, and reliable data [13-15]. Several chemicals have been applied to modify electrodes in the electrochemical detection of 4-NP, such as metal nanoneedles [16], reduced graphene oxide [17], polymer materials [18], cyclodextrin materials [19] and carbon materials [20], indicating the high applicable potential of electroanalysis in detecting 4-NP.

Indium silver sulfide is an attractive semiconductor with a relatively large absorption coefficient and suitable energy band gap, which has been widely applied in optoelectronics and photovoltaic areas [21, 22], such as solar cells [23], light-emitting diodes [24], photocatalysis [25], copper (II) detection [26] and opto-electrical properties [27]. However, the reports regarding modified electrodes based on indium silver sulfide are very limited.

To our knowledge, the study of indium silver sulfide modified GCE for the determination of 4-NP has not been mentioned in any previous reports. Herein, we reported a significantly simple and facile precipitation method to prepare tremella-like indium silver sulfide and the electroanalysis of 4-NP based on tremella-like indium silver sulfide modified glassy carbon electrodes (TLISS/GCEs) was investigated. The construction of the designed electrochemical sensing platform and the electron transport scheme are shown in Scheme 1.



Scheme 1. (a) The illustration of indium silver sulfide sensing 4-NP by an electrochemical strategy; (b) The scheme of electron transfer in the detection of 4-NP.

2. EXPERIMENTAL

2.1 Instruments and chemicals

The instruments and chemicals are shown in supporting information.

2.2 Preparation of indium silver sulfide by the co-precipitation method

Indium silver sulfide was synthesized by a co-precipitation process. $InCl_3 \cdot 4H_2O$ (1.2005 g, 4.09 mmol) and $AgNO_3$ (0.1077 g, 0.63 mmol) were dissolved in 25 ml of ethylene glycol under vigorous stirring for 30 min. Afterwards, the $AgNO_3$ solution was poured into an $InCl_3$ solution to form the metal precursor (the molar ratio of In/Ag = 6.49); then thioacetamide (0.7540 g, 10.04 mmol) was added to the above solution under magnetic stirring for 3 h at 70°C until a homogeneous dark-red solution was formed. The mixture was cooled to room temperature naturally and aged for 12 h. Subsequently, the obtained brick-red sample was thoroughly washed by deionized water and absolute ethanol for several alternating cycles. Lastly, the products were dried at 60°C for 12 h.

2.3 Electrode modificated by indium silver sulfide

The surface of the glassy carbon electrode (GCE) was polished using a polishing kit containing 0.3 μm alumina fine powder to a mirror finish. Then, the electrode was rinsed with deionized water several times. Subsequently, the electrode was subjected to sonication in an aqueous solution of water/concentrated nitric acid (1/1, v/v) and water/ethanol (1/1, v/v) for 5 min. Approximately 15 μl of indium silver sulfide aqueous dispersion (1 mg/ml) prepared by the co-precipitation method was drop-cast on the surface of the pre-cleaned GCE and dried at 60°C for 30 min.

2.4 4-NP detection

The modified electrodes were submitted to voltammetric cycles in 1 M H_2SO_4 at 100 mV s^{-1} in the presence of 4-NP. Differential pulse voltammetry (DPV) was employed to detect 4-NP. The measurements were conducted in 1 M H_2SO_4 and 298 K.

ABBREVIATIONS:
NP: nitrophenols; 4-NP: 4-nitrophenol; TLISS/GCE: tremella-like indium silver sulfide modified glassy carbon electrodes; GCE: glassy carbon electrode; DPV: differential pulse voltammetry; CV: cyclic voltammetry; EIS: electrochemical impedance spectroscopy; LOD: limit of detection

3. RESULTS AND DISCUSSION

3.1 Characterization of the TLISS/GCE

The morphology of as-fabricated indium silver sulfide was investigated by SEM. The SEM images of drop-cast indium silver sulfide on ITO glass under the same conditions as the modified GCE electrode are shown in Fig. 1. Fig. 1a indicates that the synthesized products exhibited sphere-like shapes with diameters in the range of 1 ~ 5 μm. These spheres were zoomed in and shown in Fig. 1b and 1c. From these zoomed in imagines, it is clear that these spheres were assembled by several lamellar structures with thicknesses of approximately 20 nm. The SEM investigation showed that the morphology of as-synthesized indium silver sulfide was similar to tremellas (as a reference, an image of nature tremella is shown in Fig. 1d).

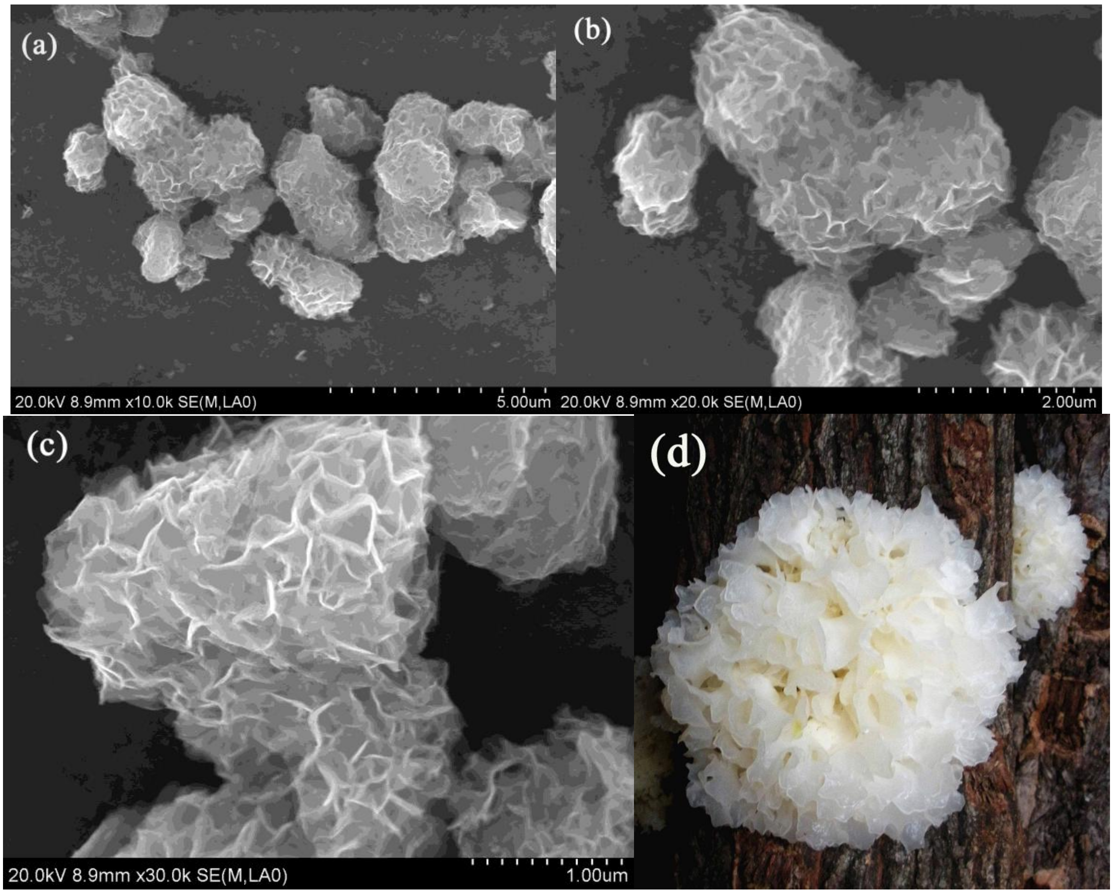


Figure 1. (a-c) SEM images of the tremella-like indium silver sulfide samples at different magnifications; (d) An image of native tremella

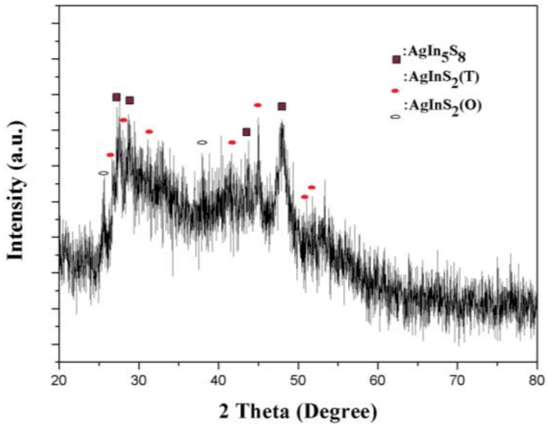


Figure 2. XRD pattern of the indium silver sulfide sample prepared by the co-precipitation method

The XRD pattern of as-synthesized indium silver sulfide is shown in Fig. 2. The characteristic peaks were attributed to the tetragonal structure (JCPDS 65-5163), orthorhombic structure (25-1328) of $AgInS_2$ [27] and cubic structure of $AgIn_5S_8$ (JCPDS 26-1477), which further confirmed that indium silver sulfide was successfully synthesized.

3.2 Electrochemical study of the TLISS/GCE and bare GCE

Cyclic voltammetry (CV) of 2.84×10^{-4} M 4-NP in 1 M H_2SO_4 was chosen to study the barrier changes between the TLISS/GCE and bare GCE. The CV data of TLISS/GCE had a higher peak and a more negative peak than those of the bare GCE (Fig. 3a), indicating a higher electron transport rate on the TLISS/GCE than that of the bare GCE.

To further investigate the sensing performance of 4-NP, differential pulse voltammetry (DPV) (Fig. 3b) was carried out in 1 M H_2SO_4 containing 2.84×10^{-4} M 4-NP for the TLISS/GCE and bare GCE. A significantly larger peak of 4-NP was obtained on the TLISS/GCE than on the bare GCE, indicating that TLISS/GCE exhibited a significantly higher sensitivity.

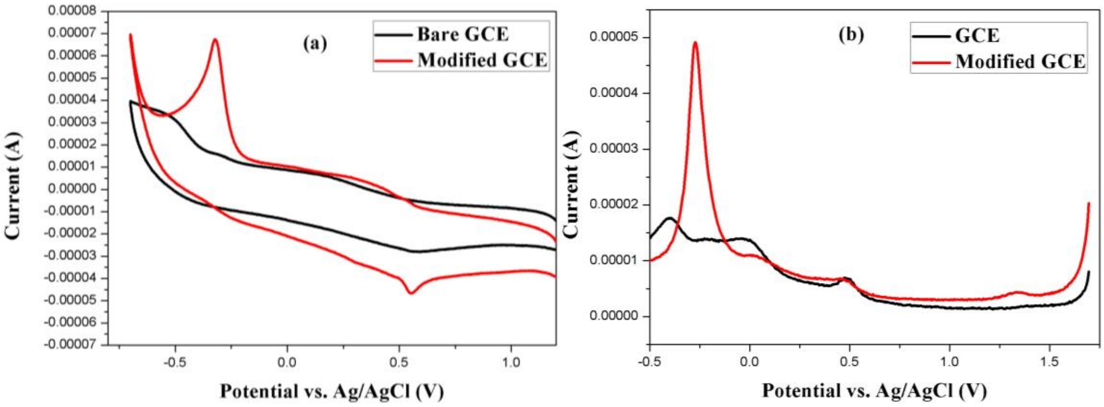


Figure 3. CV (a) and DPV (b) of 2.84×10^{-4} M 4-NP in 1 M H_2SO_4 for bare GCE and TLISS/GCE

3.3 Electrochemical behavior of the TLISS/GCE

DPV of different substances on the TLISS/GCE was investigated, and the diagrams are shown in Fig. 4. Although the TLISS/GCE exhibited a similar peak potential (E_p) to the different substances (N,N-diethyl -aniline (- 0.240 V), phenol (- 0.252 V), hydroquinone (- 0.252 V), catechol (- 0.240 V) and 4-NP (-0.228 V)), the peak currents (I_p) were significantly different. As a result, 4-NP could be detected by I_p because the peak current of 4-NP (I_p = 10.71 μA) was significantly higher than that of others (2-NP (I_p = 7.713 μA), N,N-diethylaniline (I_p = 1.035 μA), phenol (I_p = 1.518 μA), hydroquinone (I_p = 1.016 μA) and catechol (I_p = 1.291 μA)). It is suggested that nitrophenol was more sensitive than other substances on the modified GCE. Therefore, 4-NP could be determined by the TLISS/GCE via the peak current of DPV at approximately -0.228 V.

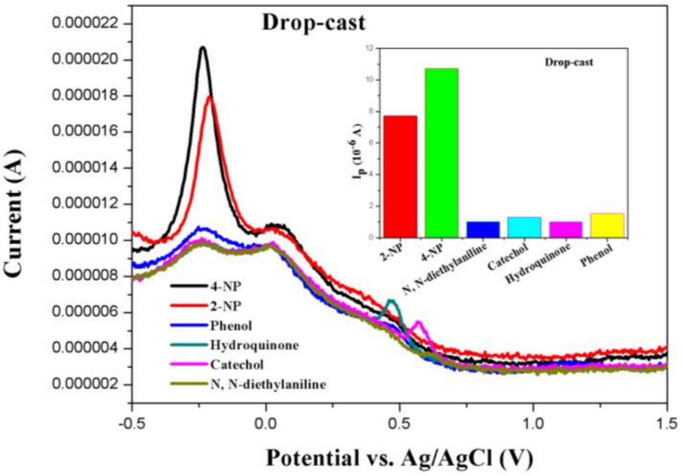


Figure 4. DPV diagrams and peak current (I_p) of 4-NP, 2-NP, phenol, catechol, N,N-diethylaniline and hydroquinone in 1 M H_2SO_4 for TLISS/GCE (The concentration of all the substances were 2.84×10^{-4} M)

The electron transfer capacity of 4-NP on the bare GCE and TLISS/GCE were studied by electrochemical impedance spectroscopy (EIS) to discuss the improved oxidation signals. As shown in Fig. 5, the semicircle that appeared on the bare GCE showed a significantly larger diameter than that of the semicircle that appeared on the TLISS/GCE. This phenomenon indicated that the electron transfer capacity of 4-NP on the surface of the TLISS/GCE was significantly faster than that on the bare GCE [28], that is, the charge transfer ability of the active species was significantly improved by the TLISS modification.

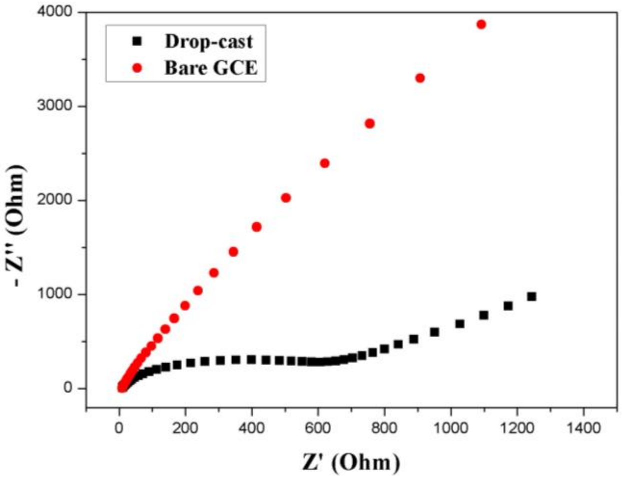


Figure 5. Nyquist plots of 2.84×10^{-4} M 4-NP in 1 M H2SO4 for the bare GCE and TLISS/GCE, the frequency range: 10 kHz to 1 Hz; amplitude: 5 mV; and initial potential: 0.52 V

3.4 Electrochemical determination of 4-NP by the TLISS/GCE

The pH effect on the CV behaviors of the TLISS/GCE in 1 M H_2SO_4 with 2.84×10^{-4} M 4-NP was investigated. In Fig. 6, the peak current exhibited an obvious increase with a decrease in the pH value. This result displayed that a pH value of 0 could be applied to effectively determine 4-NP by the TLISS/GCE because of the highest peak current.

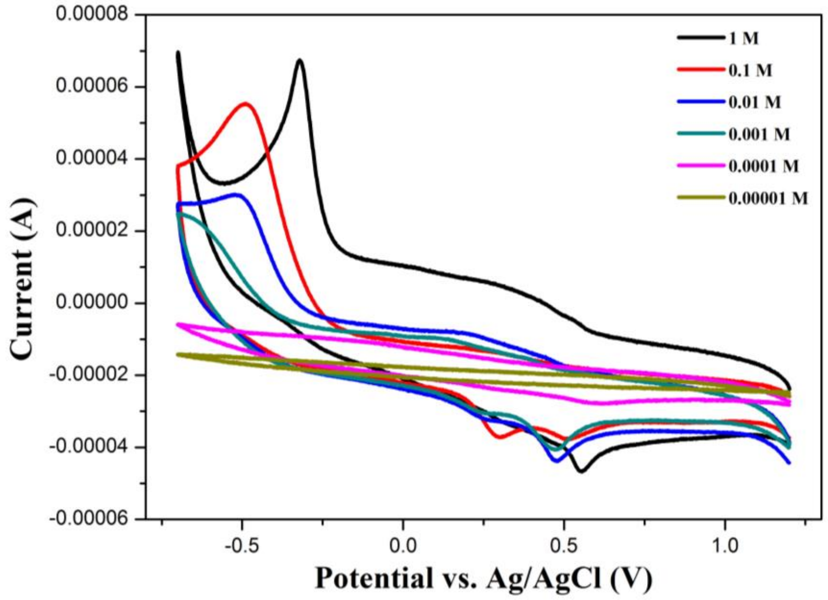


Figure 6. Effect of the H_2SO_4 concentration on the CV behaviors of the TLISS/GCE with 2.84×10-4 M 4-NP

Under the above optimized condition, the electrochemical response of the TLISS/GCE towards 4-NP with different concentrations in 1 M H_2SO_4 were studied by DPV (Fig. 7a). One could see that the peak currents increased with an increase in the 4-NP concentration. Furthermore, as shown in Fig. 7b, the peak current exhibited a linear increase with an increase in the 4-NP concentration. There were two linear ranges of the 4-NP concentration, namely, 1.43 to 55.93 μM and 55.93 to 553.7 μM, with different coefficients. These results indicated that 4-NP could be measured in the range of 1.43 to 553.7 μM by the TLISS/GCE with the electroanalysis method.

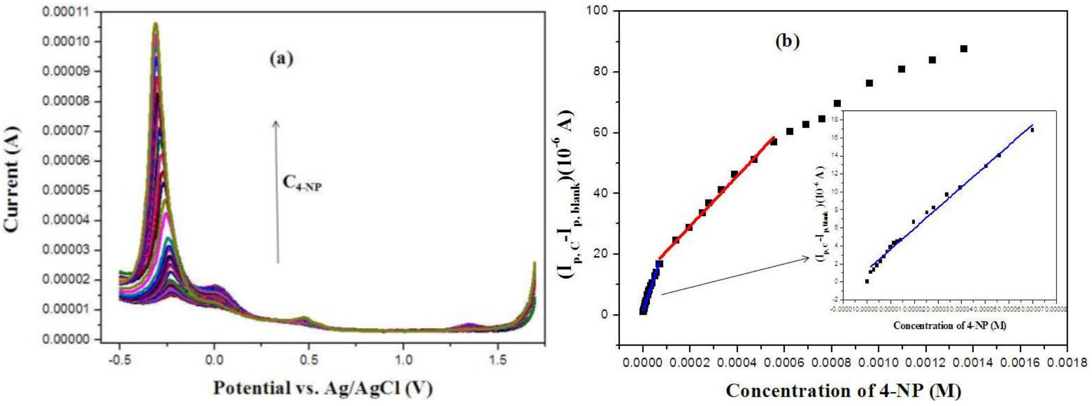


Figure 7. (a) DPV curves of the TLISS/GCE at different 4-NP concentrations in 1 M H2SO4; and (b) the corresponding calibration curves of 4-NP detection

The regression equations can be described as:

$I_{p,\ C} - I_{p,\ Blank} = 231060.89114\ C + 1.31826$ ($R^2 = 0.9914$)

for 1.43~55.93 μM and

$I_{p,\ C} - I_{p,\ Blank} = 82625.9329\ C + 12.76424$ ($R^2 = 0.99167$)

for 55.93~553.7 μM

where $I_{p,\ C}$ was the peak current (μA) of the TLISS/GCE at different concentrations of 4-NP ($C_{4\text{-}NP}$, mol/L) in 1 M H_2SO_4 and $I_{p,\ Blank}$ was the peak current (μA) of the TLISS/GCE when $C_{4\text{-}NP}$ was 0 M in 1 M H_2SO_4. Furthermore, a detection limit of 1.09 μM was estimated using the formula of the LOD = 3S / m (where S is standard deviation of the peak current of the blank (N = 11) and m is the slope of the calibration curve ($m = 0.2311\ \mu A\cdot\mu M^{-1}$)). In addition, the TLISS/GCE retained 98.0% of the initial response to 4-NP after being stored in air for four weeks, indicating the good stability of this modified electrode.

The 4-NP sensing performance of the TLISS/GCE was compared with those of some previously reported sensors, and the summary is shown in Table 1. From Table 1, although rGO-Ag, PMO, chitosan-crafted ZnO nanoneedles, β-cyclodextrin functionalized mesoporous silica, OMCs, the sodium montmorillonite-anthraquinone chemically modified glassy carbon electrode and AgNWs/GCE have lower detection limits than that of the TLISS/GCE, most of them (PMO, Chitosan-crafted ZnO nanoneedles, β-cyclodextrin functionalized mesoporous silica OMCs, the sodium montmorillonite-anthraquinone chemically modified glassy carbon electrode and AgNWs/GCE) have a smaller linear range than that of the TLISS/GCE, indicating that the TLISS/GCE has a wider application range than most of them. Although rGO-Ag exhibited outstanding performance with wider linear range and lower detection limit than those of the TLISS/GCE, rGO-Ag needed to be synthesized by microwave irradiation [4], which is more complicated with higher energy costs than the co-precipitation method applied in TLISS/GCE preparation. The comparison showed that the TLISS/GCE has a relatively wide application range and a lower detection limit, indicating that it is among the most excellent platforms for 4-NP examination that have ever been reported.

Table 1. Comparison of various electrodes for the electrochemical determination of 4-NP.

Modified Electrode	Linear range (μM)	Detection limit (μM)	References
Poly(3,4-ethylenedioxythiophene: poly(styrenesulfonate) (PEDOT:PSS)	-	4.51	[1]
Reduced graphene oxide - silver (rGO-Ag)	1~1100	0.32	[4]
poly(methyl orange) (PMO)	0.6~10	0.11	[5]
Chitosan-crafted ZnO nanoneedles	0.5~400.6	0.23	[16]
β-Cyclodextrin functionalized mesoporous silica	0.2~1.6	0.01	[19]
Ordered mesoporous carbons (OMCs)	2~90	0.1	[20]
Reduced graphene oxide	50~800	42	[29]
Nanogold	10~1000	8	[30]
Graphene-Nafion/Screen-printed electrode	25~620	3.5	[31]

Inorganic-organic/Pt	30~90	8.23	[32]
Ni-Cox nanoparticles	7~682	4.8	[33]
sodium montmorillonite-anthraquinone chemically modified glassy carbon electrode	2.2~323.7	0.14	[34]
AgNWs modified glassy carbon electrode (AgNWs/GCE)	0.6~32	0.05	[35]
reduced graphene oxide modified glassy carbon electrode	50~800	42	[36]
TLISS/GCE	1.43~55.93 55.93~553.7	1.09	This work

3.5 Practical applicability

The applicability in real sample analysis of the as-prepared TLISS/GCE was evaluated by using tap water and river water. No 4-NP was present in these water samples before the analysis, and the standard addition method was applied. The concentration of 4-NP was measured by the DPV method. The as-prepared TLISS/GCE showed good recoveries, ranging from 94.97% (RSD 2.325%) to 103.06% (2.196%) (Table 2). The obtained recovery range indicated that the developed TLISS/GCE fabrication and optimized protocol could be applied to 4-NP determination in real waters.

Table 2. Analytical results obtained from the analysis of real water samples using the proposed method.

Samples	Add (µM)	Found (µM)	Recovery (%)	RSD (%)
Tap water	7.85	8.09	103.06	2.196
River water	1.99	1.89	94.97	2.325

4. CONCLUSION

Tremella-like indium silver sulfide was successfully synthesized by a simple co-precipitation method. A voltammetric sensor for 4-NP based on indium silver sulfide modified glass carbon electrode has been developed. The indium silver sulfide was modified onto the GCE by a drop-cast method, and the modified GCE exhibited high sensitivity and a low detection limit for the selected determination of 4-nitrophenol by an electrochemical approach at 298 K. The prepared indium silver sulfide modified GCE sensor could effectively detect 4-NP at a low detection limit (1.09 µM) and large linear-dynamic range (1.43~55.93 µM, 55.93~553.7 µM). Furthermore, this electrode exhibited satisfactory analytical results during the detection of 4-NP in tap and river waters, indicating its high potential in practical applications.

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References

1. B. M. Hryniewicz, E. S. Orth, M. Vidotti, *Actuat. B-Chemical.*, 257 (2018) 570.
2. L. Chen, L. Ji, J. Zhao, X. Zhang, F. Yang, J. Liu, *J. Electroanal. Chem.*, 801 (2017) 300.
3. G. G. Gerent, A. Spinelli, *J. Hazard. Mater.*, 330 (2017) 105.
4. A. M. Noor, P. Rameshkumar, N. Yusoff, H. N. Ming, M. S. Sajab, *Ceram. Int.*, 42 (2016), 18813.
5. K. Giribabu, Y. Haldorai, M. Rethinasabapathy, S. C. Jang, R. Suresh, W. S. Cho, Y. K. Han, C. Roh, Y. S. Huh, V. Narayanan, *Curr. Appl. Phys.*, 17 (2017) 1114.
6. F. Qu, P. Chen, S. Zhu, J. You, *Spectrochim. Acta* A, 171 (2017) 449.
7. A. Escarpa, M. D. Morales, M. C. González, *Anal. Chim. Acta*, 460 (2002) 61.
8. A. Almási, E. Fischer, P. Perjési, *J. Biochem. Bioph. Meth.*, 69 (2006) 43.
9. M. Amjadi, T. Hallaj, *J. Lumin.*, 171 (2016) 202.
10. Q. Zhang, M. Lei, J. Zhang, Y. Shi, *J. Lumin.*, 180 (2016) 287.
11. T. Li, Y. Shao, S. Zhang, J. Qin, L. Fan, L. Liu, B. Wang, Z. Yang, Y. Wang, *J. Lumin.*, 181 (2017) 345.
12. N. I. Ikhsan, P. Rameshkumar, N. M. Huang, *Electrochim. Acta*, 192 (2016) 399.
13. D. R. Kumar, S. Kesavan, M. L. Baynosa, J. J. Shim, *Electrochim. Acta*, 246 (2017) 1131.
14. S. Mu, *J. Electroanal. Chem.*, 743 (2015) 31.
15. A. Khan, A. A. P. Khan, M. M. Rahman, A. M. Asiri, Inamuddin, K. A. Alamry, S. A. Hameed, *Appl. Surf. Sci.*, 433 (2018) 696.
16. B. Thirumalraj, C. Rajkumar, S. M. Chen, K. Y. Lin, *J. Colloid Interf. Sci.*, 499 (2017) 83.
17. C. Li, Z. Wu, H. Yang, L. Deng, X. Chen, *Sensor. Actuat. B-Chem.*, 251 (2017) 446.
18. C. Yao, H. Sun, H. F. Fu, Z. C. Tan, *Electrochim. Acta*, 156 (2015) 163.
19. X. Xu, Z. Liu, X. Zhang, S. Duan, S. Xu, C. Zhou, *Electrochim. Acta*, 58 (2011) 142.
20. T. Zhang, Q. Lang, D. Yang, L. Li, L. Zeng, C. Zheng, T. Li, M. Wei, A. Liu, *Electrochim. Acta*. 106 (2013) 127.
21. C. H. Wang, K. W. Cheng, C. J. Tseng, *Sol. Energ. Mat. Sol.* C., 95 (2011) 453.
22. S. Lugo, Y. Pena, M. C. Rodriguez, C. López-Mata, M. L. Ramón, I. Gómez, A. Acosta, *Appl. Surf. Sci.*, 263 (2012) 440.
23. C. Cai, L. Zhai, Y. Ma, C. Zou, L. Zhang, Y. Yang, S. Huang, *J. Power Source.*, 341(2017), 11.
24. J. Lv, X. Liang, *Opt. Mater.*, 72 (2017) 805.
25. F. deng, F. Zhong, D. Lin, L. Zhao, Y. Liu, J. Huang, X. Luo, S. Luo, D. D. Dionysiou, *Appl. Catal. B-Environ.*, 219 (2017) 163.
26. Y. Liu, M. Deng, T. Zhu, X. Tang, S. Han, W. Huang, Y. Shi, A. Liu, *J. Lumin*. 192(2017), 547.
27. M. A. Sunil, J. Nagaraju, G. M. Rao, *Surfaces and Interfaces.*, 10 (2018) 45.
28. Xin Zhang, Youli Wei, Yaping Ding, *Analytica Chimica Acta.*, 835(2014), 29.
29. P. Wiench, B. Grzyb, Z. González, R. Menéndez, B. Handke, G. Gryglewicz, *J. Electroanal. Chem.*, 787 (2017) 80.
30. L. Chu, L. Han, X. Zhang, *J. Appl. Electrochem.*, 41 (2011) 687.
31. A. Arvinte, M. Mahosenaho, M. Pinteala, A. M. Sesay, V. Virtanen, *Microchim Acta.*, 174 (2011) 337.
32. S. Lupu, C. Lete, M. Marin, N. Totir, P. C. Balaure, *Electrochim. Acta.*, 54 (2009) 1932.
33. K. A. Zeynali, E. Delnavaz, *J. Iran. Chem. Soc.*, 14 (2017) 2229.
34. S. H. Hu, C. L. Xu, G. P. Wang, D. F. Cui, *Talanta*, 54 (2001) 115.

35. C. Zhang, S. Govindaraju, K. Giribabu Y. S. Huh, K. Yun, *Sensor Actuat. B-Chem.*, 252 (17) 616.
36. P. Wiench, B. Grzyb, Z. González, R. Menéndez, B. Handke, G. Gryglewicz, *J. Electroanal. Chem.*, 787 (2017) 80.