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Sensitive electrochemical sensor of tryptophan based on Ag@C core–shell nanocomposite modified glassy carbon electrode

Shuxian Mao, Weifeng Li*, Yumei Long*, Yifeng Tu, Anping Deng

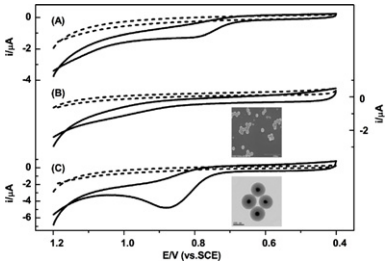
College of Chemistry, Chemical engineering and Materials Science, Soochow University, Suzhou 215123, China

HIGHLIGHTS

- The electrochemical behavior of Ag@C core–shell nanocomposite was firstly proposed.
- Ag@C/GC electrode exhibited favorable electrocatalytic properties towards Trp.
- The good electrocatalysis was due to the synergistic effect of Ag-core and C-shell.
- The Ag@C/GC electrode displayed excellent analytical properties in determining Trp.

GRAPHICAL ABSTRACT

Ag@C and Colloidal carbon sphere modified glassy carbon electrodes were prepared. It was clear that the Ag@C/GCE exhibited enhanced electrocatalytic activity towards Trp, which could result from the synergistic effect between Ag core and carbon shell. The Ag@C/GCE showed excellent analytical properties in the determination of Trp.



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ABSTRACT

We here reported a simple electrochemical method for the detection of tryptophan (Trp) based on the Ag@C modified glassy carbon (Ag@C/GC) electrode. The Ag@C core–shell structured nanoparticles were synthesized using one-pot hydrothermal method and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), and Fourier transform-infrared spectroscopy (FTIR). The electrochemical behaviors of Trp on Ag@C/GC electrode were investigated and exhibited a direct electrochemical process. The favorable electrochemical properties of Ag@C/GC electrode were attributed to the synergistic effect of the Ag core and carbon shell. The carbon shell cannot only protect Ag core but also contribute to the enhanced substrate accessibility and Trp-substrate interactions, while nano-Ag core can display good electrocatalytic activity to Trp at the same time. Under the optimum experimental conditions the oxidation peak current was linearly dependent on the Trp concentration in the range of 1.0×10^{-7} to 1.0×10^{-4} M with a detection limit of 4.0×10^{-8} M (S/N = 3). In addition, the proposed electrode was applied for the determination of Trp concentration in real samples and satisfactory results were obtained. The technique offers enhanced sensitivity and may trigger the possibilities of the Ag@C nanocomposite towards diverse applications in biosensor and electroanalysis.

1. Introduction

In the last decades, electrochemical techniques have been the most attractive methods for the determination of amino acids due to their favorable properties, such as high sensitivity, accuracy, easy operation and low cost [1–3]. However, the voltammetric response of electrochemical process is not satisfactory because of slow heterogeneous electron transfer at the electrode surface and consequent high overpotentials of the electrochemical oxidation [4,5]. Therefore, one of main challenges in this field is to get the suitable materials for electrode modification that will enhance the direct electron transfer between the electrode and redox molecule.

* Corresponding authors. Tel.: +86 512 65880089; fax: +86 512 65880089.
E-mail addresses: liweifeng@suda.edu.cn (W. Li), yumeilong@suda.edu.cn (Y. Long).

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Silver has the highest electrical conductivity among all metals and is probably the most important material in plasmonics [6]. However, Ag nanostructures are considered to be toxic and instable [7]. It is well established that applying a coating of different material can eliminate the reactivity and toxicity of nano-Ag [6,8]. The core–shell heteronanostructure is one of the significant systems for its enhanced properties from core to shell components and their synergy, which are promising for potential applications as electrocatalysts, drug delivery and fluorescent biological labels [9–12]. Recently, carbonaceous shell has attracted much attention due to its low preparation cost, chemical activity [13], and biocompatibility [14]. Carbon coating cannot only increase the core particle stability with a subsequent increase in catalytic properties, biocompatibility, and non-toxicity [15–17], but also allow interface functionalization to load other functional molecules for bio-analysis. In particular, the synthesis of Ag@C nanoparticles is convenient [18,19] and Ag nanoparticles encapsulated by carbonaceous shell already exhibit potential applications as plasmonic photocatalyst [20]. However, the electrocatalytic properties of Ag@C nanocomposites and its application in electrochemistry have not been reported yet.

Trp is a vital constituent of proteins and indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [21]. Especially, the improper metabolization of Trp can create a waste product in the brain and cause hallucinations and delusions [22]. Therefore, it is of great significance to develop a simple, accurate, rapid and inexpensive method for the determination of Trp and some works have been reported [1,23–28].

In the present work, Ag@C nanocomposite has been synthesized through hydrothermal method and the resulting nanocomposite can be used as a new modified electrode material. The Ag@C/GC electrode demonstrates favorable electrocatalytic activities in the oxidation towards Trp, thereby the concentrations of Trp in real samples are determined and the satisfying results are obtained.

2. Experimental

2.1. Materials

Trp and other amino acids, ascorbic acid (AA), uric acid (UA) and dopamine were obtained from Sangon Biotech Co. Ltd. (Shanghai, China). Amino acid injection (18 AA, Lot No. 110908M5) was brought from Anhui Fengyuan Pharmaceutical Co., Ltd., China. A rat blood serum sample was obtained from Medical College of Soochow University. All other reagents were of analytical grade and used without further purification. The phosphate buffer solution (PBS, 0.1 M, pH 2.0) was chosen as the supporting electrolyte and doubly distilled water was used throughout the experiment.

2.2. Instrumentation

Electrochemical measurements were performed on a CHI611D electrochemical workstation (Chenhua Instruments Co., Shanghai, China). The measurements were based on a conventional three-electrode system, which includes the Ag@C/GC electrode as working electrode, a platinum electrode as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode, respectively. All measurements were carried out in PBS at room temperature ($25 \pm 2\,^{\circ}C$). Electrochemical impedance spectroscopy (EIS) was performed on a RST5000 electrochemical workstation (Suzhou Risetest Instrument Co. Ltd., China) in a background solution of 0.1 M KCl containing 1.0×10^{-3} M $[Fe(CN)_6]^{3-/4-}$.

The Ag@C core–shell nanocomposites were characterized by scanning electron microscope (SEM, Hitachi s-4700), TEM (FEI Tecnai G20, an acceleration voltage of 200 kV), and FTIR spectroscopy (Prostar LC240).

2.3. Procedures

Ag@C nanocomposites were synthesized by hydrothermal method [18]. 4 g of glucose was dissolved in 38 mL of doubly distilled water. Next 2 mL of $AgNO_3$ aqueous solution (0.03 M) was dropwise added into the above-mentioned solution under vigorous stirring. The mixture was stirred for another 10 min and then transferred to a Teflon-lined autoclave (50 mL in volume) and hydrothermally treated at 180 °C for 4 h. After reaction, the autoclave was cooled to room temperature. The suspension was centrifuged at 6000 revolutions per minute (rpm) for 20 min and the resulting products cleaned by four cycles of centrifugation/washing/re-dispersion in water and in ethanol. Colloidal carbon sphere (CCS) was prepared following a similar procedure in the absence of $AgNO_3$. Finally, the as prepared products were dried at 60 °C overnight.

Before coating, GC electrode (3 mm in diameter) was polished using 1.0-, 0.3- and 0.05-μm alumina slurries in sequence, washed with doubly distilled water and ethanol. The electrode was pretreated electrochemically in 1.0 M H_2SO_4 aqueous solution by potential cycling ranged from −1.0 to 1.0 V at a scan rate of 50 mV s^{-1} until a stable cyclic voltammogram was obtained. After that, 10 μL of Ag@C ethanol suspension was dropped on the pretreated GC electrode surface and dried at room temperature to form Ag@C modified GC electrode. For comparison, the CCS/GC electrode was also prepared with the same procedure.

3. Results and discussion

3.1. Characterization of the Ag@C nanocomposites

The detailed structure of the Ag@C nanocomposites revealed by SEM, TEM and FTIR is shown in Fig. 1A–D. SEM micrographs show that the spherical particles are the primary product for the colloidal carbon (Fig. 1A) and hybrid Ag@C composite (Fig. 1B) samples. Both samples have similar particle size from 200 nm to 400 nm. TEM image shown in Fig. 1C clearly demonstrates the core/shell structure of Ag@C nanocomposite, which has the Ag core with diameters in the range of 50–80 nm and carbon shell with thickness about 100 nm. Fig. 1D shows the FTIR spectra of the Ag@C and CCS, which can clearly identify the functional groups present after hydrothermal treatment. The signature peaks at about 1710 and 1620 cm^{-1} correspond to C=O and C=C vibrations, respectively, which results from the aromatization of glucose during the hydrothermal treatment. The absorption band ranging from 1000 cm^{-1} to 1300 cm^{-1} is ascribed to the C—OH stretching and OH bending vibrations, which suggests the existence of large numbers of residual hydroxyl groups. Partially dehydrated residues in which reductive OH and CHO are covalently bonded to the carbon frameworks improve the hydrophilicity and stability of the nanospheres in aqueous systems, and greatly widen their potential applications in biochemistry, diagnostics, and drug delivery [19]. These functional groups outside can enhance the immobility of the Ag@C composites on the GC electrode and increase the absorption to the polar molecules.

3.2. Voltammetric response of Trp on Ag@C/GC electrodes

The electrochemical behaviors of Ag@C/GC electrode are evaluated using cyclic voltammogram (CV) to investigate their response to Trp. Fig. 2A presents the CVs of bare GC (a), CCS/GC (b) and Ag@C/GC (c) electrodes in PBS with and without 1.0×10^{-4} M Trp at a scan rate of 50 mV s^{-1}. It can be seen that no peak can be found in the absence of Trp for all electrodes (dot lines). On the other

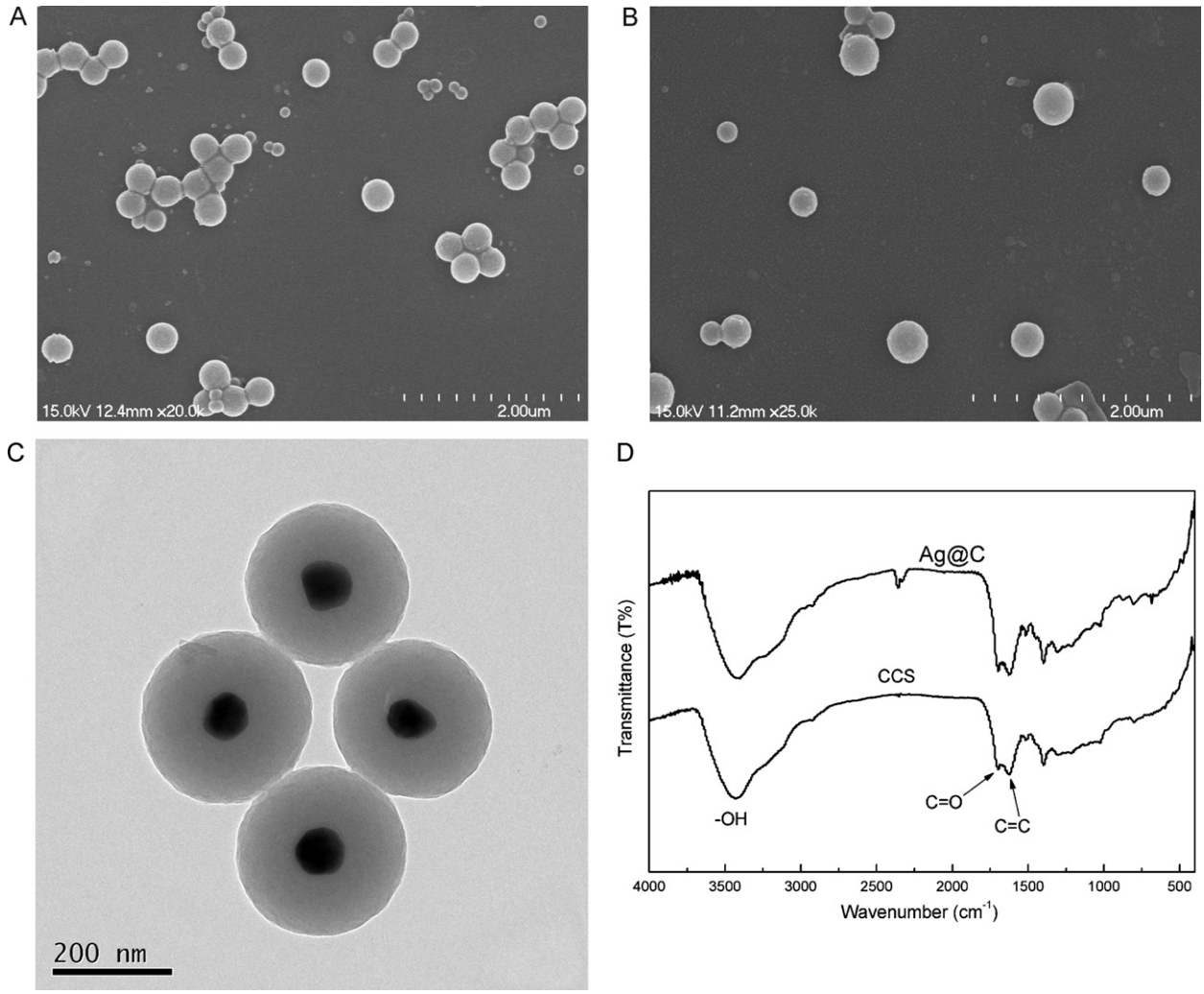

Fig. 1. SEM micrographs of (A) colloidal carbon sphere and (B) Ag@C nanoparticles, (C) TEM image and (D) FTIR of the Ag@C nanocomposite.

hand, one stable oxidation peak occurs in the potential range of 0.4–1.1 V with the introduction of Trp (solid lines), which reveals that the electrocatalytic activities is not from the electrode materials but Trp and Trp undergoes an irreversible redox process at the electrodes. In the case of the bare GC electrode, the oxidation peak of Trp is about +0.797 V (a). However, the oxidation peak is absent by the modification of CCS and the background current of the CCS/GC electrode increases (b). The phenomena show that the CCS could suppress the electrocatalysis effect of the electrode to Trp but increase the surface roughness. It should be noted that the oxidation peak shifts to +0.876 V using the Ag@C/GC electrode and the oxidation peak current is much higher (4.5-fold) than that of the bare GC electrode (c). The amplified signal can be attributed to the following factors. Firstly, charged functional groups outside the Ag@C could easily adsorb and accumulate Trp on the electrode surface via the electrostatic interaction, providing opportunities for enhanced substrate accessibility and Trp–substrate interactions. Secondly, the carbon shell can protect the nano-Ag core and make the system stable. Finally, nano-Ag core can maintain its excellent catalytic performance in the Ag@C system [20] and the high electrical conductivity of silver would favor the transfer of electrons. Therefore, it is expected that the Ag@C/GC electrode could exhibit an efficient electrocatalytic response towards Trp.

The EIS is an efficient tool to probe the features of surface-modified electrode. The electron transfer resistance of the electrochemical reaction, R_{et}, corresponds to the semicircle diameter of the Nyquist plot of $-Z''$ against Z' and it reveals the electron transfer kinetics of the redox electrochemical probe at the electrode interface. Fig. 2B shows impedance spectra on a bare GC electrode (a), a CCS/GC electrode (b) and an Ag@C/GC (c) electrode, respectively. It can be seen that the R_{et} of the CCS/GC electrode (curve b) is much larger than that of the bare GC electrode (curve a), indicating that the CCS could self-assemble on the electrode surface and hindered the electron transfer from the redox probe, $[Fe(CN)_6]^{3-/4-}$, to the electrode surface. On the other hand, R_{et} of the Ag@C/GC electrode (curve c) significantly decreases compared to the CCS/GC electrode (curve b), attributing to the excellent conductivity of nano-Ag core.

3.3. Influence of scan rate on the voltammertric response of Trp

It has been well established that the electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Fig. 3 shows the cyclic vlotammograms of the Ag@C/GC electrode in the presence of 1.0×10^{-4} M Trp in PBS at different scan rates. As can be seen, the oxidation peak current (I_{pc}) increases linearly with the square root of the of the scan rates (inset of Fig. 3), suggesting that the electrocatalytic oxidation reaction of Trp on the Ag@C/GC electrode is a diffusion-controlled process. The linear regression equation is $I_{pc}\,(\mu A) = 1.1478 - 0.753\nu^{1/2}$ $(mV\,s^{-1})^{1/2}$ with a correlation coefficient of $R = 0.995$. In addition, the peak potential shifts positively in response to the increase of

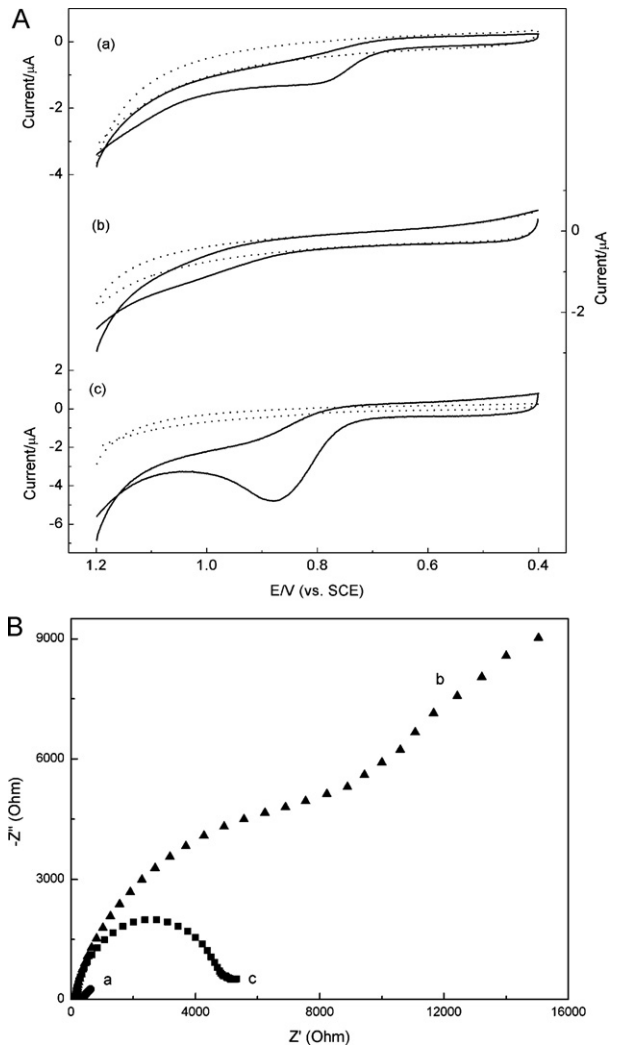

Fig. 2. (A) Cyclic voltammograms of (a) bare GC, (b) CCS/GC and (c) Ag@C/GC electrodes in PBS with (solid line) and without (dot line) 1.0×10^{-4} M Trp. Scan rate, 50 mV s^{-1}. (B) Electrochemical impedance spectra of (a) bare GC, (b) CCS/GC and (c) Ag@C/GC electrodes.

the scan rate. The resulting regression is $E_{pa} = 0.7954 + 0.0703 \log \upsilon$ ($R = 0.998$). According to Laviron's equation, the slope is equal to $2.303RT/\alpha n_\alpha F$. As for a totally irreversible electrode process, α can be assumed as 0.5, and thus the electron transfer number (n_α) is calculated to be 2.06. This result suggests that two electrons are involved in the oxidation process of Trp at the Ag@C/GC electrode and the electrochemical reaction equation can be expressed as in Fig. 4 [26].

3.4. Effect of pH values

The effect of pH on the electrochemical responses of Trp at Ag@C/GC electrode has been examined with 1.0×10^{-4} M Trp in 0.1 M PBS. Plot of peak current against pH over the range of 1.0–8.0

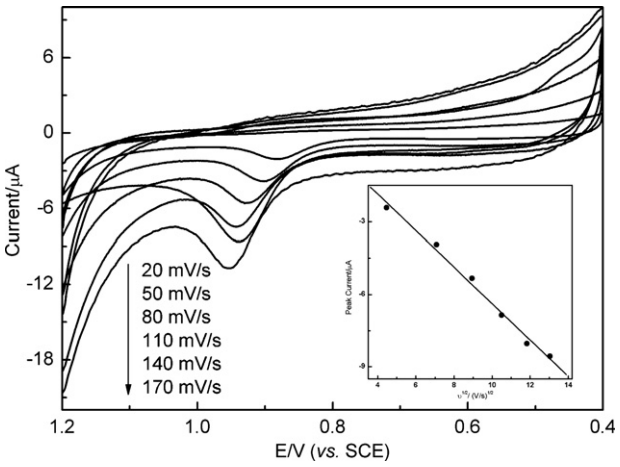

Fig. 3. Cyclic voltammograms of 1.0×10^{-4} M Trp in PBS on Ag@C/GC electrode at different scan rates: 20, 50, 80, 110, 140, 170 mV s^{-1}. (Inset) The oxidation peak current of Trp vs. the square root of the scan rate.

are shown in Fig. 5. It is clear that a maximum in peak current can be observed at pH 2.0. However, the oxidation peak current gradually decreases when the pH increases further from 2.0 to 8.0. It may be the fact that pH could influence the charge property and charge density of Trp and Ag@C. As a result, the electrostatic interaction between Trp and carbon shell increases. Therefore, the pH of 2.0 was chosen for the subsequent analytical experiments.

3.5. Analytical applications

Linear sweep voltammetry (LSV) of Trp on Ag@C/GC electrode at different concentrations are shown in Fig. 6. As can be seen, the LSV peak currents increase linearly with Trp concentration. The inset of Fig. 6 shows the linear calibration curve for the detection of Trp using Ag@C/GC electrode and the linear range is from 1.0×10^{-7} to 1.0×10^{-4} M with a detection of 4.0×10^{-8} M (S/N = 3). The linear regression equation is expressed as I_{pc} (μA) = −0.4725 − 51691C (M) with a correlation coefficient of 0.998.

Under the optimized experiment conditions described above, the possible interferences for Trp (1.0×10^{-5} M) determination at the Ag@C/GC electrode have been investigated. Eight essential amino acids (100 times content), including cysteine, lysine, valine, leucine, serine, threonine, histidine and isoleucine, have no influence on the current response for Trp. It is also found that 10-fold concentration of AA, UA and dopamine cannot interfere with the determination of Trp at Ag@C/GC electrode. The results suggest the Ag@C/GC electrode possesses high selectivity for the detection of Trp.

The utilization of the proposed method in real samples is assessed by the analysis of Trp in amino acid injection and in rat blood serum using the standard addition method. Before they are analyzed, the injection sample is diluted 10-fold and the blood serum is diluted 20-fold with 0.1 M PBS (pH 2.0). The results are presented in Table 1. As can be seen, the obtained recoveries are in the range of 97–104%, suggesting that the proposed method is

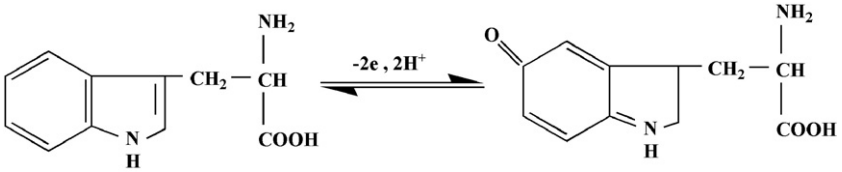

Fig. 4. Scheme of the electrochemical reaction process for Trp on Ag@C/GC electrode.

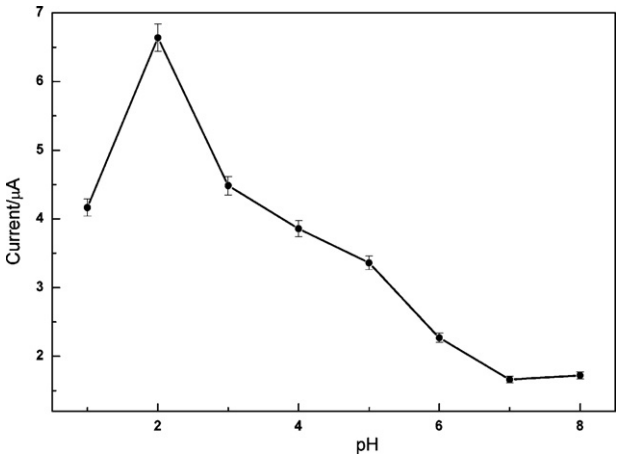

Fig. 5. The dependence of the oxidation peak current on pH values with 1.0×10^{-4} M Trp in 0.1 M PBS. Scan rate: 50 mV s^{-1}.

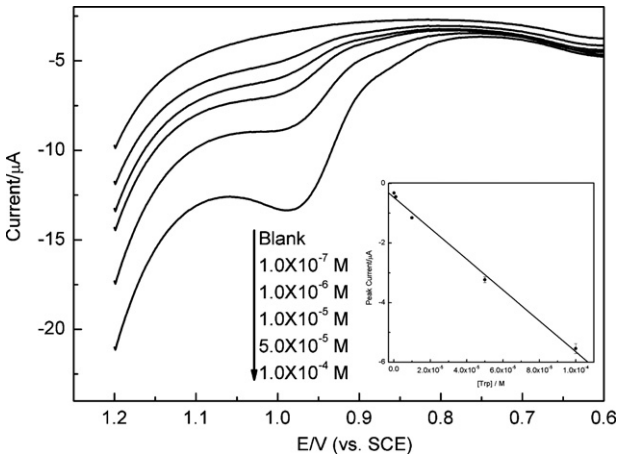

Fig. 6. LSVs recorded on Ag@C/GC electrode in PBS containing different concentrations of Trp (1.0×10^{-7}, 1.0×10^{-6}, 1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} M). Scan rate: 50 mV s^{-1}. (Inset) Linear relationship between peak current and Trp concentration.

selective for Trp and can be successfully developed for the assay of Trp in real samples. The specific features of Ag@C/GC electrode for detecting Trp are listed in Table 2. It can be seen that the Ag@C/GC electrode exhibits reasonable linear range and lower detection limit compared with some of previous reports.

3.6. Electrochemical sensor reproducibility and stability

The operational stability of the Ag@C/GC electrode has been assessed by consecutive measurements of a 1.0×10^{-4} M Trp sample. The relative standard deviation is 3.9% for 10 measurements. In addition, five Ag@C/GC electrodes prepared independently but following the same fabrication protocol is used to determine 1.0×10^{-4} M Trp. All five electrodes exhibit similar amperometric responses and a relative standard deviation is 4.1%. These experimental results indicate the proposed electrochemical sensor possesses a good reproducibility. The long-term stability of the Ag@C/GC electrode has also been studied. The Ag@C/GC electrode retains 93% of its initial activity after 1 month, demonstrating high stability. The good stability and reproducibility of the Ag@C/GC electrode could result from the rich functional groups on the surface of carbon shell, which is helpful for the attachment of Ag@C onto the GC electrode via the electrostatic interaction.

Table 1
Determination of Trp in pharmaceutical sample and rat blood matrix.

Sample	Added (μM)	Founded (μM)[a]	Recovery (%)
Amino acid injection	0.0	9.9 (±0.1)	–
	0.3	10.0 (±0.2)	97.3
	0.6	10.4 (±0.2)	98.8
	1.0	11.4 (±0.1)	103.8
Rat blood serum	0.0	0.0	–
	5.0	5.2 (±0.2)	104.0
	10.0	15.2 (±0.1)	101.3
	15.0	29.6 (±0.3)	98.7

[a] Mean values ± standard deviations ($n = 3$).

Table 2
Comparison of electrochemical methods for determining Trp.

Method	Detection limit (mol L^{-1})	Linear range (mol L^{-1})	References
Ni(II)/ACDA-AuNP-Au	2.3×10^{-8}	8.5×10^{-8} to 4.3×10^{-5}	[1]
β-CD-MNPs/GCE	5.0×10^{-7}	8.0×10^{-7} to 3.0×10^{-4}	[23]
AuNP/GCE	8.0×10^{-8}	9.0×10^{-8} to 5.0×10^{-5}	[24]
TiO_2/GCE	7.0×10^{-7}	5.0×10^{-6} to 1.4×10^{-4}	[25]
4-ABA/GCE	2.0×10^{-7}	1.0×10^{-6} to 1.0×10^{-4}	[26]
AuNP-MWNT/ITO	2.5×10^{-8}	5.0×10^{-7} to 9.0×10^{-5}	[27]
AuNP-CNT/GCE	1.0×10^{-8}	3.0×10^{-8} to 2.5×10^{-6}	[28]
Ag@C/GCE	4.0×10^{-8}	1.0×10^{-7} to 1.0×10^{-4}	Present work

ACDA: 2-amino-1-cyclopentene-1-dithiocarboxylic acid; β-CD-MNPs: β-cyclodextrin functionalized Fe_3O_4 magnetic nanoparticles; 4-ABA: poly(4-aminobenzoic acid).

4. Conclusions

We demonstrated that Ag@C could be a potential electrode modification nanocomposite. The electrochemical experiments proved that Ag@C/GC electrode not only shows a fast direct electron transfer but also displays good electrocatalytic response to Trp. The good electrochemical performance of Ag@C/GC electrode should be related to the rich functional groups on the carbon shell and the enhanced electron transfer resulting from nano-silver core. Therefore, Ag@C might provide a new promising platform for further study on the direct electrochemistry of other redox bio-molecules. The method described here is simple, rapid, sensitive and selective. In addition, the proposed sensor was also employed for the determination of Trp in the real samples with reproducible results.

Acknowledgments

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References

[1] M.B. Gholivand, A. Pashabadi, A. Azadbakht, S. Menati, Electrochim. Acta 56 (2011) 4022–4030.
[2] S. Szunerits, Y. Coffinier, E. Galopin, J. Brenner, R. Boukherroub, Electrochem. Commun. 12 (2010) 438–441.
[3] C.Y. Deng, J.H. Chen, X.L. Chen, M.D. Wang, Z. Nie, S.Z. Yao, Electrochim. Acta 54 (2009) 3298–3302.
[4] A. Babaei, M. Zendehdel, B. Khalilzadeh, A. Taheri, Colloids Surf. B: Biointerfaces 66 (2008) 226–232.
[5] P.J. Vandeberg, D.C. Johnson, Anal. Chem. 65 (1993) 2713–2718.

[6] M. Rycenga, C.M. Cobley, J. Zeng, W.Y. Li, C.H. Moran, Q. Zhang, D. Qin, Y.N. Xia, Chem. Rev. 111 (2011) 3669–3712.
[7] L. Li, J. Sun, X.R. Li, Y. Zhang, Z.X. Wang, C.R. Wang, J.W. Dai, Q.B. Wang, Biomaterials 33 (2012) 1714–1721.
[8] D.V. Goia, E. Matijevic, New J. Chem. 22 (1998) 1203–1215.
[9] X.Y. Lai, J. Li, B.A. Korgel, Z.H. Dong, Z.M. Li, F.B. Su, J. Du, D. Wang, Angew. Chem. Int. Ed. 50 (2011) 2738–2741.
[10] J. Ahmed, A. Ganguly, S. Saha, G. Gupta, P. Trinh, A.M. Mugweru, S.E. Lofland, K.V. Ramanujachary, A.K. Ganguli, J. Phys. Chem. C 115 (2011) 14526–14533.
[11] Z.G. Gu, S.P. Yang, Z.J. Li, X.L. Sun, G.L. Wang, Y.J. Fan, J.K. Liu, Electrochim. Acta 56 (2011) 9162–9167.
[12] M.L. Pang, J.Y. Hu, H.C. Zeng, J. Am. Chem. Soc. 132 (2010) 10771–10785.
[13] A. Stein, Z.Y. Wang, M.A. Fierke, Adv. Mater. 21 (2009) 265–293.
[14] S.R. Guo, J.Y. Gong, P. Jiang, M. Wu, Y. Lu, S.H. Yu, Adv. Funct. Mater. 18 (2008) 872–879.
[15] G.B. Yu, B. Sun, Y. Pei, S.H. Xie, S.R. Yan, M.H. Qiao, K.N. Fan, X.X. Zhang, B.N. Zong, J. Am. Chem. Soc. 132 (2010) 935–937.
[16] Y. Wang, H.J. Zhang, L. Lu, L.P. Stubbs, C.C. Wong, L. Lin, ACS Nano 4 (2010) 4753–4761.
[17] V.R. Galakhov, A.S. Shkvarin, A.S. Semenova, M.A. Uimin, A.A. Mysik, N.N. Shchegoleva, A.Y. Yermakov, E.Z. Kurmaev, J. Phys. Chem. C 114 (2010) 22413–22416.
[18] X.M. Sun, Y.D. Li, Langmuir 21 (2005) 6019–6024.
[19] X.M. Sun, Y.D. Li, Angew. Chem. Int. ed. 43 (2004) 597–601.
[20] S.M. Sun, W.Z. Wang, L. Zhang, M. Shang, L. Wang, Catal. Commun. 11 (2009) 290–293.
[21] M.H. Fernstrom, J.D. Fernstrom, Life Sci. 57 (1995) 97–102.
[22] W. Kochen, H. Steinhart, L-Tryptophan – Current Prospects in Medicine and Drug Safety, de-Gruyter, Berliin, 1994.
[23] H.X. Wang, Y.H. Zhou, Y.J. Guo, W.J. Liu, C. Dong, Y.H. Wu, S.D. Li, S.M. Shuang, Sens. Actuators B: Chem. 163 (2012) 171–178.
[24] C.Y. Li, Y. Ya, G.Q. Zhang, Colloids Surf. B: Biointerfaces 76 (2010) 340–345.
[25] Y. Fan, J.H. Liu, H.T. Lu, Q. Zhang, Microchim. Acta 173 (2011) 241–247.
[26] K.J. Huang, C.X. Xu, W.Z. Xie, W. Wang, Colloids Surf. B: Biointerfaces 74 (2009) 167–171.
[27] R.N. Goyal, S. Bishnoi, H. Chasta, M.A. Aziz, M. Oyama, Talanta 85 (2011) 2626–2631.
[28] Y.J. Guo, S.J. Guo, Y.X. Fang, S.J. Dong, Electrochim. Acta 55 (2010) 3927–3931.