In-situ growth of Cu@CuFe Prussian blue based core-shell nanowires for non-enzymatic electrochemical determination of ascorbic acid with high sensitivity and reusability

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**ABSTRACT**

Ascorbic acid (AA) is an important deoxidizer contained in food, drink and medicine. However, existing detection methods are time-consuming and complex to industrial production and quality testing. Here, we proposed a core-shell nanowires constructed electrochemical sensor to achieve the highly sensitive and selective recognition of AA with a long-term reusability. Cu nanowires with 30 nm diameter were served as both structure skeleton and reactant to induce in-situ growth of Cu-Fe Prussian blue layer with 10 nm thickness covering its surface to form a core-shell architecture. This nanocomposite couples advances of Cu and Prussian blue to possess both high electrocatalysis and conductivity. The as-prepared sensor shows an excellent sensitivity with an ultrawide linear range, together with the remarkable reusable ability during 30 days with 300 times of repetitive detection. Used for four kinds of juice and bear as real samples, this sensor can accurately report AA concentration within 5 s.

1. Introduction

Ascorbic acid (AA), also known as vitamin C, is a non-toxic and mild antioxidant attributed to the reductive enediol group in its molecules [1]. It has been wildly applied as the deoxidizer to inhibit the enzymatic browning of fruit and vegetables, passivate metal ions and cure the sepsis, as well as a common additive in drink to keep flavor and color to prolong the fresh period [2,3]. The worldwide demand of AA has reached more than 200,000 tons per year to produce economy value beyond 1500 million dollars. Currently, the main production technology of AA is “Two-step fermentation” method [4]. It uses high-pressure hydrogenation of glucose to first obtain sorbitol, and then uses black vinegar bacteria to ferment sorbitol into sorbose. After that, the second step is carried out to extract gulonic acid from the fermentation broth to generate sodium salt of AA, and then purify to obtain AA. In this process, the monitor of AA content is essential to evaluate the equilibrium transformation of both fermentation and chemical reactions for the process control to determine the conversion rate and product quality [5]. At present, the popular test methods of AA in industry are UV–Vis spectrophotometry [6], mass spectroscopy [7] and chromatography [8]. However, UV–Vis spectrophotometry will be easily interfered by the colority and turbidity of samples to affect its accuracy. The test periods of mass spectroscopy and chromatography are time-consuming and limited by the highly cost instruments to hardly achieve in-situ and online detection.

To address above issues, the electrochemical sensor is attracting more and more attentions to propose various rapid and accurate strategies for the quantitative recognition of AA in the last decade [9-11]. Among them, there are mainly two kinds of detection principles based on the enzymatic reaction and non-enzymatic catalysis. The work of enzymatic AA sensor relies on the ascorbate oxidase (AOX) to oxidize AA to produce the response signal associated with the concentration [12,13]. Although using AOX enables to ensure the selectivity due to its high specificity, this enzyme protein is easy to lose activity caused by the temperature, composition of testing system and storage condition [14]. Therefore, repetitive use of the enzymatic sensor is a main challenge to the practical application in the industrial production. Another sensing route of non-enzymatic catalysis can effectively solve this deficiency [15-18], which directly oxidize L-Ascorbic acid \((\text{C}_6\text{H}_8\text{O}_6)\) to generate Dehydro-l-ascorbic acid \((\text{C}_6\text{H}_7\text{O}_5)\) and the detection signal by the positive potential without the assistance of enzymes. Its reaction mechanism is described as following equation:

\[
\text{C}_6\text{H}_7\text{O}_5^- \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2e^-
\]  

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This kind of sensor is of higher sensitivity and stability than the enzymatic sensor, however, its low selectivity is always an obstacle due to the oxidation of other co-existences in system to produce obvious interfering signal [19]. Therefore, a high-performance electrode material with both excellent selectivity and repetitive stability is desired to construct a non-enzymatic AA sensor for the industrial application.

Prussian blue (PB) and its analogues (PBA) are famed by its enzyme-mimic performance in the detection of various physiological indices because of their high electrocatalysis [20]. In this unit cell, there are two kinds of iron atoms with different valances of +2 and +3 to promote the redox ability during sensing, which is beneficial to increase the target signal to noise ratio [21]. However, PB or PBA is a semiconductor with the band gap of ca. 1–2 eV, showing a poor conductivity which will decrease the sensitivity and prolong the response time [22]. Thus, employ of high conductive materials to composite with PBA is often adopted to reduce the resistance of the electrode material. Among these adopted materials, nanostructured Cu is advanced due to its high electron mobility of 32 cm²/(V·s) [23], controllable nanostructure and low cost. Nevertheless, Cu in nanoscale is poor at the chemical stability to easily be oxidized, causing the difficulty in the practical application.

Here we proposed an ultrahigh sensitive and selective electrochemical non-enzymatic AA sensor through constructing a core–shell nano-wire architecture of Cu@CuFe-PBA as the recognizer (as shown in Fig. 1). Cu nanowires with the diameter of 50 nm were first synthesized to serve as the skeleton, and then their surfaces were electrochemically oxidized to produce Cu ions as one of reactants for the further growth of CuFe-PBA (Cu3[Fe(CN)6]2) by an electrodeposition strategy. The in-situ formed PBA shell showing a thickness of 10 nm enables to effectively protect the Cu core during the electrochemical sensing. The as-prepared non-enzymatic sensor exhibits an ultrahigh sensitivity and selectivity for recognizing AA among multiple interfering substances with an outstanding reusing stability beyond 30 days of repetitive detections. Moreover, it also performed accurate and rapid tests of AA in the real juice and bear within 1 min.

2. Experimental

2.1. Reagents and apparatus

Potassium ferricyanide (III) (K3[Fe(CN)6]·3H2O) and D-Glucose were obtained from Sigma-Aldrich. 1-hexadecylamine (HDA) was purchased from Alfa-Aesar. Copper (II) chloride dihydrate (CuCl2·2H2O) and ascorbic acid were acquired from Shanghai Lingfeng Chemical Reagent Co. Ltd. (China). d-Fructose, lactate, glutamate, pyruvate, lysine, phenol and sucrose were provided from Shanghai Macklin Biochemical Co., Ltd. All the chemicals in this work were directly used without further purification. All aqueous solutions were prepared with deionized water (≥18.2 MΩ, Smart2Pure 6, Thermo Fisher Scientific, USA).

A field emission scanning electron microscopy (FESEM) (Hitachi, ModelS-4800II, Japan) and transmission electron microscopy (TEM) (JEOL JEM-2010 UHR) were used to observe the micromorphology of Cu nanowires and Cu@CuFe-PBA. Zeta potential (Zetasizer Nano ZS90, Malvern, UK) was used to characterize the potential change on the surface of the ITO. X-ray diffractometer (XRD) (D/MAX 2500 V/PC) with Cu-Kα radiation (0.15419 nm) was employed to measure the characteristic peaks of Cu nanowires and Cu@CuFe-PBA. X-ray photoelectron spectrometer (XPS) (ESCALAB MKLL) was utilized to analyze the elemental valence states of Cu and Fe.

2.2. Preparation of CuNWs/ITO electrode

The synthesis of the Cu nanowires (CuNWs) follows the reported procedure with minor modification [24–26]. In a typical procedure, 0.17 g CuCl2·2H2O and 0.391 g glucose were added into 80 mL distilled water, after adequate stirring for 30 min, 1.44 g HDA was added to the solution in batches within 5 h. Then the suspension was poured into a stainless steel...
tank and the ITO was immersed to react at 120 °C for 10 h. After the end of the hydrothermal reaction, wait for the hydrothermal kettle to cool to room temperature, took out the CuNWs/ITO electrode and rinsed with deionized water and ethanol 3 times.

2.3. Preparation of Cu@CuFe-PBA/ITO electrode

Cu@CuFe-PBA was in-situ synthesized through electrodeposition method. First, electrodeposition solution was prepared by 5 mM K₃[Fe(CN)₆]·3H₂O, 50 mM KCl and 0.1 M HCl. Then, the CuNWs/ITO electrodes, the Pt wire counter electrode and the Ag/AgCl reference electrode are immersed into the as-prepared electrodeposition solution. The Cu@CuFe-PBA/ITO electrode was formed by cyclic voltammetry (20 cycles between 0 V and 0.6 V at a scan rate of 100 mV/s) electrodeposition. Then the modified electrode was rinsed with distilled water and dried at room temperature.

2.4. Electrochemical measurements

All electrochemical experiments, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronamperometry (IT), were performed with a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). In addition, 0.05 M of phosphate buffer solution (PBS, Ph = 6.8) containing 0.1 M of KCl was used for the electrochemical tests. A conventional three electrode configuration was employed during the experiment. The Cu@CuFe-PBA/ITO electrode, a Pt wire and an Ag/AgCl (saturated KCl) electrode were utilized as the working electrode, counter electrode and reference electrode, respectively.
3. Results and discussion

3.1. Nanostructure evolution of core-shell nanowires

In our design, the core–shell structure is expected to not only protect Cu for avoiding oxidation to enhance stability, but also build an expressway for the electron transfer produced by the electrocatalysis of the PBA shell [21]. Thereby, a nanowire shape of Cu was first prepared to provide a core skeleton for the further coverage of PBA [27]. As shown in Fig. 1, a chemical reduction method was proposed under a hydrothermal environment to realize the in-situ growth of CuNWs on an ITO substrate [28]. In this process, the reaction time was carefully investigated to associate with the morphology evolution. Initially, small nanoparticles presenting a cube-like structure dominated the ITO surface, which accompanying with few nanowires (Fig. 2A). Some evidences have revealed that some Cu crystals preferred to further grow along the axial direction to increase the length-diameter ratio. Then prolonging the reaction time to 5 h, particles and nanowires still coexisted (Fig. 2B), but the amount of nanowires increased obviously. Till 10 h, individual particles can hardly be observed, and lots of nanowires stacked together to obtain a high porosity (Fig. 2C). However, if more nanowires were generated, a dense film would be harvested with reduced porous sites to greatly decrease the surface area [29]. XRD results in Fig. 2E indicates that the intensities of peaks located at 43.2, 50.2 and 73.9° which represent the typical crystal faces of (111), (200) and (220) of Cu obviously increased with the synthesis time. As reported, (111) and (200) is closely related to the radial growth of the wire structure. Hence, the length of the CuNWs gradually grew with the hydrothermal time. However, too long nanowires have caused the excessive stack together. In this case, the morphology of CuNWs prepared at 10 h was selected as the optimum skeleton for the further growth of PBA.

The synthesis rate of PBA is always fast to produce huge amount of crystals, which may result in partial aggregation instead of the coverage of nanowire surface [30]. In order to realize the core–shell structure, the CuNWs were directly served as one of two synthesis reactants of CuFe-PBA (Cu₃[Fe(CN)₆]₂). As shown in Fig. 3A, the prepared CuNWs/ITO electrode was electrochemically oxidized by a DPV treatment between 0 and 0.6 V to transform the Cu simple substance to ions of the nanowire surface in a potassium buffer solution [31]. After 5 repetitive oxidation cycles, the XPS pattern of the electrode showed typical Cu⁺ peaks at 951.67 and 931.87 eV, and Cu²⁺ peaks at 953.98 and 933.87 eV, respectively (Fig. 3B). Moreover, the results of Z potential revealed that the film charge of CuNWs exhibited an obvious difference after this electrochemical treatment. The fresh film presented an always negative surface in various pH values from 5 to 9. However, after the electrochemical oxidation, the surface charge was gradually closer to the positive feature (Fig. 3C). Especially at the neutral environment, the Z potential reached + 4.19 mV, indicating the reversion of the original film charge to positive state attributed to the formation of copper ions [32,33]. The synthesis of CuFe-PBA was designed to adopt following reaction:

$$3\text{Cu}^{2+} + 2[\text{Fe(CN)}_6]^{3-} \rightarrow \text{Cu}_3[\text{Fe(CN)}_6]_2$$

(Fig. 3. (A) DPV scanning curves of the electrochemical oxidation process on CuNWs/ITO. (B) Zeta potential evolution of the Cu and Cu²⁺/ITO surface in different pH environments. (C) XPS spectra of CuNWs after the electrochemical oxidation. (D) XRD patterns of CuNWs and Cu@CuFe-PBA.)
Based on above principle, the positive CuNWs can provide not only Cu\(^{2+}\) ions as one of the synthesis reactants, but also an electrostatic adsorption field to attract [Fe(CN)\(_6\)]\(^{3-}\) ions on the nanowire surface for in-situ crystallization [34], boosting the formation of shell structure. On the contrary, if the electrochemical oxidation was not applied, the negative CuNWs would reject the adsorption of [Fe(CN)\(_6\)]\(^{3-}\) from the charge repulsion to block the shell building of PBA.

The PBA shell was prepared through an electrodeposition method. The positive CuNWs/ITO was first immersed in a buffer solution containing 10 mM K\(_3\)Fe(CN)\(_6\) solution, and then applied CV technique to accelerate the crystallization rate [35]. In this process, the influence of the CV scanning time on the film morphology was investigated according to the samples prepared from 10 to 40 cycles. According to the XRD results (Fig. 3D), the prepared film showed the typical peaks of Cu and PBA to confirm the successful crystallization process on CuNWs. Then the morphology evaluation related to the deposition cycle was further investigated. As shown in Fig. 4A, there were only a few small particles grown on partial sites of some nanowires to show rare evidence of the core–shell structure. If an extra 10 cycles were imposed, different with the smooth CuNWs, a rough surface composed of tiny nanoparticles was observed to cover the whole surface of each nanowire. Meanwhile, the gaps formed by the stack of these CuNWs were still retained. However, when we continued to add the deposition cycle to 30 times, lots of nanocubic crystals with the size of ca. 200 nm were created to form an intergrowth layer which covered almost cavities to hardly distinguish the nanowire structure. Till 40 cycles, this layer had been a dense film to hide all nanowires, resulting in the significant decrease of the surface area. These four samples were then characterized by CV and EIS methods to study their electrocatalysis and conductivity, respectively. As shown in Fig. 4E, the values of both...
reduction and oxidation peaks at 0.68 and 0.72 V derived from the redox reaction of \([\text{Fe(CN)}_6]^{3-}/4^-\) evidently raised with the increase of the deposition cycle. The PBA coverage amount on ITO surface \(\Gamma_{\text{PBA}}\) was calculated through following equation [36]:

\[
\Gamma_{\text{PBA}} = \frac{Q}{nFA}
\]

where \(Q\), \(A\) and \(F\) are the single peak area, electrode area and Faraday constant, respectively; \(n\) is the average electrons transfer which was calculated by \(57/\Delta E\) (the difference value between potentials of redox peaks). The surface concentration of PBA in above samples were obtained as 4.4, 5.3, 6.3 and 8 nmol/cm\(^2\) for 10–40 deposition cycles, respectively. Because the prepared PBA was served as the main electrocatalytic material due to its good reversible redox ability, the more PBA was deposited on the electrode, the higher current intensity was harvested [33]. However, as proved in Fig. 4F more coverage had caused a stronger resistance. Before the growing of CuNWs, the charge transfer resistance of bare ITO was 10 \(\Omega\), and increased to 13 after modified to CuNWs/ITO. The deposition of PBA from 20 to 30 layers resulted in the great increase of charge transfer resistance from 23 to 31 \(\Omega\), owing to the enhancement of the film thickness and independent crystals to block the electron transfer.

To prove the core–shell structure, the Cu@CuFe-PBA film prepared by 20 electrodeposition cycles was then characterized by HRTEM to study the structure composition. As shown in Fig. 5A and B, a core–shell nanowire morphology can be clearly revealed to present a very thin shell with 10 nm thickness covering a 30 nm diameter of nanowire. Through further magnification in Fig. 5C, there was no obvious interface gap between these two materials. This is because that we served the surface of the CuNWs as the reactant during the synthesis of PBA to effectively eliminate the crystal gap for the stability enhancement. The interplanar spacings of the core and shell were measured as 0.211 and 0.165 nm which corresponds to the (1 1 1) plane of Cu and (2 2 0) of PBA, respectively (Fig. 5D). According to the EDX results in Fig. 5E and F, the Cu element were almost concentrated to the core region, and the Fe element uniformly existed the surface. Then XPS was applied to further investigate the chemical composition of this sample. As shown in Fig. S2, after the electrodeposition of CuFe-PBA, Cu, Fe, K, N and C elements were found in XPS survey, corresponding to the composition of \(\text{Cu}_{3}\{\text{Fe(CN)}_6\}\). The peak of C=N bond was observed at 284.07 eV in Fig. 5G to present the unit of \([\text{Fe(CN)}_6]^{3-}\). Compared with the Cu2p spectrum of only CuNWs in Fig. 3B, the deposition of PBA remarkably enhanced the 2p3/2 peak at 934.80 eV, which represented more generation of \(\text{Cu}^{2+}\) participating in the formation of PBA (Fig. 5H). The Fe2p spectrum (Fig. 5I) shows two couples of peaks at 720.90 and 707.92 eV, 725.61 and 709.8 eV which were attributed to the \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) orbits of the \([\text{Fe(CN)}_6]^{3-}\) unit. Above evidences confirmed that the core–shell nanostructure of Cu@CuFe-PBA nanowires was obtained by constructing a thin CuFe-PBA layer covered CuNWs.

Fig. 5. (A-B) TEM image of the Cu@CuFe-PBA electrodeposited at 20 cycles and (C-D) shows its diffraction image. (E-F) EDX mapping results for Cu and Fe respectively. XPS spectra of Cu@CuFe-PBA and magnified element map of (G) C1s-K2p, (H) Cu2p and (I) Fe2p.
3.2. Electrochemical behaviors of the Cu@CuFe-PBA nanowires

In order to investigate the intrinsic properties, benefits of core–shell nanowires on electrochemical performance were first studied by using CV to scan three electrodes of bare ITO, CuNWs/ITO and Cu@CuFe-PBA/ITO in PBS solution. As comparison in Fig. 6A, the prepared Cu@CuFe-PBA/ITO presented the highest current intensity, demonstrating its advanced electrocatalysis. And we also investigated the electrocatalytic activity by CV to scan three electrodes in an indicator solution ([Fe(CN)₆]³⁻/⁴⁻). In this process, the redox of [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ will occur in the CV cycle and a redox peak will be generated by the following equation:

\[
\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}
\]

The stronger peak current indicates the stronger electrocatalytic activity of the electrode. As shown in Fig. S3, the redox peak current difference of bare ITO, CuNWs/ITO and Cu@CuFe-PBA/ITO were ± 0.2 mA, ± 0.4 mA and ± 0.8 mA, respectively. Indicating a better electrocatalytic activity of nanocomposite.

Furthermore, only CuFe-PBA modified ITO was prepared to compare Cu@CuFe-PBA/ITO about the redox performance. In a buffer solution, the redox peaks derived from the electron transfer of the [Fe(CN)₆]³⁻/⁴⁻ unit in PBA showed a quite difference of potential in PBS solution. For PBA only, the reduction and oxidation peaks were revealed at 0.53 and 0.93 V with the potential difference of 0.4 V. Nevertheless, when applying CuNWs to form the core–shell nanostructure, the PBA obtained an obvious improvement on the conductivity to exhibit a much lower potential difference of 0.16 V, illustrating a better electrochemical reversal ability attributed from the introduction of CuNWs to provide an efficient path for electron transfer [37].

In addition, the kinetic control mechanism of the prepared Cu@CuFe-PBA electrode for AA detection was investigated through the repetitive CV tests accompanying with continuous elevation of the scan rate from 10 to 110 mV/s in 0.05 M PBS presenting 0.1 mM of AA. According to Fig. 6C, both peak currents were being enhancing with increasing scan rate. Their peak values enabled to follow the linear relations with the root of the scan rate (v¹/²), confirming the diffusion control principle of the electrode during its electrocatalytic reaction to AA. Furthermore, the electrochemical effective surface areas of the bare ITO, CuNWs/ITO and Cu@CuFe-PBA/ITO was calculated for comparison through the Randles-Sevcik equation [38]:

\[
\frac{I_p}{\sqrt{v}} = (2.69 \times 10^5)n^{3/2}D_v^{1/2}C^{*}A
\]

where \(I_p\) is the peak current of the redox couple, \(v\) is the scan rate, \(n\) is the total number of electronic transfers in the redox process, \(D_v\) is the diffusion coefficient of the molecules, \(C^{*}\) is the concentration of the probe molecules and \(A\) is the effective electrode area. Here, \(A\) of the bare ITO is 0.18 cm². Obviously, \(A\) is proportional to \(I_p/v^{1/2}\). Based on the data of the CV results in Fig. 7A–C, the calibration relations of these three electrodes can all follow the linear correlations (Fig. 7D) which were fitted to obtain the effective surface areas of the fabricated
CuNWs/ITO and Cu@CuFe-PBA/ITO as 0.20 and 0.31 cm$^2$, respectively. This result confirms that the construction of the core–shell nanostructure enables to provide a high surface area for active sites, benefiting the promotion of electrocatalysis [39].

3.3. Sensing performance of the Cu@CuFe-PBA/ITO to ascorbic acid

Before the sensing test, the prepared Cu@CuFe-PBA/ITO was first repeatedly scanned for 30 cycles by CV measurements to prove its electrochemical stability. As shown in Fig. 8A, after 30 times of the repetitive scan between 0 and 1.2 V, the shape and peak current value of the CV curve showed rare change to ensure the accuracy of the further detection of AA under the electrochemical process. After that, AA was added from 0.1 to 0.5 mM to judge the electrochemical reaction of the prepared electrode to AA. It can be found that the introduction of AA has aroused the increase of oxidation current and decrease of reduction current which indicates an electrochemical oxidation reaction on AA (Fig. 8B). Although an ultrahigh current response had been observed when the potential was beyond 0.6 V, the high operation potential would result in strong interference of the detection signal derived from the oxidation of other substances in target system. We further investigated the current response of bare ITO and CuNWs/ITO to AA (Fig. S4), both presented a current response to AA but less than Cu@CuFe-PBA/ITO. Indicating the benefits of Cu@CuFe-PBA on the electrocatalytic ability to AA. Then we compared the electrocatalytic abilities of the bare ITO, CuNWs/ITO and Cu@CuFe-PBA/ITO through the chronoamperometry at 0.4 V. When 25 μM AA was continuously injected, both three electrodes enabled to produce stable current steps (Fig. 8C). Among them, the Cu@CuFe-PBA/ITO was of the strongest electrocatalysis to exhibit nearly double intensity of the response current to other electrodes. According to the linear fitting in Fig. 8D, their electrocatalytic abilities were respectively calculated as 4.82 ± 0.1, 5.5 ± 0.08 and 9.63 ± 0.5 μA mM$^{-1}$ for the bare ITO, CuNWs/ITO and Cu@CuFe-PBA/ITO. This result indicates that only CuNWs is of a weak electrocatalysis on AA oxidation, and the deposition of PBA to form the core–shell structure can greatly improve the electrochemical activity of the CuNWs due to the valance transition of [Fe(CN)$_6$]$^{3−/4−}$ in PBA. As confirmed before in Fig. 6B, the architecture of CuNWs was capable to reduce the electron transfer resistance, accelerating the electron movement to present strong current response. In this case, the synergistic effect integrating both advances of CuNWs and CuFe-PBA was expected to produce excellent electrochemical performance.

Owing to the dominant influence of potential on sensing performance, the prepared Cu@CuFe-PBA based sensor was examined at different potentials from 0.1 to 0.5 V. As shown in Fig. 8B, the oxidation peak potential is ca. + 0.7 V when adding AA to show higher sensitivity under this high working potential, but this condition is not friendly to the practical applications. Similarly, +0.5 V as the working potential can obtain highest current response, it can be observed that the signal showed lots of noises to present an unstable state (Fig. 9A). Besides, a high working potential may cause more interference [40,41]. For balancing the sensitivity and accuracy, a relatively low potential is more appropriate. Except for this condition, other potentials were able to produce stable and continuous steps for each addition of AA. According to the linear fitting of current density vs. AA concentration (Fig. 7).

Fig. 7. CV traces of bare ITO (A), CuNWs/ITO (B) and Cu@CuFe-PBA/ITO (C) in a solution of 10 mM K$_3$[Fe(CN)$_6$] and 3 M KCl at scan rates of 50, 100, 150, 200, 250 and 300 mV/s. (D) The calibrations plot of the peak current (Ip) against the square root scan rates ($\nu^{1/2}$).
concentration, the sensitivities were calculated as 7.9 ± 1.3, 15.37 ± 1.33, 28.35 ± 1.73, 49.03 ± 2.56 and 56.91 ± 4.44 μA·mM⁻¹·cm⁻² at the working potentials from 0.1 to 0.45 V, respectively. To ensure the accuracy, 0.4 V was selected as the optimum sensing potential for the AA detection.

The influence of the solution pH was investigated with IT. As shown in Fig. S5, the sensor was detected in different pH value of 0.05 M KCl. When the pH value increased from pH 6 to 8, the sensitivity increased, especially under alkaline conditions. It has been demonstrated that, in alkaline conditions, large quantities of small-sized hydroxyl anions (OH⁻) can easily diffuse to the nanoparticle surface, and OH⁻ can be easily oxidized into •OH radicals, which can easily diffuse through solution to oxidize AA with a faster rate [42,43]. However, the sensitivity dropped sharply in alkaline conditions when second detection. This can be interpreted that OH⁻ can break the Fe-CN-Cu bond, hence CuFe-PBA was destroyed [44]. Due to this result, we suggest a neutral conditions to detect AA because of its better stability. Then the linear range of the as-prepared sensor was tested through recording its current response during the continuous additions of AA from low to high concentration. As shown in Fig. 9C, initially several injections of 0.1 μM AA hardly produced evident change of the current. Till adding 1 μM into the buffer solution, an identifiable response was revealed. Then the concentration of the added AA kept increasing until the current step showing reduction. In this detection process, the response time was less than 5 s to reach stable, resulted from the excellent conductivity of the core-shell structure to rapidly balance the electrochemical reaction.

After the linear fitting of above data, there were two parts of linear ranges for this sensor. One was from 0.001 to 0.5 mM, which exhibited the sensitivity of 42.78 ± 1.56 μA·mM⁻¹·cm⁻², and another was from 0.5 to 4.5 mM with the sensitivity of 14.77 ± 0.35 μA·mM⁻¹·cm⁻². The detection limit was further investigated with low concentrations of AA (0.1, 0.5 and 1 μM) as shown in Fig. S6. The results showed the current response to 0.5 μM AA (ΔI = 5.37nA) was about 12 times higher than the noise level (i.e. the standard deviation, N = 0.41nA), while the response for 0.1 μM AA (ΔI = 1.13nA) was smaller than 3 times of noise level. Then the test was repeated by using the same electrode for 3 times. The current responses were 5.37, 5.86 and 5.59nA which all beyond S/N = 3, showed a good repeatability to the detection limit. Therefore, a low detection limit of 0.5 μM was achieved in the sensor system.

Above performance was compared with those of other reported AA sensors in Table 1. It can be concluded that noble metals and carbon materials were preferred to adopt in the fabrication of AA sensors. Among them, although the reported PB/CS/CC-5 based sensor enabled to present ultrahigh sensitivity as 1.64 A·mM⁻¹, the preparation route of this sensor is so complicate with preparation of carbon cloth which may constrain its stability in practical applications. Besides, the listed CuS@PB/GCE electrode is of an ultrahigh sensitivity of 256.91 μA·mM⁻¹·cm⁻² and low detection limit of 0.24 μM, however its working potential is too high, which may easy oxidize other co-existed substances in drink to affect its accuracy. By comparison, the as-prepared Cu/PBA enables to exhibit a superior sensitivity, linear range and detection limit under a mild potential of 0.4 V, attributed...
to the integration of both high electrocatalysis of PBA and conductivity of Cu through the construction of a core–shell nanostructure.

3.4. Anti-interference ability, reproducibility and stability

The main deficiency of the non-enzymatic sensor is always the poor selectivity due to the easy oxidation of non-target substances under a high working potential [54]. Therefore, we carefully study the anti-interference ability of our prepared sensor through adding various common analytes in fermentation or drink. Fig. 10A shows the current response of eight interfering substances whose added concentrations are 50 times than AA during the detection process. It can be observed that the additions of these interfering substances produced rare change of the current step derived from AA injections. And CV measurement was further used to explore the anti-interference ability, as shown in Fig. S7, no current response appeared when interfering substances added, but an obvious response when AA added. These results proving the excellent selectivity of the as-prepared sensor to ensure the accu-

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**Table 1**

Performance comparison of various nanomaterials based AA sensors reported in the literature.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential (V)</th>
<th>Sensitivity (μA mM⁻¹ cm⁻²)</th>
<th>Linear range (μM)</th>
<th>Low detection limit (μM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB/XOD</td>
<td>−0.1</td>
<td>9.98</td>
<td>0–50</td>
<td>4.93</td>
<td>[12]</td>
</tr>
<tr>
<td>ZnO/CNTs</td>
<td>+0.61</td>
<td>80 (μA mM⁻¹)</td>
<td>0.1–450</td>
<td>0.07</td>
<td>[45]</td>
</tr>
<tr>
<td>PDDA/graphite</td>
<td>+0.35</td>
<td>49.15</td>
<td>50–1200</td>
<td>0.8</td>
<td>[46]</td>
</tr>
<tr>
<td>Au/ZnSe/ZnO</td>
<td>+0.2</td>
<td>113.75</td>
<td>0–2000</td>
<td>0.119</td>
<td>[47]</td>
</tr>
<tr>
<td>MoOx@PB/GF</td>
<td>+0.26</td>
<td>0.37 (A/M)</td>
<td>0.0125–293</td>
<td>0.5</td>
<td>[48]</td>
</tr>
<tr>
<td>AuNPs/RGO/SPCE</td>
<td>+0.3</td>
<td>53.57</td>
<td>0–500</td>
<td>0.5</td>
<td>[49]</td>
</tr>
<tr>
<td>poly(ethylene glycol)/PEGDGE/SPCE</td>
<td>+0.45</td>
<td>13.5 (μA mM⁻¹)</td>
<td>10–450</td>
<td>10</td>
<td>[50]</td>
</tr>
<tr>
<td>PB/CS/CC-S</td>
<td>+0.26</td>
<td>1.64 (A/M)</td>
<td>0.3–300</td>
<td>0.25</td>
<td>[44]</td>
</tr>
<tr>
<td>PAA-Fc/MMPS/Au</td>
<td>+0.18</td>
<td>12.2</td>
<td>50–1000</td>
<td>27</td>
<td>[51]</td>
</tr>
<tr>
<td>CuS@PB/GCE</td>
<td>+0.7</td>
<td>256.91</td>
<td>5–3075</td>
<td>0.24</td>
<td>[52]</td>
</tr>
<tr>
<td>SiO₂@PANI/CPE</td>
<td>+0.4</td>
<td>21.88</td>
<td>150–8000</td>
<td>3.375</td>
<td>[53]</td>
</tr>
<tr>
<td>Cu@PBA/ITO</td>
<td>+0.4</td>
<td>42.78</td>
<td>1–500</td>
<td>0.5</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 9. Chronoamperometry diagrams (A) and linear calibrations (B) of Cu@CuFe-PBA/ITO under different working potential to the repeated addition of AA every 50 s in 0.05 M PBS. The linear range test (C) and linear calibration (D) of the Cu@CuFe-PBA/ITO at 0.4 V in 0.05 M PBS, three insets showing magnifications of the curve from 100 to 850 s, the response time and linear calibration at low concentration respectively.
racy. Then ten sensors were respectively prepared to test their sensitivities in order to evaluate the reproducibility of our proposed Cu@CuFe-PBA based sensors. The performance of these 10 sensors exhibited in Fig. 10B confirmed a 6.49% relative standard deviation (RSD) of the sensitivity to reveal a good reproducibility in the sensor fabrication. For a single sensor, it was further repetitively used once a day for one month to monitor its change of sensitivity. After each use, the sensor was cleaned by deionized water and kept storage in 4 °C fridge. After 30 days of tests, this sensor still remained 56.79% of the initial sensitivity (Fig. 10C) to indicate its excellent usage stability.

3.5. Real samples analysis

The analysis accuracy of the as-prepared sensor in the practical samples of several drinks via a standard addition method. As shown in the Fig. S8, an AA sample with a known concentration (0.1 mM) was injected to get a standard current signal \( \Delta i_{\text{standard}} \), and then the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (μM)</th>
<th>Found (Sensor, μM)</th>
<th>RSD (n = 3)/%</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juice 1</td>
<td>5</td>
<td>4.702</td>
<td>−4.8</td>
<td>94.04</td>
</tr>
<tr>
<td>Juice 2</td>
<td>10</td>
<td>10.6</td>
<td>3.4</td>
<td>106</td>
</tr>
<tr>
<td>Bear 3</td>
<td>15</td>
<td>14.96</td>
<td>2.27</td>
<td>99.73</td>
</tr>
<tr>
<td>Bear 4</td>
<td>20</td>
<td>19.32</td>
<td>3.1</td>
<td>96.6</td>
</tr>
</tbody>
</table>

Table 2
Results of the AA detections in real drink samples using our prepared AA sensor.
Table 2 listed the results of four different kinds of juice and bear with different added concentrations of AA. Overall, the relative standard deviation (RSD) of the prepared sensor for detecting AA was less than 5% with a remarkable recovery between 94.04 and 106. This indicates that our designed sensor is capable of high accurate detection of the practical AA concentration in drink, as well as a short detection period within 5 s.

4. Conclusions

In this work, a core–shell nanowire architecture of Cu@CuFe-PBA was successfully in-situ constructed as an ultra-high sensitive and selective AA sensor through coupling the hydrothermal reaction and electrodeposition. This nanostructure contributed an outstanding synergic effect performing both strong electrocatalysis from PBA shell and conductivity from CuNWs core, promoting the current intensity and shortening detection period during the AA detection. The as-prepared sensor enables to exhibit a wide linear range and a short detection limit, together with an excellent selectivity, reproducibility and reuse stability after the repetitive usage of 30 days. Using four kinds of juice and bear as the practical samples, the AA concentration can be accurately and fast recognized with a good recovery. The synthesis strategy in this work enables to provide a new inspiration on the design of core–shell nanostructure of various composites, and this high-performance non-enzymatic sensor is promising to be further applied in the online process control of industrial AA production and onsite quality testing of food and drink.

CRediT authorship contribution statement

Jingyu Feng: Data curation, Formal analysis, Investigation, Methodology, Software, Supervision, Writing – original draft. Yu Liu: Data curation, Formal analysis, Investigation, Methodology, Software, Supervision, Writing – original draft. Yuansheng Shan: Data curation, Formal analysis, Methodology, Software, Writing – original draft. Zhenyu Chu: Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing - review & editing. Wanqin Jin: Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing - review & editing. Yuhua Li: Conceptualization, Data curation, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ellechem.2021.115718.

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