Screen-printing of core-shell $\text{Mn}_3\text{O}_4@\text{C}$ nanocubes based sensing microchip performing ultrasensitive recognition of allura red

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**A R T I C L E  I N F O**

Handling Editor: Dr. Jose Luis Domingo

Keywords:
- Azo dyes
- Core-shell nanocubes
- Manganese oxides
- Ultrawide linear range
- Real drink detection

**A B S T R A C T**

Allura red (AR) is a member of azo dyes is commonly used as an additive in foods and soft drinks. However, due to the special harm of the azo structure to the human body, the dosage control of AR becomes particularly necessary. The present detection methods are time-consuming, expensive and complicated. In order to address the above issues, a core-shell nanocubes constructed sensor has been developed to determine the ultrawide detection range and selective recognition of AR with a long-term reusability. The core-shell architecture is composed of carbon material of 12.64 nm thickness covering 600 nm Mn$_3$O$_4$ nanocube. This nanocomposite combines the advantages of Mn$_3$O$_4@$C, possessing high electrocatalysis and chemical stability. As confirmed in using sports drinks as real samples, the as-prepared AR sensor exhibits excellent selectivity with a ultrawide linear range from 0.1 to 1748.4 μM, and meanwhile, this sensor can also meet the requirements of remarkable anti-interference and reusability over 30 days.

1. **Introduction**

As the largest category of synthetic dyes, there are more than 3000 kinds of azo dyes in the world, accounting for approximately 65% of the commercial dye market (Bessegato et al., 2019). Allura red (AR), which is one of the most applied red pigments, is commonly used as a major additive in food and soft drinks owing to its color increasing and non-fading characteristics (Gan et al., 2013; Li et al., 2020; Moarefdouse et al., 2021; Nagles et al., 2021). However, AR has been confirmed to possess clear toxic effects on the liver and kidney of humans; especially children, as a result of a distinctive azo structure (with a $-\text{N}═\text{N}-$ group) (Moarefdouse et al., 2021; Penagos-Llanos et al., 2019a,b). Hence, the acceptable daily intake (ADI) of this additive is a topic, which must be concerned. According to the research by the European Food Safety Authority (EFSA), the actual ADI value of AR in food is 7.0 mg/kg. However, this value is frequently exceeded in our daily lives (Sierra-Rosales et al., 2019). Taking human health into consideration, it is imperative to carry out rapid and accurate detection of AR. (Amin et al., 2010; Darabi and Shabani-Nooshabadi, 2021; Zhang et al., 2010). At present, traditional AR detection methods include liquid chromatography, Raman spectroscopy, mass spectrometry and UV/visible spectrophotometry (Al-Deqs, 2009; Chen et al., 2014; Ou et al., 2018). Among these, high performance liquid chromatography (HPLC) is the most widely used. Although HPLC shows good selectivity and high detection sensitivity, time consumption and complicated operation make it unsatisfactory in terms of both high precision and real-time detection at the same time (Yu et al., 2016). Other methods are also limited by their requirements of special and expensive instruments (Ceyhan et al., 2013; Soylak et al., 2011).

Electrochemical sensing technology is advanced due to its fast response, high selectivity and low cost. Hence, it has been widely applied in clinical diagnosis, pollution monitoring and fermentation detection (Maduraiveeran et al., 2018; Zhang et al., 2021a). The detection principle of electrochemical sensing relies on the electrochemical reaction between the analyte and electrode material to convert the chemical quantity into an electrical quantity during its sensing process (Lakhdari et al., 2021; Le et al., 2021). AR is a complex organic compound containing a chromophore group ($-\text{N}═\text{N}-$) and a auxochromic group ($-\text{OH}$), which can be electrochemically oxidized or reduced to possibly arouse the change of the electric signal (Silva et al., 2020; Uruc et al., 2021). Therefore, without the assistance of any enzymes or other specific recognition substances, an electrochemical sensor for direct oxidation of AR can be expected to be constructed as following equation (Penagos-Llanos et al., 2019a,b):

\[ \text{Allura red } -\text{N}═\text{N}(-) \rightarrow \text{dehydro} - \text{Allura red} \]

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https://doi.org/10.1016/j.jct.2022.112908

Received 24 January 2022; Received in revised form 22 February 2022; Accepted 5 March 2022

Available online 7 March 2022

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During the above electrochemical process, electrode material is a key factor determining the detection sensitivity and selectivity because of its direct contact and reaction with the AR (Chen et al., 2012; Rana et al., 2019; Wang and Zhao, 2015) (Priya and Berchmans, 2012; Staaf et al., 2014).

Various electrode materials such as noble metals, alloys, carbon materials, transition metal oxides and so on have been successfully used to prepare different non-enzymatic sensors. Being important functional metal oxides, manganese oxides (MnO, MnO₂, Mn₂O₃ and MnO₄) have attracted considerable attention in electrocatalysis or sensors on account of their low price, high carrier mobility, fine biocompatibility and chemical stability (Bhuyan et al., 2021; Ji et al., 2015; Kalantar-zadeh et al., 2016; Liu et al., 2004; Rai et al., 2015; Smith et al., 2019) (Guo et al., 2017; Li et al., 2013; Wang et al., 2014). Among these, MnO₂ is the most stable and possesses abundant active sites due to its unique spinel structure (Zhang et al., 2021b). Furthermore, its reversible mixed valence states (Mn⁴⁺, Mn³⁺) yielded excellent redox properties that could enhance the target signal for improving the selectivity (Yang et al., 2015). However, because of its wide band gap (2.23 eV), the electron transfer will be strongly constrained to greatly reduce the detection sensitivity (Yang et al., 2015). In this case, it is desired to solve the softening of poor electrical conductivity of a single MnO₂ material by in-situ calcination of the carbon layer, which is expected to bring high sensitivity and selectivity for the AR recognition.

In this work, a screen-printed microchip sensor has been developed to obtain ultrasensitive AR detection with an ultrawide linear range and excellent selectivity through designing a core-shell nanocubic architecture of MnO₂@C as the sensor (as shown in Fig. 1). This core-shell nanostructure was constructed through the high temperature co-calcination of a polydopamine in situ covered with MnCO₃ nanocubes in a N₂ atmosphere. The special morphology of the sensor provides high electrocatalysis, surface area and satisfactory conductivity, promoting the electrochemical redox and electron transfer processes. This nanocubic composite directly served as a printing ink to fabricate a three-electrode sensing microchip. The as-prepared sensor exhibited ultrahigh sensitivity and selectivity with an ultrawide linear range for the AR recognition and outstanding stability beyond 30 days of repetitive detections. Moreover, this microchip was proved to perform accurate and rapid tests of AR in four kinds of real sports drinks within 30 s.

2. EXPERIMENTAL

2.1. Reagents and apparatus

Manganese sulfate monohydrate (MnSO₄·H₂O), dipotassium hydrogen phosphate (K₂HPO₄), potassium dihydrogen phosphate (KH₂PO₄) and potassium chloride (KCl) were purchased from Shanghai Lingfeng Chemical Reagent Co. (China). Ammonium hydrogen carbonate (NH₄HCO₃) was obtained from Sinopharm Chemical Reagent Co. Sudan I was provided by Shanghai Yien Chemical Co. Tartrazine and Sunset Yellow were supplied by Shanghai Macklin Biochemical Co. (China). Allura red was purchased from Shanghai Aladdin Biochemical Technology Co. 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).

The electrochemical experiments including cyclic voltammetry (CV), chronoamperometry (IT) and electrochemical impedance spectroscopy (EIS) were performed using a CHI 660E Electrochemical Workstation (Shanghai Chenhua Instrument Co.). EIS characterization was carried out in the presence of 5 mM [Fe(CN)₆]³⁻/⁴⁻ solution containing 0.1 M KCl at the frequency range of 0.01 Hz–10 MHz. The effective area was tested in the solutions of 10 mM K₃[Fe(CN)₆] and 3 M KCl. In all CV tests, the scan rate and sampling frequency were 0.1 V/s and 0.001 V, respectively. All the experiments in the electrochemical detection were carried out in 0.5 M PBS. Moreover, a conventional three-electrode cell was used composed of Pt wire, Ag/AgCl, and Au as the counter, reference and working electrodes, respectively. For fabrication of the screen-printed microchips (SPMs), a 245 DEK screen printing machine (Weymouth, United Kingdom) was utilized. Field emission scanning electron microscopy (FESEM) (Hitachi, ModelS-4800II, Japan) and transmission electron microscopy (TEM) (JEOL JEM-2010 UHR) were used to investigate the micromorphology of MnCO₃ nanocubes and MnO₂@C nanocubes. X-ray diffractometry (XRD) (D/MAX 2500 V/PC) with Cu-Kα radiation (0.15419 nm) was employed to study the characteristic peaks of MnCO₃ and MnO₂@C nanocubes. Thermogravimetric analysis (TGA) (STA 449F5) was utilized to analyze the effect of calcination temperature on the composition of MnO₂@PDA. X-ray photoelectron spectroscopy (XPS) (ESCALAB MKLL) was utilized to analyze the elemental valence states of Mn, O and C. Fourier transform infrared spectroscopy (FTIR) (Thermo Electron, Nicolet- 8700) was utilized to determine the functional groups present in the samples.

2.2. Synthesis of MnO₂@C nanocomposite

For the one step facile synthesis of MnCO₃ precursor, two solutions were prepared: solution A: 4 mM MnSO₄ (50 mL) and solution B: 200 mM NH₄HCO₃ (50 mL). Solution A was preheated in a 50℃ water bath for 10 min and then directly poured into solution B. The mixed solution started to become cloudy within 1 min under continuous stirring, after

Fig. 1. Schematic of the synthesis strategy of MnO₂@C nanocubes based screen-printed microchip for AR sensing. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
which it was kept for 5 h in a 50 °C water bath. Upon the completion of the reaction, the MnCO₃ nanocubic precursor was obtained by adding deionized water, centrifugation three times at the speed of 8000 rpm and drying at 60 °C for 12 h.

Core-shell structured Mn₃O₄@C nanocubes were prepared via initial PDA coating on the MnCO₃ core and subsequent calcination in N₂. Briefly, 1 g of MnCO₃ powder was dispersed in 100 mL of deionized water under stirring. 0.13 g of Tris powder was then dissolved into the above dispersion under magnetic stirring for 30 min. Afterwards, 0.20 g of dopamine hydrochloride was added into the above mixture. The color of the mixture was found to gradually darken with the self-polymerization of dopamine. After 24 h of magnetic stirring at room temperature, a black suspension was obtained, which was then washed with deionized water and dried at 60 °C before being loaded into a tube furnace. After 2 h of calcination at 600 °C at a ramping rate of 5 °C min⁻¹ in N₂, the final Mn₃O₄@C nanocubes was obtained.

2.3. Screen-printing of the sensing microchip

The screen-printed microchips (SPMs) were mass produced by a screen printer. The length and width of the sensing microchip prepared by screen printing technology were 26 mm and 8 mm, respectively, and the area of its working electrode was 0.07065 cm². The ink of the working electrode was prepared by uniformly mixing Mn₃O₄@C and carbon ink at a suitable mass ratio using a silver chloride slurry as the reference electrode. The counter electrode and the connected portion were carbon ink.

3. RESULTS and discussion

3.1. Nanostructure evolution of core-shell Mn₃O₄@C nanocubes

As shown in Fig. 1, a core-shell morphology is desired to achieve both high conductivity and electrocatalysis, which are derived from the core and shell materials, respectively. However, since the morphology of Mn₃O₄ is normally difficult to control, a core precursor of MnCO₃ with a regular nanostructure was first introduced to serve as the growth skeleton. During the preparation of the core precursor, self-assembly precipitation was applied to precisely control the crystallization reaction of MnCO₃ using various reactant concentrations of Mn²⁺ ions (Xie et al., 2017) (Fig. 2a). As it can be observed, the nanostructure of the obtained MnCO₃ has obviously changed with the continuous increase of Mn²⁺ concentration. Under the lowest Mn²⁺ concentration (2 mM), the particles presented a rhombohedral cube appearance with a wide angle of ca. 103° (Fig. 2b). The crystal surface was smooth and the average particle size was ca. 500 nm. When the concentration increased slightly from 2 mM to 4 mM, the edge angle of a single particle was ca. 90° (Fig. 2c), confirming the formation of a cubic morphology. The size of the cubic particle was ca. 600 nm with round edges. Further increasing the concentration to 6 mM resulted in the generation of a transition region between the cubic and spherical particles (Fig. 2d). The average particle size was not significantly different from that of the former cubes. However, if a large number of Mn²⁺ ions participated in the crystallization, the shape of the MnCO₃ particles would transform to a ball-like rough feature composed of numerous sharp corners (Fig. 2e). Considering the uniformity and convenience for the further formation of the shell structure, the nanocubic morphology was selected as the optimum precursor.

In order to obtain Mn₃O₄ from MnCO₃, high temperature calcination is required. As previously indicated, if only MnCO₃ is used as the electrode, its poor conductivity will greatly decrease the sensing performance. Therefore, polydopamine (PDA) was employed to cover the whole surface of the MnCO₃ nanocubes by in situ polymerization of dopamine before the calcination operation (Wang et al., 2017). In this way, a carbon layer will be expected to form through the thermal decomposition of PDA during the formation of Mn₃O₄ crystals. Using different calcination temperatures (Fig. 3a–c), overall, the cubic shape was still retained. However, the crystal treated at 600 °C presented a complete coverage on the nanocubic surface while the one treated at 400 °C produced some deficiencies of the shell layer to reveal the core material, and the one treated at 800 °C caused the damage of some nanocubes with lots of cracks. Subsequently, TEM characterization was applied to further investigate the shell structure. As shown in Fig. 3d, a very thin layer of 2.64 nm thickness can be observed. According to the EDX analysis (Fig. 3e–h), this layer was composed of carbon derived from the decomposition of the PDA layer. The material in the core was found to mainly contain Mn and O. The TGA image indicated the thermal behavior of MnCO₃@PDA during the calcination (Fig. 3i). The total weight loss of the crystal was 45.29%, considering that the trapped H₂O and organic matter were burnt to produce the Mn₃O₄@C nanocubes. Moreover, the XRD results (Fig. 3j) confirmed that the first weight loss of about 32.15% from 20 to 400 °C was mainly attributed to the decomposition of MnCO₃ into MnO and CO₂ while the second weight loss of about 13.34% was due to the conversion of MnO into Mn₃O₄.

For more clarity, MnCO₃ and core-shell Mn₃O₄@C crystals were further characterized by XRD to determine the elemental changes before and after calcination. As shown in Fig. 4a, MnCO₃ shows typical peaks at 24.2°, 31.3°, 34.2°, 37.5° and 41.4°, which correspond to the crystal
Fig. 3. FESEM images of the MnCO$_3$@PDA calcined at different temperatures: (a) 400 °C, (b) 600 °C and (c) 800 °C. (d) TEM image of the single Mn$_3$O$_4$@C nanocube. (e) Mixed HAADF image of C, Mn and O three elements. (f–h) EDX mapping results for C, Mn and O respectively. (i) TGA curve of the synthesized MnCO$_3$@PDA. (j) XRD patterns of varying the temperature to the MnCO$_3$@PDA under 25 °C, 400 °C and 600 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. (a) X-ray diffraction (XRD) patterns of MnCO$_3$ and Mn$_3$O$_4$@C. (b) Sum map of MnCO$_3$ and Mn$_3$O$_4$@C and each magnified element map of (c) Mn 2p, (d) O 1s and (e) C 1s. (f) Repetitive CV tests of the prepared sensor for the stability investigation, and the insets are the magnifications of the redox peaks. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
faces of (1 0 1), (1 1 2), (2 0 0), (1 0 3) and (2 1 1), respectively. The XRD image of the prepared Mn₃O₄@C presents peaks at 18.0°, 28.8°, 31.0° and 32.3°, associated with the typical crystal faces of (1 0 1), (1 1 2), (2 0 0) and (1 0 3), respectively. In addition, the chemical composition and elemental valence state of Mn₃O₄@C nanocomposite was studied by XPS. The full spectra of MnCO₃ and Mn₃O₄@C proved that these two compounds were mainly composed of Mn, C and O (Fig. 4b). The difference between these two compounds was the peak corresponding to N in Mn₃O₄@C, which was derived from the PDA. Specifically, as shown in Fig. 4, the Mn 2p spectrum consisted of a pair of peaks located at 642.90 eV, corresponding to Mn 2p₃/2 and Mn 2p₁/2, respectively, which indicated the introduced oxygen containing groups –C, –O and O –C=O at 284.7, 285.9 and 288.3 eV, respectively, which indicated the introduced oxygen containing groups in the composite. Despite lacking some bridge force for connection, Mn₃O₄@C nanocubes were able to exhibit excellent electrochemical stability during repetitive CV scans for 30 times (Fig. 4f), suggesting the stable structure of this core-shell framework.

3.2. Electrochemical behaviors of the Mn₃O₄@C nanocubes

The electrochemical behavior of the prepared Mn₃O₄@C nanocube was first compared with those of the bare electrode and MnCO₃ nanocube using CV. As compared in Fig. 5a, the Mn₃O₄@C nanocubes produced the highest redox currents, which proved that the coexisting Mn²⁺ and Mn³⁺ possessed rather strong redox abilities. According to the EIS test (Fig. 5b), the electron transfers resistances of the bare Au electrode, MnCO₃ and Mn₃O₄@C modified electrodes were calculated as 130.64, 151.40 and 140.58 Ω, respectively. Although Mn₃O₄@C nanocube has a weaker conductivity compared with Au, it is superior to MnCO₃ nanocube. This demonstrated that the formation of the carbon shell after the calcination treatment improved the electron transfer ability. Furthermore, the electrochemical effective surface areas of the bare Au electrode, MnCO₃ and Mn₃O₄@C were investigated through the Randles-Sevcik equation:

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

where \(I_p\) is the redox peak current, \(v\) is the scan rate, \(n\) is the total number of electrons transferred during the redox process, and \(D\), \(C_p\) and \(A\) correspond to the molecular diffusion coefficient, probe molecule concentration and electrode area, respectively. Obviously, the effective catalytic area was proportional to \(\frac{I_p}{\sqrt{v}}\). Fig. 5c–e presents the CV diagrams of these three electrodes in a 10 mM probe solution of [Fe(CN)₆]³⁻/⁴⁻, respectively. By fitting Eq. (2) (Fig. 5f), the effective areas of the bare Au electrode, MnCO₃ and Mn₃O₄@C modified electrodes were calculated as 0.0314, 0.0460 and 0.0495 cm², respectively. As a result, the core-shell nanostructure can also contribute more active sites to improve the electrocatalytic performance.

3.3. Sensing performance of the Mn₃O₄@C printed microchip

To considerably promote the reproducibility and reusability of the proposed electrochemical sensor, the screen-printing technique was employed to fabricate Mn₃O₄@C based microchip in large scale. In this preparation, the obtained Mn₃O₄@C nanocomposite was mixed with a commercial carbon paste to directly serve as a printing ink, satisfying the viscosity and mobility requirements for printing the working electrode. The unchanged typical XRD peaks of the Mn₃O₄@C in the prepared ink (Fig. 6a) show that this mixing process cannot destroy the original crystal structure. Furthermore, the mixed ink showed an extra characteristic peak at 26.3°, which belonged to the (0 0 2) crystal plane.

Fig. 5. (a) Comparison of cyclic voltammetry (CV) values of the bare gold electrode, MnCO₃ and Mn₃O₄@C modified gold electrodes at a scan rate of 0.05 V/s in a 0.05 M PBS solution. (b) EIS diagram of the above three electrodes at a scanning frequency range from 0.1 to 100 kHz; inset: electrical equivalent circuit. CV diagrams of bare gold electrode (c), MnCO₃ (d) and Mn₃O₄@C (e) modified gold electrodes in a solution of 10 mM K₃[Fe(CN)₆] and 3 M KCl at scan rates of 10, 30, 50, 70, 90 and 110 mV/s. (f) Calibration curves of the peak current versus the square root of the scan rate of three electrodes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
of carbon ink, according to the standard card of carbon ink (PDF#41–1487), indicating the stable co-existence of carbon and Mn$_3$O$_4$@C in the mixed ink. The FTIR spectra in Fig. 6b showed two significant peaks at 640 and 535 cm$^{-1}$, corresponding to Mn–O vibration. Similarly, there was no obvious change after mixing carbon ink with Mn$_3$O$_4$@C, confirming the good stability of the prepared ink. In order to fabricate a three electrode microchip, a silver chloride slurry and carbon ink were used to print the reference and counter electrodes, respectively.

Subsequently, the as-prepared screen-printed microchip (SPM) was used in the electrochemical detection of AR. The CV curves of Mn$_3$O$_4$@C/SPM were scanned before and after the addition of 20 μM AR (Fig. 7a). It was shown that when AR standard solution was added to the buffer solution, a significant increase in current occurred at the potential of ca. 0.9 V, indicating the electrochemical oxidation of AR to dehydro-AR. Therefore, this potential was selected to test the sensing performance of the microchip. Different concentrations of AR were continuously injected into the electrolyte cell to study the electrochemical response by a DPV technique. As shown in Fig. 7b, upon increasing the AR concentration from 0.1 to 1748.4 μM, the value of the current peak located at 0.9460 V showed gradual enhancement. Even at the ultralow AR concentration (0.1–2 μM), this peak showed a clear increase (Fig. 7c). According to above DPV results, the response current can follow a piecewise linear relation with the AR concentration (Fig. 7d) from 0.1 to 108.4 μM, which corresponds to the fitting line of $j = 1.60056C_{AR} + 5.07797$ ($R^2 = 0.92441$) and another from 168.4 to 1748.4 μM, fitting the line of $j = 0.19304C_{AR} + 155.24757$ ($R^2 = 0.97599$).

This performance has been compared with those of other reported AR sensors in Table 1. It can be observed that metal oxides and carbon materials preferred to adopt in the fabrication of AR sensors. Among these, although the reported Er-BTC/CPE based sensor exhibited an extremely low detection limit (0.0003 μM), the very narrow linear range still limited its practical application in most industrial purposes. Furthermore, the listed CoO$_x$/CPE was of a high sensitivity of 33.69 μA μM$^{-1}$. However, the linear range was also too narrow (0.1–1 μM). By
In comparison, the prepared Mn$_3$O$_4$@C/SPM sensor could exhibit superior sensitivity, linear range and selectivity together, attributed to the integration of both high electrocatalysis of Mn$_3$O$_4$ and conductivity of carbon through the construction of a core-shell nanostructure.

### 3.4. Anti-interference ability, reproducibility and stability

Anti-interference performance is a vital parameter to ensure the accuracy of the proposed sensor during the analysis of food or drink. Here, the common azo dyes present in food and beverages such as Sunset Yellow (SY), Tartrazine (TZ) and Sudan I were selected to serve as typical interfering compounds to examine the selectivity of the as-prepared SPM. According to the DPV scanning (Fig. 8a), while injecting 10 μM AR, a clear current peak appeared. However, no significant changes were observed at this current peak after 10 μM. Sunset Yellow (SY), Tartrazine (TZ) and Sudan I were injected with the same concentration, indicating the excellent anti-interference performance of our SPM.

In order to evaluate the reproducibility of this sensor, seven sensors were prepared to test and compare their sensitivities (Fig. 8b). The performance of these sensors exhibited a 1.19% relative standard deviation (RSD) of the sensitivity, indicating the good reproducibility in the sensor fabrication. For a single sensor, it was further repetitively used once a day for one month to monitor the fluctuations of its sensitivity. After each use, the sensor was cleaned by deionized water and stored in a fridge at 4 °C. After 30 days of repetitive tests (Fig. 8c), this sensor still retained 28.43% of the initial sensitivity, which indicated its excellent reusability.

### 3.5. Analysis of real drink samples

The analysis accuracy of the as-prepared AR sensor was tested in the real samples of several sports drinks via a standard addition method. First, an AR sample with a known concentration was injected to obtain a standard current signal, $\Delta i_{\text{[standard]}}$, followed by the addition of a drink sample containing a certain AR content to report a response current, $\Delta i_{\text{[sample]}}$. The sample concentration can be calculated using the following equation:

$$C_{\text{[sample]}} = \frac{C_{\text{[standard]}} \times \Delta i_{\text{[sample]}}}{\Delta i_{\text{[standard]}}}.$$  

Table 2 lists the results of four different kinds of sports drinks with different added concentrations of AR. Overall, the relative standard deviation (RSD) of the prepared sensor for detecting AR was less than 8% with a remarkable recovery between 98.60% and 100.68%. This indicates that our designed sensor is capable of highly accurate detection of the practical AR concentration in drinks as well as a short detection period within 30 s.

### 4. Conclusions

In summary, a core-shell architecture of Mn$_3$O$_4$ nanocubes has been constructed to fabricate an ultrasensitive sensing microchip for achieving the accurate recognition of AR within only 30 s. Compared with the single Mn$_3$O$_4$ material, this special composite nanostructure can produce high electrocatalysis and good electrical conductivity under the synergistic effect of the Mn$_3$O$_4$ core and C shell layers. The as-prepared sensor could exhibit an ultralow linear range and an ultralow detection limit in the detections of various real sport drinks, together with an excellent selectivity, reproducibility and reusability.

#### Table 1

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Method</th>
<th>Linear range (μM)</th>
<th>Low detection limit (μM)</th>
<th>Sensitivity (μA μM$^{-1}$)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>In$^{3+}$-NiO/GCE</td>
<td>DPV</td>
<td>0.01–700</td>
<td>0.0041</td>
<td>0.256</td>
<td>Moarefdouse et al. (2021)</td>
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<tr>
<td>TiO$_2$-ErGO/GCE</td>
<td>DPV</td>
<td>5.0–800</td>
<td>0.05</td>
<td>0.076</td>
<td>Li et al. (2013)</td>
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<tr>
<td>IL-CB/GCE</td>
<td>SWAdASV</td>
<td>0.0398–0.909</td>
<td>0.00091</td>
<td>27.4</td>
<td>Silva et al. (2020)</td>
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<tr>
<td>Ptre/PGE</td>
<td>DPV</td>
<td>0.25–100</td>
<td>0.075</td>
<td>0.4334</td>
<td>Uruc et al. (2021)</td>
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<tr>
<td>MoO$_3$/CPE</td>
<td>SWV</td>
<td>1–15</td>
<td>0.38</td>
<td>0.69</td>
<td>Nagles et al. (2021)</td>
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<tr>
<td>Er-BTC/CPE</td>
<td>DPV</td>
<td>0.061–0.1</td>
<td>0.0003</td>
<td>–</td>
<td>Cai et al. (2020)</td>
</tr>
<tr>
<td>MWCNT/GCE</td>
<td>DPV</td>
<td>1–9</td>
<td>0.028</td>
<td>–</td>
<td>Sierra-Rosales et al. (2019)</td>
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<tr>
<td>CoO$_2$/CPE</td>
<td>SWV</td>
<td>0.1–1</td>
<td>0.05</td>
<td>33.69</td>
<td>Penagos-Llanos et al. (2019)</td>
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<td>DPV</td>
<td>0.05–10</td>
<td>0.008</td>
<td>1.17</td>
<td>Yu et al. (2016)</td>
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<td>IL-GO-MWCNT/GCE</td>
<td>SWV</td>
<td>0.0098–0.5</td>
<td>0.0005</td>
<td>–</td>
<td>Wang et al., 2015</td>
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<tr>
<td>Mn$_3$O$_4$@C/SPM</td>
<td>DPV</td>
<td>0.1–168.4</td>
<td>0.033</td>
<td>0.11308</td>
<td>This work</td>
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#### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (μM)</th>
<th>Found (Sensor, μM)</th>
<th>RSD (n = 3)/%</th>
<th>Recovery (%)</th>
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<tr>
<td>Sample 1</td>
<td>10</td>
<td>9.86</td>
<td>6.08</td>
<td>98.60</td>
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<tr>
<td>Sample 2</td>
<td>15</td>
<td>14.98</td>
<td>6.81</td>
<td>99.87</td>
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<td>Sample 3</td>
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<td>19.93</td>
<td>5.51</td>
<td>99.65</td>
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<tr>
<td>Sample 4</td>
<td>25</td>
<td>25.17</td>
<td>7.77</td>
<td>100.68</td>
</tr>
</tbody>
</table>

Fig. 8. (a) Anti-interference ability of the as-prepared sensor to Sunset Yellow (SY), Tartrazine (TZ) and Sudan I. The addition concentrations of interfering substances and AR were 10 μM. (b) Sensitivities of the prepared 7 sensors through independent tests. (c) Monitor on the sensitivity of a single sensor during the repetitive usage in 30 days. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)


