Design of Double-Shelled CuS Nanocages to Optimize Electrocatalytic Dynamic for Sensitive Detection of Ascorbic Acid

Tong Yang, Liangliang Tian, Enmin Zhou, Daidong Chen and Yu Lei

Abstract

Although transition metal sulfides have presented prospect in electrochemical sensing, their electrocatalytic performance still cannot meet the demands for practical applications due to the difficulties in mass transport and electron transfer. In this work, double-shelled CuS nanocages (2-CuS NCs) were prepared for enzyme-free ascorbic (AA) sensor through a Cu₂O-template method. The unique double-shelled hollow structure displayed large specific surface areas, ordered diffusion channels, increased volume occupying rate, and accelerated electron transfer rate, resulting in enhanced electrochemical dynamic. As a sensing electrode for AA, 2-CuS NCs modified glassy carbon electrode (2-CuS NCs/GCE) exhibited eminent electrocatalytic activity in terms of satisfying sensitivity (523.7 μA mM⁻¹ cm⁻²), short response time (0.31 s), and low limit of detection (LOD, 0.15 µM). 2-CuS NCs look promising for analytical sensing of AA in electrochemical sensors thanks to its prominent electrocatalytic kinetics issued from double-shelled hollow porous structure.

Keywords: CuS, Double-shelled nanocages, Cu₂O template, Electrochemical sensors, Ascorbic acid detection

Background

AA plays a key role in biological metabolism for human health. Accurate and fast detection of AA can avoid diseases such as scurvy, diarrhea, and stomach convulsion [1]. A series of methods have already been established to accurately detect AA [2–4]. Thereinto, electrochemical method has attracted lots of attention due to fast response, high sensitivity, simple operation, and low cost. Transition metal materials present great prospect in enzyme-free electrochemical sensors due to their abundant reserves, variable valence states, active redox couples, and accessibility for the detection species [5, 6]. As active materials for electrochemical sensors, transition metal sulfides are a new surge of interest due to their higher electric conductivity compared with transition metal hydroxides or oxides [7].

As we know, the performance of electrochemical sensors closely correlates with the properties of electrocatalysts. Inspired by the structure-activity theory, high-active electrocatalysts can be obtained by controlling their unique morphology and fine structure [8]. Accordingly, researchers have focused on the rational design of electrocatalytic materials with different structures, such as nanosheets, nanorods, nanoplates, nanocubes, and nanospheres. Thereinto, hollow porous structures (HPSs) afford large specific surface areas and sufficient active sites for redox reactions. Moreover, the ultrathin porous shells also shorten distances of ion diffusion or electron transfer [9, 10]. Notably, most of the prepared HPSs are composed of single shells. These single-shelled HPSs commonly suffer from low volume occupying rate (V_active/V_total) and limit the further improvement of electrochemical performance [11]. Recently, the attempts to fabricate multi-shelled HPSs have been proposed to circumvent this issue. For example, Shen et al. synthesized NiCo₂S₄ ball-in-ball hollow structures with an enhanced specific capacitance of 705 F g⁻¹ at 20 A g⁻¹ compared with that of single-shelled NiCo₂S₄ hollow structures (567 F g⁻¹ at 20 A g⁻¹) [12]. According to the report of Wang and his coworkers, double-shelled Co₃O₄ with higher volume occupying...
rate exhibited superior specific capacity to the single-shelled one with lower volume occupying rate [11]. Compared with conventional simple single-shelled counterparts, multi-shelled structures with larger surface area and higher volume occupying rate maximize the advantages of HPSs, which means the opportunity to improve physical/chemical properties of active materials and contribute to prominent electrocatalytic performance. Thus, the design of hollow structures with multiple shells is both significant and interesting for electrochemical sensors.

Among transition metal sulfides, CuS is a great candidate for electrochemical sensors, thanks to its effective redox pair of Cu$^{2+}$/Cu$^{3+}$ and metal-like electrical conductivity [13, 14]. In this work, 2-CuS NCs were synthesized through a Cu$_2$O-templated method. The prepared 2-CuS NCs have combined advantages of cage-like structure and double-shelled feature, and acquired large specific surface area, desirable porosities and increased volume-occupying rate. As expected, 2-CuS NCs/GCE presented higher electrocatalytic activity in terms of shorter response time (0.31 s), higher sensitivity (523.7 μA mM$^{-1}$ cm$^{-2}$), and lower LOD (0.15 μM) compared with single-shelled CuS nanocages modified GCE (1-CuS NCs/GCE).

**Methods/Experimental**

**Reagents**

CuCl$_2$·2H$_2$O, Na$_2$S, Na$_2$S$_2$O$_3$·5H$_2$O, Na$_2$HPO$_4$, polyvinylpyrrolidone (PVP, Mw = 40,000), and NaOH were purchased from Chengdu Kelong Chemical Reagent Corporation. Glucose (Glu.), dopamine (DA), lactose (Lac.), fructose (Fruc.), L-ascorbic acid (AA), uric acid (UA), and Nafion solution (5 wt% in mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich without further purification.

**Preparation of Cu$_2$O Templates**

Cu$_2$O templates were obtained according to our previous work [15]. Sixty milliliters of NaOH solution (2 M) was dropped into the stirred CuCl$_2$·2H$_2$O (600 mL, 0.01 M) at 55 °C. After 30 min of reaction, 60 mL AA (0.6 M) was added into the above solution. The brickred products were washed and collected by concentration after 3 h, followed by drying in vacuum at 40 °C for 12 h.

**Preparation of 2-CuS NCs**

Briefly, 15 mg of Cu$_2$O templates were dispersed into a mixed solution of water and alcohol (15 mL, volume ratio 1:1). After fully stirred, 0.45-mL Na$_2$S (0.086 M) was added into the solution. The sulfidation lasted for 30 s, and then Cu$_2$O@CuS products were collected by centrifugation. Next, Cu$_2$O@CuS products were dispersed into 15 mL of mixed solution of water and alcohol (1:1), and 3 mL Na$_2$S$_2$O$_3$ (1 M) was added to etch Cu$_2$O for 1 min. After a repeated sulfidation process for 2 min, Cu$_2$O templates were completely etched by Na$_2$S$_2$O$_3$ (1 M) for 1 h. The final products were washed and collected by centrifugation, and then dried in vacuum at 60 °C for 12 h. 1-CuS NCs samples were obtained without a repeated sulfidation process (see FESEM and TEM images in Additional file 1: Figure S1).

**Electrochemical Measurements**

All electrochemical measurements were carried out in 0.1 M phosphate solution (PBS) on an electrochemical workstation (ψIII Autolab). The modified GCEs, Ag/AgCl, and Pt electrodes were considered as working electrodes, reference electrode, and the counter electrode, respectively. GCEs (Φ = 3 mm) were firstly polished by 1, 0.5, and 0.05 μm alumina slurry. Then, the polished GCEs were successively cleaned with diluted HNO$_3$, water, and ethanol under ultrasonic. Afterward, 5 mg products (2-CuS NCs or 1-CuS NCs) were dispersed into a mixture of 0.9 mL water and 0.1 mL Nafion. Five microliters of suspension was then dropped onto pretreated GCEs and dried at room temperature. The modified GCEs were denoted as 2-CuS NCs/GCE and 1-CuS/GCE, respectively.

**Apparatus and Instruments**

Crystal structures of the samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2400). The compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) with the C 1s peaks (284.8 eV) as an internal standard. The morphologies were observed via field emission scanning electron microscope (FESEM, SU8020) and high-resolution transmission electron microscope (HRTEM, FEI20). Brunauer-Emmett-Teller (BET, Belsort-max) was utilized to analyze the specific surface area and pore structure.

**Results and Discussions**

**Characterizations of the Products**

Schematic illustration of synthetic process for 2-CuS NCs is depicted in Fig. 1. Firstly, Cu$_2$O templates were evenly distributed into the mixed solution of water and alcohol (volume ratio 1:1) under the assistance of ultrasonic. The sulfidation process was driven by S$^{2-}$ ions released from Na$_2$S, and a thin layer of CuS was formed around Cu$_2$O templates (reaction 1). Then, S$_2$O$_3^{2-}$ ions were introduced and the etching of
Cu$_2$O occurred (reaction 2) due to soft interaction between Cu$^+$ and S$_2$O$_3^{2-}$ [16], resulting in the formation of gap between CuS and Cu$_2$O. Afterwards, the above-prepared Cu$_2$O@CuS structure was sulfurized for 2 min to generate the inner CuS shell around the residual Cu$_2$O templates. Finally, 2-CuS NCs were obtained by complete etching of Cu$_2$O templates for 1 h using S$_2$O$_3^{2-}$ ions. The coordinated control of etching rate of Cu$_2$O and precipitation of CuS led to the formation of well-defined 2-CuS NCs. TEM images of the products obtained at different stages are also displayed in Fig. 1 (inset a–d). The observed formation process agreed well with the above-deduced mechanism.

\[
\text{Cu}_2\text{O} + \text{S}^{2-} + \text{O}_2 + 4\text{H}_2\text{O} \rightarrow 4\text{CuS} + 8\text{OH}^- \quad (1)
\]

\[
\text{Cu}_2\text{O} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow [\text{Cu}_2(\text{S}_2\text{O}_3^{2-})]_x + 2\text{OH}^- \quad (2)
\]

As shown in Fig. 2a, all diffraction peaks of final products agreed well with PDF#06-0464, and no diffraction peaks of Cu$_2$O was observed, indicating successful preparation of hexagonal CuS. Furthermore, the detailed information on chemical compositions and electronic states of the final products was measured by XPS. The survey spectroscopy demonstrated Cu 2p and S 2p peaks (Fig. 2b), revealing the main composition of the samples. As depicted in Fig. 2c, the two major peaks at 931.8 eV and 951.7 eV were assigned to Cu 2P$_{3/2}$ and Cu 2P$_{1/2}$, respectively. The binding energy separation was about 20 eV, which was the typical characteristic of Cu$^{2+}$ in CuS [8]. Besides, two satellite (Sat.) peaks at 944.1 eV and 962.5 eV were observed in the Cu 2p spectrum, further demonstrating the existence of Cu$^{2+}$ [17]. In the S 2p spectrum (Fig. 2d), the typical peak from 160 to 164 eV was fitted by two peaks located at 161.8 eV and 162.9 eV, which was the feature of S-Cu [8, 18]. A characteristic peak at 168.9 eV also indicated the existence of metal sulfides [19]. The results of XRD and XPS data confirmed the successful preparation of hexagonal CuS.

In Additional file 1: Figure S2, Cu$_2$O templates exhibited exquisite cubic morphology with an average edge length about 500 nm. As shown in Fig. 3a, the prepared CuS exactly duplicated structural and morphological features of Cu$_2$O templates. The shell of CuS was porous and composed of randomly assembled nanoparticles (Fig. 3b). As shown in Fig. 3c, the broken cube revealed cage-like feature and double-shelled structure of CuS products. The internal CuS NCs further increased the contact area between
electrode and electrolyte to provide more electroactive sites, leading to enhanced electrocatalytic activity. The detailed structure of 2-CuS NCs is studied by TEM. As shown in Fig. 3d, the final CuS products presented a typical double-shelled cage-like structure compared with 1-CuS NCs (inset of Fig. 3d). Notably, the inner CuS NCs were not in the central place, and an obvious gap between the two cages was observed (Fig. 3e). As shown in Fig. 2f, the thicknesses of outer and inner shells were about 60 nm and 8 nm, respectively. The decrease of the inside shell thickness can be attributed to the shielding effect of the outside CuS shell. Two distinct lattice fringes of 0.190 nm and 0.282 nm observed in Fig. 3g were consistent with (110) and (103) crystal planes of CuS (PDF#06-0464), respectively. Simultaneously, the selected area electron diffraction pattern in the inset revealed polycrystalline feature of 2-CuS NCs. The results of FESEM and TEM demonstrated the successful preparation of 2-CuS NCs.

To verify the porosity, N\textsubscript{2} absorption-desorption isothermal and corresponding pore size distributions are recorded in Fig. 3h, i. The curve of 2-CuS NCs was considered as a 4-type isotherm with a H3 hysteresis loop, suggesting the existence of mesopores [20]. The pore size distribution of 2-CuS NCs (inset of Fig. 3h) ranging from 2.4 to 18.5 nm further confirmed the mesoporous feature. Especially, the pore volumes of 2-CuS NCs and 1-CuS NCs were estimated as 0.045 cm\textsuperscript{3} g\textsuperscript{-1} and 0.011 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. The mesopores served as suitable channels for ion diffusion and played a key role in facile mass transport during electrocatalytic reactions [21]. Moreover, the surface area of 2-CuS NCs (28.3 m\textsuperscript{2} g\textsuperscript{-1}) was much larger than that of 1-CuS NCs (10.03 m\textsuperscript{2} g\textsuperscript{-1}). Furthermore, 2-CuS NCs also had larger surface area compared with the previously reported CuS materials, including nanosheets [22], nanoplates [23], nano-flowers [24], and nanospheres [25]. Generally, high porous volume and large surface areas benefited the accessibility of reactant molecules to the inner shells of 2-CuS NCs, leading to enhanced electrocatalytic activity.

**Electrochemical Performance of 2-CuS NCs/GCE**

Cyclic voltammetry (CV) was performed to study the electrocatalytic activity of 2-CuS NCs/GCE towards AA. Figure 4a displays the CVs of bare GCE, 1-CuS NCs/GCE, and 2-CuS NCs/GCE in the absence and presence of 50 \(\mu\)M AA. Obviously, bare GCE had a small background current, whereas the modified GCE had much better conductivity compared with bare GCE. After the addition of 50 \(\mu\)M AA, extremely weak current response was investigated on bare GCE.
Fig. 4  

a: CVs of 2-CuS NCs/GCE, 1-CuS NCs, and bare GCE at 50 mV s$^{-1}$.  
b: The catalytic mechanism of AA oxidation on 2-CuS NCs/GCE.  
c: Nyquist plot of 2-CuS NCs/GCE and 1-CuS NCs/GCE.  
d: $i$-$t$ response towards 25-$\mu$M AA.
interior cavities [18, 26]. Sued from enhanced porosity of the shells and cal, demonstrating a low ion diffusion resistance is the imaginary axis for 2-CuS NCs/GCE was subverted. Notably, the slope in the low frequency region alongtron collection efficiency and elevated electron transfer resistance can be ascribed to the high electron lower electron transfer resistance. The lower electron semicircle than that of 1-CuS NCs/GCE, revealingance. Obviously, 2-CuS NCs/GCE showed a smaller portion in low frequency. The semicircle corresponded to the electron transfer resistance, and the linear portion was related to the ion diffusion resistance. Obviously, 2-CuS NCs/GCE showed a smaller semicircle than that of 1-CuS NCs/GCE, revealing lower electron transfer resistance. The lower electron transfer resistance can be ascribed to the high electron collection efficiency and elevated electron transfer rate provided by the double-shelled structure. Notably, the slope in the low frequency region along the imaginary axis for 2-CuS NCs/GCE was subvertical, demonstrating a low ion diffusion resistance issued from enhanced porosity of the shells and interior cavities [18, 26].

In order to study the kinetics advantages, electrochemical impedance spectroscopy (EIS) was recorded. As shown in Fig. 4c, the Nyquist plots were consisted of a semicircle portion in high frequency and a linear portion in low frequency. The semicircle corresponded to the electron transfer resistance, and the linear portion was related to the ion diffusion resistance. Obviously, 2-CuS NCs/GCE showed a smaller semicircle than that of 1-CuS NCs/GCE, revealing lower electron transfer resistance. The lower electron transfer resistance can be ascribed to the high electron collection efficiency and elevated electron transfer rate provided by the double-shelled structure.

In Additional file 1: Figure S4, the effect of scan rates on CVs of 2-CuS NCs/GCE was recorded. The redox peak current linearly changed with square root of scan rates (inset), indicating a diffusion-controlled process on the surface of 2-CuS NCs/GCE [27]. Additional file 1: Figure S5a and Figure S5b displayed the chronoamperometry (CA) response for 1-CuS NCs/GCE and 2-CuS NCs/GCE in 0 mM and 0.5 mM of AA, respectively. In a static AA solution, a large diffusion current was produced once the potential was applied in the CA because of the high concentration gradient. Then, the diffusion current gradually decreased with the decrease of concentration gradient. Finally, a stable diffusion current was maintained due to the stable diffusion of AA from solution to electrode. The diffusion coefficient \(D\) of AA can be calculated according to Cottrell’s equation [28]:

\[
I_{\text{cat}} = nFAD^{1/2}C_0\tau^{-1/2}t^{-1/2}
\]

where \(I_{\text{cat}}\) is the current of the electrode in 0.5 mM AA, \(n\) represents the number of electrons transferred, \(F\) is the Faraday constant, \(A\) is the area of the electrode, \(C_0\) is the substrate concentration, \(D\) is the diffusion coefficient, and \(t\) expresses the elapsed time.

In Additional file 1: Figure S5c showed the plots of \(I_{\text{cat}}/I_L\) vs. \(t^{1/2}\) according to the CA curves. Thus, the value of \(D\) for 2-CuS NCs/GCE could be calculated to be 2.77 \(\times\) 10^{-5} \(\text{cm}^2\text{s}^{-1}\), which was larger than 1-CuS NCs/GCE (4.16 \(\times\) 10^{-7} \(\text{cm}^2\text{s}^{-1}\)). The catalytic rate constant \(K_{\text{cat}}\) of AA oxidation can be calculated according to the following equation:

\[
I_{\text{cat}}/I_L = (nk_{\text{cat}}C_0)^{1/2}
\]

where \(I_{\text{cat}}\) and \(I_L\) are the diffusion currents of the electrode in 0.5 mM and 0 mM AA, respectively. \(C_0\) is the substrate concentration, and \(t\) is the elapsed time. According to Additional file 1: Figure S5d, the value of \(K_{\text{cat}}\) was estimated to be 0.08 \(\times\) 10^{-3} \(\text{M}^{-1}\text{s}^{-1}\), which was larger than that of 1-CuS NCs/GCE (0.02 \(\times\) 10^{-3} \(\text{M}^{-1}\text{s}^{-1}\)). Generally, the elevated values of \(D\) and \(K_{\text{cat}}\) would result in higher electrocatalytic activities.

Detection of AA

To obtain the optimal working potential, \(i-t\) curves at different potentials are gathered in Fig. 4d. Obviously, the current response at 0.25 V was higher than that at 0.2 V, and the relationship between concentration and response current at 0.25 V showed a better linearity than 0.3 V (inset of Fig. 4d). Moreover, severe interference to the oxidation of AA easily emerged at more positive potential, so 0.25 V was selected as the optimal working potential. As demonstrated in Fig. 5a, 2-CuS NCs/GCE exhibited superior amperometric response to 1-CuS/GCE. Once AA was added to the electrolyte, the response current immediately reached 95% of the steady-state current within 0.31 s for 2-CuS NCs/GCE and 0.46 s for 1-CuS NCs/GCE (Fig. 5b), suggesting that 2-CuS NCs/GCE had faster response towards AA. As shown in Fig. 5c, the response current linearly increased with AA concentrations between 5 and 1200 \(\mu\text{M}\), and the regression equation was expressed as \(I (\mu\text{A}) = 0.037C (\mu\text{M}) + 0.06 (R^2 = 0.996)\). The sensitivity was calculated as 523.7 \(\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}\), which was higher than that of 1-CuS/GCE (324.4 \(\mu\text{A}\text{mM}^{-1}\text{cm}^{-2}\)). Furthermore, the 2-CuS NCs/GCE presented a LOD as low as 0.15 \(\mu\text{M}\) at signal-to-noisy ratio of 3. The enhanced electrocatalytic performance of 2-CuS NCs can be attributed to the coupling of two hollow structures (Fig. 5d).

---

Larger surface areas and more active sites were acquired to improve redox reactions. This point was proved by BET analysis; (2) larger volume occupying rate and ample mesopores effectively promoted the
utilization of the double-shelled cage-like structure; (3) the two thin shells of 2-CuS NCs accelerated the transfer rate of catalytic electron, which was confirmed by above EIS analysis. Compared with the previously reported literatures, 2-CuS NCs/GCE exhibited higher electrochemical performance in terms of high sensitivity and low LOD as shown in Table 1 [29–35], demonstrating that 2-CuS NCs was ideal for analytical sensing of AA.

Selectivity, Reproducibility, and Stability of the 2-CuS NCs/GCE

The selectivity, reproducibility, and stability were also of great importance in electrochemical sensing of AA. The common interfering species were injected during the $i$-$t$ measurement to evaluate the selectivity. As shown in Fig. 6a, no significant interference currents were observed, indicating ultrahigh selectivity. Moreover, the response current for the second addition of AA still retained 91% of its first injection. The attenuation in response current would be ascribed to the adsorption of trace interfering species or intermediate products on the electrode. As depicted in Fig. 6b, the response current of five different electrodes towards 100 μM AA was recorded, and the relative standard deviation (RSD) was 3.6%, suggesting good reproducibility. In terms of long-term stability, only 15% of the current

![Table 1](https://www.nanoscaleresearchletters.com/content/15/1/44)

**Table 1** Comparison of 2-CuS NCs/GCE with previously reported nonenzymatic AA sensors

| Electrodes          | Linear range (mM) | Sensitivity (μA mM$^{-1}$ cm$^{-2}$) | LOD (μM) | Reference     |
|---------------------|-------------------|-------------------------------------|----------|---------------|
| EMGON 5-1/CPE       | 0–1               | 78.63                               | 1.54     | [29]          |
| Au-PANI/GCE         | 0.01–12           | 25.69                               | 8.2      | [30]          |
| CF/ZnO/GCE          | 0.6–1.8           | –                                   | 156.7    | [31]          |
| Ag HN/GCE           | 0.00017–1.8       | 35.512                              | 0.06     | [32]          |
| GNP-Ag/GCE          | 0.001–0.2         | –                                   | 0.88     | [33]          |
| RO/Ni               | 0.57–5.7          | 296                                 | –        | [34]          |
| Bi$_2$S$_3$/TNF/GCE | 1–10              | 38                                  | –        | [35]          |
| 2-CuS NCs/GCE       | 0.005–1.2         | 523.7                               | 0.15     | This work     |

**EMGON** electroactive mesoporous materials organosilica nanocomposites, **CPE** carbon paste electrode, **Au-PANI** polyaniline, **CF** carbon fiber, **HN** hierarchical nanostructures, **GNP** graphene nanoplatelets, **RO** ruthenium oxide, **TNF** titanate nanofibers
response was lost over a long period of 1000 s (Fig. 6c). As shown in Fig. 6d, the response current of 2-CuS NCs/GCE still retained 91.2% of the initial value after 15 days. Moreover, 2-CuS NCs still maintained cubic structure after testing (inset), demonstrating remarkable stability. The excellent stability could be ascribed to the double-shelled highly porous feature, which alleviated the structure strain associated with the volume expansion during electrochemical testing.

Conclusions
In brief, we have succeeded in preparation and application of 2-CuS NCs in enzyme-free AA electrochemical sensor. Optimized double-shelled cage-like structure for CuS NCs afforded large specific surface area, increased volume occupying rate, enough diffusion channels, and confined electron transfer routes, leading to prominent electrocatalytic activity. The unique structure yielded 2-CuS NCs/GCE with short response time (0.31 s), high sensitivity (523.7 μA mM⁻¹ cm⁻²), low LOD (0.15 μM), reasonable selectivity, and acceptable reproducibility towards AA. Overall, 2-CuS NCs look promising as effective electrocatalysts for electrochemical sensing of AA.

Supplementary information
Supplementary information accompanies this paper at https://doi.org/10.1186/s11671-020-3278-2.

Additional file 1: Figure S1. (a) FESEM image and (b) TEM image of 1-CuS NCs. Figure S2. (a) FESEM image of Cu₂O. Figure S3. CVs of bare GCE at 50 mV s⁻¹. Figure S4. CVs of 50 μM AA on 2-CuS NCs/GCE at different scan rates (16, 25, 36, 49, 64, 81 and 100 mV s⁻¹). Figure S5. Chronoamperograms of (a) 2-CuS NCs/GCE and (b) 1-CuS NCs/GCE in the absence and presence of 0.5 mM AA; (c) Calibration curve of Icat versus t⁻¹/₂; (d) Calibration curve of Icat/Iref versus t¹/₂.

Abbreviations
1-CuS NCs: Single-shelled CuS nanocages; 2-CuS NCs: Double-shelled CuS nanocages; AA: Ascorbic; AA: L-ascorbic acid; BET: Brunauer-Emmett-Teller; CA: Chronoamperometry; CV: Cyclic voltammetry; DA: Dopamine; EIS: Electrochemical impedance spectroscopy; FESEM: Field emission scanning electron microscope; Fruc: Fructose; GCE: Glassy carbon electrode; Glu: Glucose; HRTEM: High-resolution transmission electron microscope; Lac: Lactose; LOD: Limit of detection; PBS: Phosphate solution; Sat.: Satellite; UA: Uric acid; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

Acknowledgements
We greatly appreciate the National Natural Science Foundation of China, the Basic and Frontier Research Program of Chongqing Municipality, the Natural Science Foundation of Yongchuan, the Academician project of Chongqing Science and Technology Bureau, and the Scientific and Technological Research Program of Chongqing Municipal Education Commission.

Authors’ Contributions
TY and LLT designed the experiment and wrote the paper. EMZ did the electrochemical measurements. DDC prepared the materials and made the characterizations. YL provided financial supports. All authors read and approved the final manuscript.
Funding
This work was funded by the National Natural Science Foundation of China (21403020, 51503022), the Basic and Frontier Research Program of Chongqing Municipality (cstc2016jcyjAX0014, cstc2019jcyj-msxmX003), and cstc2018jcyj-A15020, the Natural Science Foundation of Chongqing (cstc2017jcyj-B2602), the Academician project of Chongqing Science and Technology Bureau (cstc2018jcyj-yszx0003), and the Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJQN20181315).

Availability of Data and Materials
The datasets are available without restriction.

Competing Interests
The authors declare that they have no competing interests.

Author details
1 School of Materials and Energy, Southwest University, Chongqing, People's Republic of China. 2 Chongqing Key Laboratory of Materials Surface and Interface Science, Chongqing, People's Republic of China. 3 Chongqing Municipal Key Laboratory of Micro/Nano Materials Engineering and Technology, Chongqing, People's Republic of China. 4 Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing, People's Republic of China. 5 School of Science, Chongqing University of Posts and Telecommunication, Chongqing, People's Republic of China.

Received: 21 December 2019 Accepted: 4 February 2020
Published online: 18 February 2020

References
1. Jin LH, Zhang ZH, Zhuang ZH, Meng Z, Li C, Shen YH (2016) PdPt bimetallic alloy nanowires-based electrochemical sensor for sensitive detection of ascorbic acid. RSC Adv 6:20008-20015
2. Jia A, Kang MY, Cha A, Jang HS, Shim JH, Lee NS, Kim MH, Lee YM, Lee CM (2014) Nonenzymatic amperometric sensor for ascorbic acid based on hollow gold/ruthenium nanoshells. Anal Chim Acta 819: 94–101
3. Liu H, Na WD, Liu ZP, Chen XQ, Su XG (2017) A novel turn-on fluorescent sensing strategy for ascorbic acid using graphene quantum dots as fluorescent probe. Biosens Bioelectron 92:229–233
4. Chen J, Ge J, Zhang L, Li ZH, Li JJ, Sun YJ, Qu LB (2016) Reduced graphene oxide nanosheets functionalized with poly(styrene sulfonate) as a peroxidase mimetic in a colorimetric assay for ascorbic acid. Microchim Acta 183:1847–1853
5. Yang T, Tian LL, Zhou EM, He GG, Tian LL, Cai YH, Wu SP, Su YY, Yan HQ, Pu WR, Jk Z, Li L (2018) Sensitive nonenzymatic electrochemical glucose detection based on hollow porous NiO. Nanoscale Res Lett 13:1–3
6. Guo CY, Li H, Zhang X, Huo HH, Xu CL (2015) 3D porous CNT/MnO2 composite electrode for high-performance enzymeless glucose detection and supercapacitor application. Sens Actuators B: Chem 206:407–414
7. Gopi CVVM, Somasekha A, Reddy AE, Kim SK, Kim HJ (2018) One-step facile hydrothermal synthesis of FeO2@LiCoO2 composite as excellent supercapacitor electrode materials. Appl Surf Sci 435:462–467
8. Pan P, Lei YT, Lu SJ, Wang Q, Liu QB (2015) Three-dimensional roselike α-Ni(OH)2 assembled from nanosheet building blocks for non-enzymatic glucose detection. J Mater Sci Mater Electron 26:453–460
9. Yin DD, Bo XI, Liu J, Guo LP (2018) A novel enzyme-free glucose and H2O2 sensor based on 3D graphene aerogels decorated with Ni,N nanoparticles. Anal Chim Acta 1038:11–20
10. Qin Y, Kong XG, Lei DQ, Lei XD (2018) A facial grinding method for the synthesis of high-purity CuS nanosheets. Ind Eng Chem Res 57: 2579–2584
11. Podili S, Geetha D, Ramesh PS (2017) One-pot synthesis of CTAB stabilized mesoporous cobalt doped CuS nano flower with enhanced pseudocapacitive behavior. J Mater Sci: Mater Electron 28:15387–15401
12. Kannan PK, Rout CS (2015) High performance non-enzymatic glucose sensor based on one-step electrodeposited nickel sulfide. Chem Eur J 21:9355–9359
13. Venkadesh A, Radhakrishnan S, Mathiyarasu J (2017) Eco-friendly synthesis and morphology-dependent superior electrocatalytic properties of CuS nanostructures. Electrochem Acta 246:544–552
14. Tian LL, He GG, Chen MJ, Wang JB, Yao YC, Bai X (2018) Hollow porous Ni (OH)2 architecture for highly sensitive and reliable stability enzyme-free glucose sensors. Nanoscale Res Lett 13:342–351
15. Wang SP, Zheng H, Li YT, Peng RF, Feng B (2015) Electrochemical sensor based on reduced graphene oxide and copper sulfide hollow nanoparticles. RSC Adv 5:207318–207325
16. Tian LL, He GG, Chen MJ, Wang JB, Yao YC, Bai X (2018) Hollow porous Ni (OH)2 architecture for highly sensitive and reliable stability enzyme-free glucose sensors. Nanoscale Res Lett 13:342–351
17. Wang X, Wu XL, Guo YG, Zheng YT, Cao XQ, Ma Y, Yao JN (2010) Synthesis and lithium storage properties of Co3O4 nanosheet-assembled multishelled hollow spheres. Adv Funct Mater 20:1680–1686
18. Shen LF, Yu L, Wu HB, Yu XY, Zhang XG, Lou XW (2015) Formation of nickel cobalt sulfide ball-in-ball hollow spheres with enhanced electrochemical pseudocapacitive properties. Nat Commun 6:1–8
19. An CH, Ni Y, Wang ZF, Li XD, Liu XZ (2018) Facile fabrication of CuS micro-flower as high durable sodium-ion battery anode. Inorg Chem Front 5:1045–1052
20. Radhakrishnan S, Kim HJ, Kim BS (2015) A novel CuS microflower superstructure based sensitive and selective nonenzymatic glucose detection. Sens Actuators B: Chem 233:93–99
electroanalysis of dopamine and ascorbic acid in biological samples. Appl Surf Sci 449:558–566
34. Lee YG, Liao BX, Weng YC (2017) Ruthenium oxide modified nickel electrode for ascorbic acid detection. Chemosphere 173:512–519
35. Cabrita JF, Ferreira VC, Monteiro OC (2014) Titanate nanofibers sensitized with nanocrystalline Bi2S3 as new electrocatalytic materials for ascorbic acid sensor applications. Electrochim Acta 135:121–127

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.