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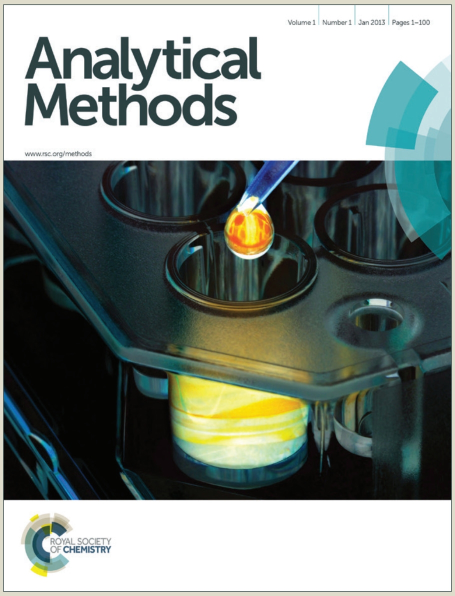

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ARTICLE

A Highly-Sensitive Electrochemical Sensor Based on Cu/Cu_2O@Carbon Nanocomposite Structures for Hydrazine Detection†

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We report a simple and large-scale fabrication of carbon-coated Cu/Cu_2O nanocomposite material (Cu/Cu_2O@carbon) and their application as sensing materials for hydrazine detection in a neutral medium. The Cu/Cu_2O@carbon nanocomposite structures were successfully synthesized using the facile, cost-effective calcination method. The morphology, crystalline structure, and composition of the prepared Cu/Cu_2O@carbon were characterized by scanning electron microscopy, X-ray diffraction, energy dispersive spectroscopy and high-resolution transmission electron microscopy. The hydrazine electrochemical sensor was fabricated by painting Cu/Cu_2O@carbon on glassy carbon electrode and immobilized using Nafion. By optimizing the Cu/Cu_2O@carbon modified quantity and evaluating the performance in cyclic voltammograms and amperometry technique, we demonstrated an optimal hydrazine electrochemical sensor with a high sensitivity of 2.37 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$, an excellent linear concentration range of 0.25 μM to 800 μM, and a low detection limit of 0.022 μM.

Introduction

In recent years, great attention has been paid to the hydrazine detection. This is ascribed to the essentiality of reliable and fast determination of hydrazine in the fields of environmental monitoring, industrial production and food industry.[1-4] Fortunately, the method of electrochemical detection offers an opportunity for rapid, simple, low-cost, and high-precision methodologies.[5,6] Therefore, more and more research on hydrazine electrochemical detection was conducted, and many noble metal nanoparticles have been used to fabricate electrochemical sensor.[7-12] Although noble metals such as Pd, Au, Pt and Ag are very effective in the determination of hydrazine, they are too expensive for practical applications.

Copper and its derivatives are inexpensive material and have been widely used, especially as sensing materials, owning to its high electrical conductivity, good catalytic activity and low cost.[13-16] In recent years, copper-based nanomaterials have been used to make electrochemical sensors for hydrazine sensing. The electrode materials which were used in these hydrazine electrochemical sensors are usually CuO, CuS or Cu/CuO nanomaterials,[17-19] but the overall performances of these sensors are poor. As an important copper oxide, cuprous oxide (Cu_2O) demonstrates a direct band gap of 2.17 eV,[20] and has potential application in photochemical catalysis,[21] and electrochemical sensor,[22-24] owning to its unique optical property and catalytic characteristic.[25,26] Thus, considering the potential applications of copper-based materials, we used the Cu/Cu_2O composite to fabricate hydrazine electrochemical sensor. To the best of our knowledge, there are few reports concerning the fabrication of hydrazine electrochemical sensor based on Cu_2O or Cu/Cu_2O nanomaterials. The Cu or Cu_2O nanomaterials are unstable in an aqueous solution containing hydrazine based electrochemical environment according to the pourbaix diagram.[27,28] Thus, the deteriorations of conductivity and catalysis caused by the instability of Cu and Cu_2O will affect the performance of the electrochemical sensor. Therefore, the key issue to have a high performance Cu/Cu_2O based electrochemical sensor is the stability of electrode materials. Until now, many chemical and physical methods have been used to protect the Cu or Cu_2O from aggressive environment by forming the protecting shell structure around the copper-based nanoparticles, which include the techniques of arc-discharge,[29] detonation decomposition,[30] hollow-cathode glow discharge,[31] and pyrolysis of copper phthalocyanine dye.[32] However, these methods are difficult to achieve mass production and meet the commercial applications, because precise control of these methods variables is difficult and expensive. Therefore, we used the calcination method which could achieve mass production in low cost to synthesize the carbon-coated Cu/Cu_2O nanoparticle composite material (Cu/Cu_2O@carbon).

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In this study, we prepared an electrochemical sensor based on Cu/Cu_2O@carbon and accomplished the electro-oxidation of hydrazine for hydrazine detection. The effect of Cu/Cu_2O@carbon modified quantity on hydrazine sensing was studied by CV, EIS, and amperometry techniques. The experimental results indicate that the optimized hydrazine electrochemical sensor possesses a high sensitivity of 2.37 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$ and a large linear response range of 0.25-800 µM.

Experimental

Preparation of Cu/Cu_2O@carbon nanocomposite structures

The Cu/Cu_2O@carbon nanocomposite structures were prepared by using cellulosic fibers as the template and $CuSO_4$ as the metal source. Firstly, the cellulosic fibers were soaked in $CuSO_4$ solution for 2 hours to adsorb Cu^{2+} sufficiently. Then the copper-impregnated cellulosic fibers were calcined for carbonization at 350 °C under N_2 for 2 hours and under steam for 1 hour.[33] The Cu/Cu_2O nanoparticles and their carbon shells formed simultaneously during the carbonization. After cooled to room temperature inside the furnace, the carbonized fibers were ground with a grinding mill to reduce their size.

Material structure characterization

The morphology of the Cu/Cu_2O@carbon nanocomposite structures were examined by scanning electron microscopy (SEM, JSM-7001F). The crystallinity and crystal phases were measured by X-ray powder diffraction (XRD, Hao Yuan DX2700, Cu-Kα_1, λ=1.5406 Å) in the range of 10°-80°. The chemical composition was analyzed using energy dispersive spectroscopy (EDS, QUANTAX200) with a 15 kV accelerating voltage. The further microstructure information of the as-synthesized Cu/Cu_2O@carbon was examined by high-resolution transmission electron microscopy (JEM-2100F).

Fabrication and detection methodology of the Cu/Cu_2O@carbon based electrochemical sensor

The hydrazine electrochemical sensor was fabricated by modifying Cu/Cu_2O@carbon on glassy carbon electrode (GCE) and immobilized by Nafion (0.5%). Prior to modification, the GCE surface was polished by using alumina particles with the diameter of 1.0 µm, 0.3 µm and 0.05 µm, sequentially, until reached a mirror-like surface. Then, the GCE was sonicated in diluted nitric acid (1:1), acetone, anhydrous ethanol, and deionized water, respectively. The Cu/Cu_2O@carbon (20 mg) was dispersed in ethanol (3 mL) by ultrasound. After that, certain amount of Cu/Cu_2O@carbon slurry was dropped on the GCE surface and dried at room temperature for 1 h. Finally, 0.5 wt% Nafion solution (5 µL) was coated onto the treated GCE surface in order to immobilize the Cu/Cu_2O@carbon. For comparison, the GCE modified with only Nafion and Nafion/carbon was also prepared. The testing hydrazine electrochemical sensor and reference sensors have been fabricated with the structures of Nafion/Cu/Cu_2O@carbon/GCE, Nafion/GCE, and Nafion/carbon/GCE, respectively. An electrochemical workstation (Zahner, Zennium, IM6) was used to evaluate the performance of the prepared hydrazine electrochemical sensors. The fabricated sensors, Pt wire and Ag/AgCl (3.5 M KCl) were used as the working electrode, the counter electrode and the reference electrode, respectively. All the experiments were carried out in an electrochemical cell which was filled with 100 ml 0.1 M phosphate buffer solutions (PBS, pH=7.4). The PBS was prepared by varying the ratio of NaH_2PO_4 to Na_2HPO_4.

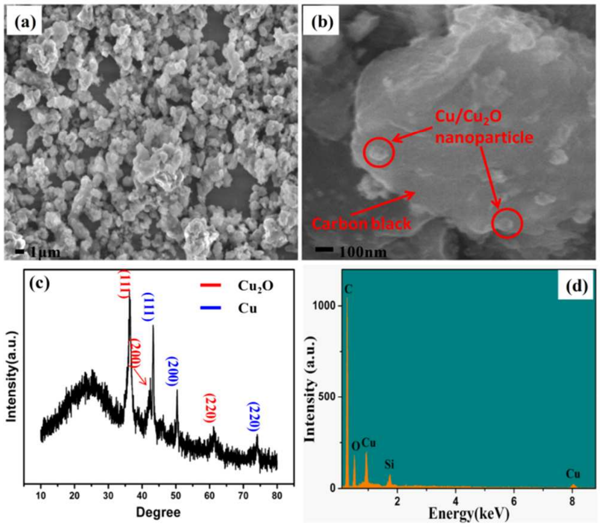

Fig. 1 The scanning electron microscopy (SEM) images (a, b), X-ray powder diffraction (XRD) (c), and energy dispersive spectroscopy (EDS) (d) of the prepared Cu/Cu_2O@carbon nanocomposite structures.

Results and discussion

Characterization of the Cu/Cu_2O@carbon nanocomposite structures

The morphology and composition of the as-prepared Cu/Cu_2O@carbon nanocomposite structures are shown in Fig. 1. The synthesized Cu/Cu_2O@carbon possesses an irregular block shape in the size of 1-3 µm as shown in Fig. 1a. Fig. 1b reveals that there are small amount of nanoparticles on the surface of the amorphous carbon block (carbon black) with a diameter of about 80-100 nm, but most of the copper-based nanoparticles were wrapped by the carbon black, so we cannot see them in the SEM images. The crystallinitiy and phase purity of the as-prepared nanoparticles were carried out by XRD. Fig. 1c shows the prominent peaks at 43.31°, 50.40° and 74.15°, which correspond to the (111), (200) and (220) planes of the Cu nanoparticles (JCPDS card No. 85-1326),[34] respectively. The peaks at 36.30°, 42.44° and 61.25° can be ascribed to the reflection of (111), (200), and (220) planes of Cu_2O nanoparticles (JCPDS card No. 78-2076).[35] And the broad peak at about 24° corresponds to the (002) graphitic planes of the carbon black.[36] The results indicate that the as-synthesized copper-based nanomaterials were coexisting substance of C, Cu and Cu_2O. Furthermore, the purity and composition of Cu/Cu_2O@carbon were also investigated using

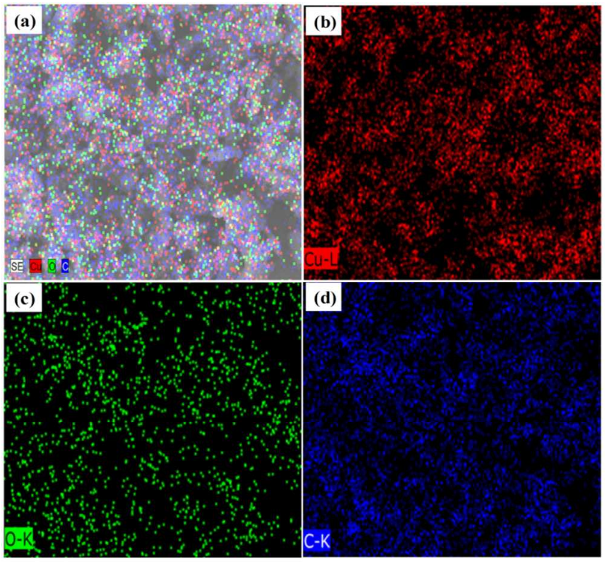

Fig. 2 The SEM image (a) and the corresponding elemental mapping images of copper (b), oxygen (c) and carbon (d) for the as-prepared Cu/Cu_2O@carbon.

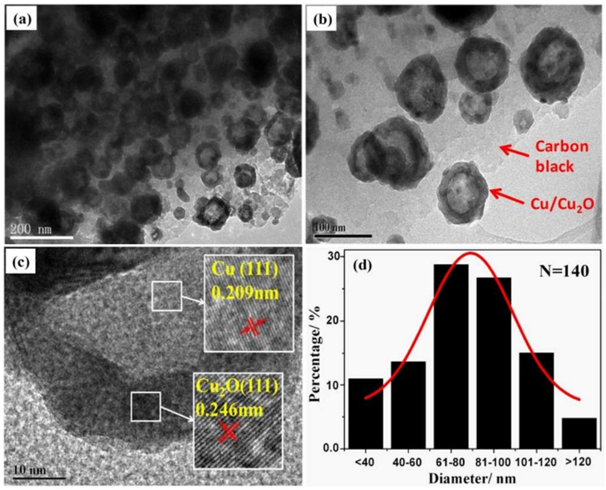

Fig. 3 TEM images of low-resolution (a, b) and high-resolution (c) of the Cu/Cu_2O@carbon; (d) size distribution of the copper-based nanoparticles.

EDS technique as shown in Fig. 1d. The measured results indicate that only C, Cu and O are involved in the products, and the Si is the substrate in experiment, which evidences that the Cu/Cu_2O@carbon possesses a high purity in composition.

The element mapping images of Cu/Cu_2O@carbon are shown in Fig. 2. Fig. 2b-2d depicts the distribution of different ions of Cu, O and C, which show that all of the elements (Cu, O and C) are uniformly distributed through entire material. Thus, the elemental mapping results further evidence that the as-synthesized Cu/Cu_2O@carbon are not only composed of high purity Cu, O and C, but also have a homogeneous composite material distribution.

The morphology and crystal structure of Cu/Cu_2O@carbon

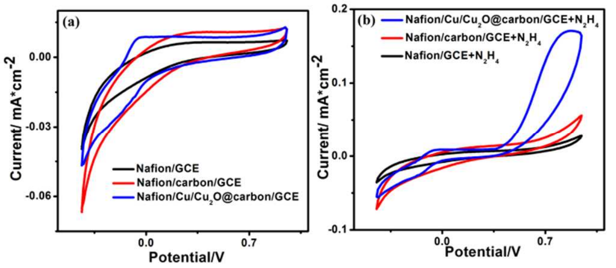

Fig. 4 Cyclic voltammograms of Nafion/GCE, Nafion/carbon/GCE and Nafion/Cu/Cu_2O@carbon/GCE in the condition of no hydrazine (a) and with 100 μM hydrazine (b) in 0.1 M PBS (pH=7.4) at the scan rate of 100 mV/s (vs. Ag/AgCl).

were further investigated by TEM and high-resolution TEM (HRTEM). The TEM images (Fig. 3a-3b) confirm that the obtained materials are granular in shape with copper based nanoparticles embedded in carbon black. Detailed structural analysis was performed by HRTEM and shown in Fig. 3c. The fringe analysis results show that lattice spacing values of 0.209 nm are corresponding to the interplanar spacing of (111) plane of the cubic phase of Cu. The lattice spacing of about 0.246 nm can be indexed to the (111) plane of cubic Cu_2O. The results suggest the as-synthesized nanoparticles are composed of crystalline Cu/Cu_2O. Based on above results of XRD, EDS, and HRTEM, we concluded that these synthesized nanoparticles which wrapped in carbon black are coexisting substance of Cu and Cu_2O. The size distribution of the nanoparticles was also summarized in Fig. 3d. The measured results reveal that about about 58% nanoparticles are within the diameter range of 60-100 nm.

Electrochemical characteristics of the prepared sensors

In order to study the electrocatalytic properties of Cu/Cu_2O@carbon for hydrazine, the cyclic voltammograms (CVs) response of the fabricated sensors toward hydrazine were investigated in 0.1M PBS (pH=7.4). No obvious oxidation peak was observed when Nafion/GCE, Nafion/carbon/GCE and Nafion/Cu/Cu_2O@carbon/GCE were exposed to PBS without hydrazine in the selected voltage range of -0.4-1.0 V as shown in Fig. 4a. When the hydrazine (100 μM) was introduced, the background current of Nafion/GCE and Nafion/carbon/GCE slight increased but no oxidation peaks emerged, which implied that hydrazine can't be electro-oxidized effectively on GCE or carbon/GCE (Fig. 4b). However, the CV for Nafion/Cu/Cu_2O@carbon/GCE demonstrated increased background current and oxidation peak when exposed to 100 μM hydrazine. And the anodic current increased starting from about 0.35 V, peaked around 0.805 V, indicating the Cu/Cu_2O@carbon based electrode exhibits a good catalytic performance towards hydrazine. In addition, there was no cathodic current peak which corresponds to hydrazine can be observed for the reducing reaction (the reverse sweep of CV), which evidences that the hydrazine oxidation reaction is irreversible under this condition. According to the previous reports,[37-39] a proposed possible reaction for hydrazine is $N_2H_4+5/2OH^-$—>$1/2N_3^-+1/2NH_3+5/2H_2O+2e^-$. A faster electron

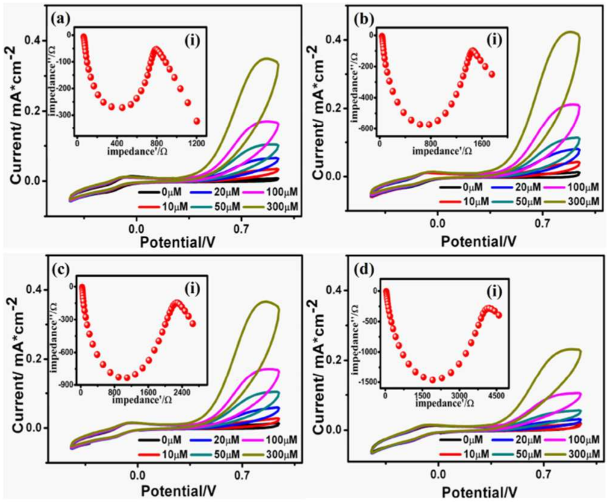

Fig. 5 Cyclic voltammograms in presence of 0 μM, 10 μM, 20 μM, 50 μM, 100 μM and 300 μM hydrazine in 0.1 M PBS (pH=7.4) at a scan rate of 100 mV/s (vs. Ag/AgCl) for Nafion/Cu/Cu_2O@carbon/GCE sensors which modified with different amounts of Cu/Cu_2O@carbon: 340 μg·cm^{-2} (a), 510 μg·cm^{-2} (b), 680 μg·cm^{-2} (c) and 1180 μg·cm^{-2} (d); Inset images: the electrochemical impedance spectroscopy of the fabricated sensors in 5 mM $K_3[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl from 100 kHz to 0.05 Hz at an ac amplitude of 5 mV under open-circuit potential conditions.

transfer reaction will lead to a sharper and well-defined peak in CVs. The experimental results indicate that Cu/Cu_2O@carbon based electrode has electrocatalytic effect on hydrazine oxidation reaction under current testing condition and can be used for hydrazine-sensing.

To evaluate the effect of Cu/Cu_2O@carbon loading quantity on the hydrazine detection, Nafion/Cu/Cu_2O@carbon/GCE sensors coated with different loading amounts of Cu/Cu_2O@carbon were fabricated and tested using electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CVs). From the results shown in Fig. 5, the higher oxidation current peaks were obtained as the hydrazine concentration increased for all of the fabricated sensors. In the presence of 300 μM hydrazine, the peaking catalytic current density values which obtained from sensors with Cu/Cu_2O@carbon loading levels of 340 μg·cm^{-2}, 510 μg·cm^{-2}, 680 μg·cm^{-2} and 1180 μg·cm^{-2} were 348.8 μA·cm^{-2}, 422.9 μA·cm^{-2}, 365.8 μA·cm^{-2} and 231.6 μA·cm^{-2}, respectively. The sensitivities of the sensor were also estimated, and the sensor modified with 510 μg·cm^{-2} Cu/Cu_2O@carbon exhibited the highest sensitivity of 0.27 μA/μM (Fig. S1†). The results suggest that excessive amount of Cu/Cu_2O@carbon will reduce the detecting sensitivity of the fabricated sensor. The electrochemical impedance spectroscopy (EIS) performance for different sensors has been evaluated and the results are shown in the inset images. The EIS results imply that the interfacial electron transfer resistance increased with the increasing loading quantity of Cu/Cu_2O@carbon, which can reach to 800 Ω, 1450 Ω, 2200 Ω and 4150 Ω, respectively. The two major competing processes (electrocatalytic capability and reaction resistance) will affect the final reaction rate of a particular process. When the Cu/Cu_2O@carbon modified quantity more than 510 μg·cm^{-2}, the negative effects of electron transfer resistance will surpasses the electrocatalytic activity of Cu/Cu_2O@carbon, which causes the sensor sensitivity decline. Since Cu/Cu_2O@carbon used in current experiments have relatively high resistivity (>10^{10} Ω/m), the excessive catalytic materials will significantly reduce the reactivity. Therefore, under current testing condition, the optimal Cu/Cu_2O@carbon loading quantity for hydrazine sensing was about 510 μg·cm^{-2} and the subsequent experiments were carried out on this basis.

The CVs of Nafion/Cu/Cu_2O@carbon/GCE sensor in presence of 100 μM hydrazine at different scan rates (10-600 mV/s), and its linear fitting curve (oxidation peak current (I_p) vs. square root of the scan rate ($V^{1/2}$)) are shown in Fig. S2†. The fitting linear of I_p vs. $V^{1/2}$ exhibits a linear relationship with the correlation coefficient of 0.993, and the fitting line through the origin. The results prove that the nature of the electrocatalytic process on Nafion/Cu/Cu_2O@carbon/GCE is diffusion controlled.

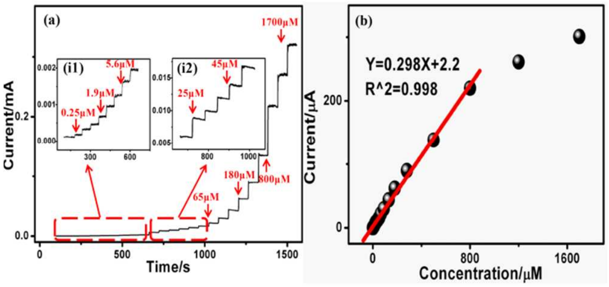

Fig. 6 (a) The amperometric current response of Nafion/Cu/Cu_2O@carbon/GCE for successive addition of hydrazine range from 1 μM to 1700 μM in 0.1 M PBS (pH=7.4); Inset image (i1): amperometric current response of a very lower concentration from 0.25-7.5 μM; Inset image (i2): amperometric current response for concentration of 17-55 μM. (b) The linear plot of oxidation current plateau value vs. hydrazine concentration.

Amperometric response of the fabricated sensors

In order to further investigate the electrocatalytic properties of Nafion/Cu/Cu_2O@carbon/GCE sensor which modified with the optimized amount of Cu/Cu_2O@carbon nanocomposite, a typical amperometric (i-t) response experiment upon the successive addition of hydrazine into continuously stirred 0.1 M PBS at the potential of 0.8 V was carried out, as shown in Fig. 6a. The hydrazine concentration varied from 0.25 μM to 1700 μM, the inset image (i1) is an amperometric current response for a very low concentration range of 0.25-7.5 μM, and the inset image (i2) is for a concentration range of 17-55 μM. The results show that the Nafion/Cu/Cu_2O@carbon/GCE exhibited a rapid and sensitive response with each introduction of hydrazine, and oxidation current reached to the 95% steady-state within 3 s, indicating the Cu/Cu_2O@carbon composite has a well enhanced electrocatalytic capability towards the hydrazine oxidation reactions.

Fig. 6b shows the plot of the plateaus current (μA) values vs. hydrazine concentration (μM) for fabricated hydrazine sensor with Cu/Cu_2O@carbon loading of 510 μg·cm^{-2}, which exhibits

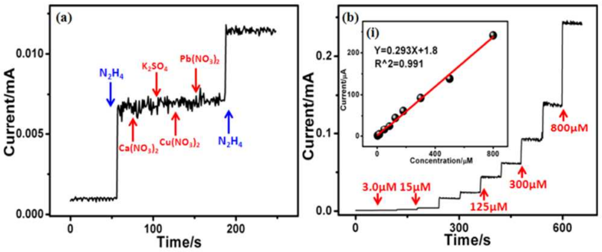

Fig. 7 (a) Interference study of the Cu/Cu$_2$O@carbon based sensor in the presence of hydrazine and interference including urea, K$^+$, Ca^{2+}, Cu^{2+}, Pb^{2+}, SO$_4^{2-}$ and NO$_3^-$; (b) Amperometric current response of Nafion/Cu/Cu$_2$O@carbon/GCE in 0.1 M PBS (pH=7.4) which contain 30 µM interference substances; Inset image: The linear plot of current vs. hydrazine concentration in interference condition.

an excellent linear relationship in the concentration range from 0.25 µM to 800 µM with a correlation coefficient (R^2) of 0.998. The linear equation can be defined as y=0.298x+2.2. Based on the equation of "sensitivity=slope/surface of the electrode"[40,41], the calculated sensitivity of Nafion/Cu/Cu$_2$O@carbon/GCE sensor can reach up to 2.37 µA·µM^{-1}·cm^{-2} with the calculated minimum detection limit of 0.022 µM. In addition, to test the repeatability of the results, much more experiments were also carried out. The corresponding results are shown in Fig. S3† and Table S1†, and the standard deviation of R^2 is only 0.0038, indicating the fabricated sensor possesses good reliability and repeatability. In order to appraise the performance of the as-fabricated Cu/Cu$_2$O@carbon composite based sensor for hydrazine detection, the previous hydrazine electrochemical sensors were summarized as shown in Table 1, including Cu-based materials and noble metal materials based sensors. It can be seen that the present Cu/Cu$_2$O@carbon based sensor possesses a relatively high sensitivity. The detection limit is below the LOD (Limit of Detection) communicated in most works. Furthermore, the overall performance is superior to the rest of the sensors.

Table 1. A response comparison of the Nafion/Cu/Cu$_2$O@carbon/GCE sensor with various hydrazine electrochemical sensors

Sensing materials	Sensitivity (µA·µM^{-1}·cm^{-2})	Linear range (µM)	LOD (µM)	Ref.
Hydrazine electrochemical sensor based on noble metal materials				
Pd/carbon black	8.86µA·µM^{-1}	20-500	8.8	7
Pd-MWCNTs/GCE	0.146µA·µM^{-1}	0.1-10	0.016	8
Au nanoparticles	--	0.1-100m	0.56	9
Pt-TiO$_2$	0.044	2-1030	0.142	10
Hydrazine electrochemical sensor based on Cu-based materials				
Cu-CuO	0.156	100-1800	--	16
CuO hollow spheres	0.007	5-10000	1.9	18
CuS-rGO	0.113	1-1000	0.3	19
CuO/Si/GCE	0.239µA·µM^{-1}	1-5000	0.25	42
CuO/GCE	0.094µA·µM^{-1}	0.1-600	0.03	43
Nano-CuO/GCE	0.73	25-1660	20	44
Cu/Cu$_2$O@carbon	**2.37**	**0.25-800**	**0.022**	**This work**

Selectivity of the Cu/Cu$_2$O@carbon based sensor

To study the selectivity of the Cu/Cu$_2$O@carbon based sensor, many cations and anions present in the form of a salt in boilers and in many of the natural water sources, such as K$^+$, Ca^{2+}, Cu^{2+}, Pb^{2+}, SO$_4^{2-}$ and NO$_3^-$ etc., and compounds like urea were introduced to electrolyte.[37] Two typical amperometric (i-t) response experiments were employed to evaluate the selectivity of the sensor and the results were shown in Fig. 7. The interference substances and hydrazine were sequentially added to the PBS. The hydrazine concentration was 15 µM, and the concentrations of interference substances were 10-fold higher than hydrazine's. Fig. 7a shows that there were only relatively small fluctuations after the interferences were added, and the noises brought to the measuring system will not affect the hydrazine detection performance of the sensor. Fig. 7b exhibits the amperometry experimental result that electrolyte (100 ml) was prepared by 0.1 M PBS with interference substances (30 µM respectively). The inset image shows that the sensor has good linearity in the range of 3.0-800 µM under the interference condition. And the Cu/Cu$_2$O@carbon based hydrazine electrochemical sensor exhibits a sensitivity of 2.32 µA·µM^{-1}·cm^{-2} in the solution with a variety of interference species, which is closed to the sensitivity of 2.37 µA·µM^{-1}·cm^{-2} under no interference environment, indicating the sensor possesses a good selectivity towards hydrazine. Moreover, the reproducible results (Fig. S4† and Table S2†) evidence that the Cu/Cu$_2$O@carbon based sensor has excellent stability for hydrazine sensing in interference conditions.

Real samples analysis

To further test the reliability of the proposed method, the Nafion/Cu/Cu2O@carbon/GCE sensor has been used to analyze spiked real samples. We prepared seven samples with different concentrations of 5, 12, 25, 60, 200, 500 and 700 µM hydrazine using tap water. Fig. S5† shows the response currents which were obtained from detecting the real samples. The results of determination of hydrazine in real samples are shown in Table 2. And the recoveries are appropriate in despite of small deviation. The results evidence that the proposed method can be used efficiently for determination of hydrazine in real sample analysis.

Table 2. Determination of hydrazine in real samples.

Sample	Hydrazine added (µM)	Hydrazine found (µM)	Recovery (%)
1	5	5.10±0.09	102.0
2	12	12.2±0.12	101.6
3	25	24.6±0.53	98.40
4	60	61.4±2.80	102.3
5	200	196.1±5.18	98.05
6	500	509.6±7.08	101.9
7	700	717.5±9.10	102.5

Conclusions

The Cu/Cu_2O@carbon nanocomposite structures were successfully synthesized by inert gas calcination method, and the as-prepared Cu/Cu_2O@carbon was used to fabricate hydrazine electrochemical sensor. Experimental results indicate that increased Cu/Cu_2O@carbon loading amount can enhance electrochemical catalytic performance at low loading level and the high loading amount will increase the overall transfer resistance significantly, resulting in a slowdown in the hydrazine oxidation processes. The optimized Cu/Cu_2O@carbon loading amount for hydrazine detection under current testing condition is about 510 $\mu g \cdot cm^{-2}$. The optimized Cu/Cu_2O@carbon based hydrazine electrochemical sensor exhibits a superior electrical catalytic property, high sensitivity (2.37 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$), outstanding linear concentration range (R^2=0.998 from 0.25 µM to 800 µM), and low detection limit (22 nM) towards hydrazine. The results also suggest that Cu/Cu_2O@carbon nanocomposite structures are a suitable material background for a stable, sensitive, and easy to use hydrazine sensor.

Acknowledgements

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Graphical abstract

A kind of carbon-coated Cu/Cu_2O nanocomposite material (Cu/Cu_2O@carbon) was coated on glassy carbon electrode for electrochemical detection of hydrazine (N_2H_4).