

Seed-mediated Preparation of CuO Nanoflowers and their Application as Hydrazine Sensor

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CuO nanoflowers made up of nanobelts (CuO NFNBs) were successfully prepared in one step by a simple and reliable seed-mediated route, employing only $\text{Cu}(\text{NO}_3)_2$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ as the starting materials. The as-prepared sample was characterized by XRD, FESEM, and TEM techniques. The growth mechanism of these nanostructures is discussed. A glassy carbon electrode modified with CuO NFNBs was then used to detect hydrazine. The results show that the CuO NFNBs show a very high activity for detecting hydrazine.

Nanostructured materials have attracted great interest in both fundamental as well as applied research areas owing to their outstanding physical and chemical properties. Construction of well-ordered, specifically oriented ensembles of nanostructures and realization of their potential applications have resulted in intensive research for the past few years. Recently, nanomaterials with a higher degree of engineering and more complex architectures, such as two-dimensional (2D) and three-dimensional (3D) nanostructures, may have potential applications in light-emission/detection, field emission, biomedical devices, gas sensors, electrode materials in batteries, and so on.^{1,2} Additionally, 2D and 3D carbon nanomaterials, 3D ZnO nanostructure arrays, and 3D NiO nanowalls have exhibited excellent physical properties and provided an opportunity for physicists to explore new physics of high-dimensional nanostructures with open boundaries.^{3,4}

As a p-type semiconductor with a narrow band gap (1.2 eV), CuO has been widely exploited for diverse applications such as heterogeneous catalysts,⁵ gas sensors,⁶ lithium-ion electrode materials,^{7,8} field emission (FE) emitters,⁹ and electrochemical sensors.^{10–12} Recently, many efforts have been directed toward the fabrication of nanostructured CuO to improve its performance in currently existing applications. Among these CuO nanostructures, 1D CuO nanomaterials (such as nanowires, nanoribbons, nanorods, and nanotubes) have been largely prepared through different routes.^{13,14} In particular, recent research indicates that 2D and 3D structures of CuO nanomaterials have been widely focused. Some high-dimensional structures of CuO nanomaterials have been prepared by material scientists.^{15,16} However, to the best of our knowledge, CuO nanoflowers made up of nanobelts (CuO NFNBs) have not been reported yet.

In this paper, we report the successful preparation of CuO NFNBs via seed mediation in a simple aqueous solution containing only $\text{Cu}(\text{NO}_3)_2$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$. The CuO NFNBs were successfully used to modify a glassy carbon electrode (GCE) to detect hydrazine with chronoamperometry (CA). Consequently, the resulting GCE found a good application to electrochemical detecting of hydrazine.

XRD analysis was used to determine the structure and phase of the samples. Figure 1a shows the XRD pattern of the samples.

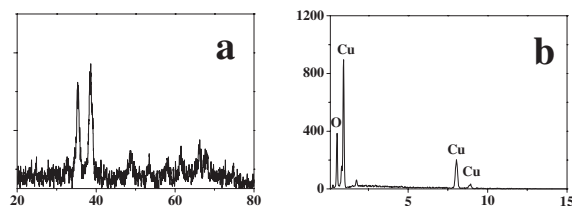


Figure 1. XRD pattern (a) and EDS (b) of the CuO NFNBs.

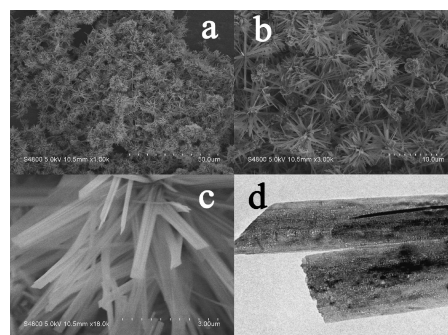


Figure 2. (a), (b) A low-magnification FESEM image, (c) a high-magnification FESEM image, (d) a TEM image of the samples prepared at 100 °C at 8 h.

All the peaks can be clearly indexed to monoclinic phase CuO (space group $C2/c$). Compared with the standard diffraction peaks from (JCPDS Card No. 41-0254), no other peak is observed belonging to the impurities, such as $\text{Cu}(\text{OH})_2$ or Cu_2O , indicating the high purity of the samples. Figure 1b is the EDS image of CuO NFNBs. The result shows that the weight rate of Cu, O, is 70.45%, 29.32% and the atom rate of Cu, O, is 47.25%, 52.22%, nearly the $\text{Cu}:\text{O} = 1:1$, showing the as-prepared sample is CuO.

The morphology and structure of the powders were observed by FESEM and TEM. These images (Figures 2a–2c) clearly indicate that the obtained sample with a high aspect ratio consisted of many nanoflowers made up of nanobelts. A low-magnification FESEM image is shown in Figure 2a, revealing that the CuO nanostructure has flower morphology with the diameter of about 1 μm . The more highly magnified FESEM images (Figures 2b and 2c) give more details about the morphology of the CuO flowers. It can be seen that these CuO NFNBs have a length up to 1–5 μm and a width about 50–200 nm. TEM observations of the product further confirmed the FESEM result (Figure 2d).

Figure S1¹⁸ shows typical FESEM images of CuO NFNBs grown at four different periods in the solution at 100 °C, namely, 0, 2, 4, and 6 h. Figure S1a¹⁸ shows a typical FESEM image of CuO nanoseed particles by using an ultrasonic process showing high-density growth of CuO nanoparticles with a uniform

particle size. These nanoparticles grew into large-scale 3D nanostructures just after completing a short period in the growth solution, typically 2 h (Figure S1b).¹⁸ In this stage, nanoflowers made up of small nanowires with length of 50–100 nm were obtained. From the image, it was also found that no CuO nanoseeds were observed, inferring effective growth of CuO nanoseeds into nanowire. With the growth time increasing to 4 h, the wire-like structure continued to grow longer and wider, its length became 150–200 nm and width became 30–50 nm as shown in Figure S1d.¹⁸ We also investigated the structure of the sample with a growth time of 6 h as shown in Figure S1e,¹⁸ and we found that the as-formed nanowires continued to grow longer and wider with lengths up to 300–400 nm and the width up to 50–100 nm. Hence, considering the previous discussions on Figure S1,¹⁸ we conclude that the CuO NFNBs growing process in the solution was a process from nanoseeds to nanoflowers made up of a wire-like structure to belt-like structure. This kind of structure growth just like that of the preparation of different CuO nanostructure by using pyrogenation of the Cu(OH)₂, which is also demonstrated in the existing literature.¹⁷

For the development of an amperometric biosensor for hydrazine, the CuO NFNBs were dispersed in Nafion, a perfluoro-sulfonated polymer, to facilitate the modification of the GCE. As shown in Figure 3a, curve 1, hydrazine shows no redox peak at a bare GCE. However, the CuO NFNBs exhibit strong electrocatalytic activity in response to hydrazine oxidation. One oxidation wave in the anodic sweep and one anodic wave in the cathodic sweep indicate the high catalytic ability of the electrode toward hydrazine oxidation. From the CV profiles (Figure 3a curve 2–6) we also find that with the addition of hydrazine, there was an enhancement in the anodic current compared with that at a bare

GCE. This suggested that the modified electrode could be applied to the determination of hydrazine.

For amperometric sensing application, electrodes are generally evaluated by measuring current response at a fixed potential with the analyte added. Figure 3b displays the amperometric response (at +0.10 V) at the CuO NFNBs/GCE to the successive addition of 1 mM hydrazine in PBS (pH 7.0). As expected from the voltammetric data (inset of Figure 3b), the CuO NFNBs/GCE showed good linear response to the changes of hydrazine concentration, producing steady-state signals within 10 s. The CuO NFNBs/GCE gives a linear dependence ($R = 0.9848$) in a hydrazine concentration range of 0.05–5 mM with a sensitivity of 0.9415 mA mM⁻¹, as depicted in Figure 3b. Exhilaratingly, the CuO NFNBs/GCE also shows high stability and reproducibility in detection of hydrazine, with a relative standard deviation about 3% in more than 20 measurements.

In summary, CuO NFNBs were successfully prepared in one step by a simple and reliable seed-mediated route, employing only Cu(NO₃)₂ and NH₃·H₂O as the starting materials. The results obtained from SEM and TEM indicate that the CuO NFNBs growing process in the solution was a process from nanoseeds to nanoflowers made up of a wire-like structure to belt-like structure. In addition, a GCE modified with CuO NFNBs was used to detect hydrazine in the solution. The result shows that the CuO NFNBs show a very high activity for detecting hydrazine. Thus, the CuO NFNBs hold promise for being developed as a hydrazine sensor at low cost.

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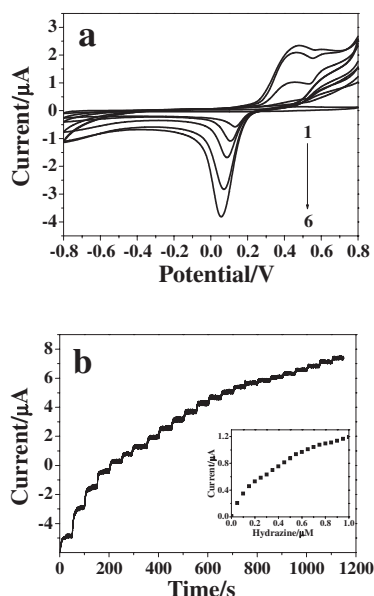


Figure 3. (a) CV performance of CuO NFNBs/GCE in the presence of a different amount of hydrazine in 50 mmol L⁻¹ PBS (pH 7.2) at a scan rate of 50 mV s⁻¹ (1 means 5 μmol L⁻¹ hydrazine in 50 mmol L⁻¹ PBS on the bare GCE, 2–6 means 1, 2, 3, 4, 5 μmol L⁻¹ hydrazine in 50 mmol L⁻¹ PBS, respectively); (b) CA response of CuO NFNBs/GCE at 0.10 V upon subsequent addition of hydrazine solution. Inset shows a linear response for hydrazine concentrations between 0.05 and 1 μM.

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