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Study of the growth mechanisms of nanoporous Ag flowers for non-enzymatic glucose detection

Jianan Chen$^1$, Chang Liu$^1$, Yu-Ting Huang, Hyeonseok Lee and Shien-Ping Feng

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Rd., Pokfulam 999077, Hong Kong

E-mail: hpfeng@hku.hk

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Abstract

Highly sensitive and selective non-enzymatic glucose detection was developed using nanoporous Ag flowers on a Ni substrate. The cyclic scanning electrodeposition (CSE) method was used to fabricate Ag flowers on a Ni substrate in an alkaline electrolyte. The nanoporous Ag flowers were then formed by repeated CSE in NaOH. The growth mechanisms of the nanoporous Ag flowers were systematically studied, and these mechanisms can be extended to the formation of other metal, bimetal or metal oxide. The synthesized three-dimensional nanoporous Ag flowers on the Ni substrate were used in the electro-oxidation of glucose, demonstrating a wide linear range (0.1 µM to 1 mM), fast response time (<2 s), low detection limit of 0.1 µM (S/N = 3) and a high sensitivity to detect glucose in the presence of uric acid (UA) and ascorbic acid (AA) at the level of their physiological concentrations. Apart from the nanoporous Ag flowers, the formation of a NiO thin layer on the Ni substrate during CSE also contributed to the high selectivity. This work indicates the potential for developing a fast, sensitive, selective and stable electrochemical sensor for diabetes diagnosis.

Supplementary material for this article is available online

Keywords: electrochemical method to fabricate nanoporous Ag flowers, proper model to study the growth mechanism, applications in non-enzymatic glucose detection, low detection limit, high sensitivity and selectivity

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, nanomaterials have played an important role in biosensing [1]. The physical and chemical properties of nanomaterials are strongly related to their morphology, size, and phase [2]. The distinct superiority of nanomaterials in catalysis reaction is their high surface area to volume ratio (SA:V) [3]. A large amount of exposed area can improve the reactivity of the catalyst due to a good contact with the analytes. Additionally, when nanomaterials have three-dimensional structures, the intercrossed framework can facilitate the electrons transfer within the catalyst [4]. These properties contribute to a low detection limit and a high sensitivity.

The measurement of glucose has been a focus in the biosensing field for many years [5]. The detection of glucose concentration is essential in many aspects, such as the clinical diagnosis of diabetes, the food industry and biological research [6, 7]. Glucose sensors can be classified into enzyme and non-enzyme based. In the 1960s, Clark, Updike and their colleagues developed the first enzyme glucose biosensors [8, 9]. Since then, considerable attention has been given to the development of glucose oxidase (GOx) based sensors. The first several generations of glucose sensors were all based on the enzyme method [10]. However, due to the intrinsic
properties of enzymes, the performance of these GOx-based sensors is affected by temperature, pH, and humidity. GOX-based sensors also tend to lose activity in hostile environments and thus suffer severe stability issues. It is therefore important to develop simple, cheap, stable, sensitive and reliable non-enzymatic glucose sensors. Many metals (e.g., Au, Pt, Cu, and Ni), metal oxides (e.g., CuO) and bimetallic materials (e.g., Pt-Pb, Au–Ag, and Ni–Cu) have been explored in the fabrication of non-enzymatic glucose sensors [11–20]. These studies show that the right material with a suitable structure could lead to enhancing sensor performance.

Among the materials used in the development of non-enzymatic glucose sensors, Ag has been regarded as one of the most suitable candidates. Ag displays very good electrical conductivity and typical noble metal characteristics. It is also biocompatible and has low toxicity [21]. Over the past few years, numerous strategies have been used to fabricate Ag nanomaterials, such as the double-reductant method, an etching technique [22], electrochemical synthesis [23] and photochemical processes [24–27]. At the same time, a wide range of Ag nanomaterials with unique morphologies have been developed, such as nanoparticles [21], nanowires [28] and nanoplates [29].

In our previous work, nanostructured Ag flower constituted by intercrossed smooth nanoplates was synthesized on FTO substrate using CSE method [30]. However, although the electrode had a high catalytic activity towards the electro-oxidation of glucose, the applied potential is too high (0.95 V) to avert the side reactions of interferences during glucose detection. Herein, we developed a facile electrochemical method to fabricate a nanoporous Ag structure on Ni substrate; with the aid of nanoporous structure and Ni substrate, the as-prepared electrode achieved a high selectivity in the presence of interferential uric acid (UA) and ascorbic acid (AA) at 0.75 V. Meanwhile, a relatively low detection limit and high sensitivity were attained. Our current electrode is more robust than our previous work, with a more potential towards the practical application. Other than the catalytic electrode, the formation mechanism of the porous structure was studied systematically. The proper model was proposed to advance our understanding, which can be extended to the formation of other metal, bimetallic and metal oxide porous structures for a wide range of applications including catalysis, electronics, and sensing.

2. Experimental section

2.1. Materials

High purity (≥99.98%) N6 type Ni foil was obtained from the Yue Grown metal materials. Sodium sulfate (Na2SO4), nickel (II) sulfate hexahydrate (NiSO4·6H2O), sodium acetate trihydrate (CH3COONa·3H2O) were supplied by Showa. Sodium hydroxide (NaOH) was purchased from Wako. We obtained 3-mercaptopropyl-trimethoxysilane (MPS) from Sigma-Aldrich. The L (+)-Ascorbic acid was supplied by Acros Organics. The commercial Ag electrolyte (MetSil 500 CNF), which is cyanide free and contains 0.28 M Ag ions, was obtained from the Metalar company. All aqueous solutions used in this work were prepared with deionized (DI) water generated by a Millipore Direct Q-5 purification system.

2.2. Preparation of nanoporous Ag flowers electrodes

We used a conventional three-electrode system with a polished Ni substrate (A = 100 mm²) as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a platinum mesh as the counter electrode. Before the fabrication process, Ni foil was sequentially polished with P800, P1200, P2000 sandpaper and 1 μm alumina slurry, then rinsed with DI water. Finally, the Ni foil was cleaned by sonication in ethanol and DI water, dried by compressed air at room temperature. The clean and polished Ni substrate was then immersed into 1 v/v% 3-mercaptopropyl-trimethoxysilane (MPS) in ethanol for 3 min at room temperature and then rinsed with ethanol. An intact Ag film was then electroplated onto the MPS-grafted Ni substrate. To convert the Ag film into the porous flower-like nanostructure, a two-step method was used. First, the Ag-coated Ni substrate was subjected to a CSE in a weak alkaline solution, which consisted of 0.312 M CH3COONa, 0.078 M NiSO4, and 0.1 M Na2SO4 (pH = 7.26). During the cyclic scanning, the Ag went through an anodic stripping process and then a reduction process. The nanostructured Ag flowers with smooth petals were then fabricated on the Ni electrode. To get a higher surface to volume ratio, the prepared electrode was immersed into 0.1 M NaOH electrolyte (pH = 13), and after cyclic scanning from −0.3 to 1 V several times, the nanoporous silver flowers electrode was finally obtained. All electrochemical syntheses and measurement were carried out at room temperature (25 ± 2 °C).

2.3. Apparatus and electrochemical measurements

All electrochemical syntheses were carried out using a CHI 660E electrochemical workstation (CH Instrument Inc., USA). The morphologies of the Ag nanostructures were characterized by a field-emission scanning electron microscope (SEM; Hitachi S-4800). The detailed morphology and selected area electron diffraction were carried out using a transmission electron microscope (TEM; Philips CM100).

3. Results and discussion

3.1. The formation and characterization of the nanoporous Ag flowers

A layer of Ag (150 nm) was electroplated onto the MPS-treated Ni foil. The Ag-coated substrate was subsequently subjected to a CSE in the electrolyte that consisted of CH3COONa, NiSO4, and Na2SO4. During the CSE, the Ag
layer was stripped into Ag\(^+\) ions during the anodic scan and was re-electroplated on the Ni foil during the reverse scan. Figure 1(a) shows the corresponding current-potential response of the CSE. Figures 1(b) and (c) show SEM images of the nanostructured Ag flowers. The average diameter of the flowers is about 6 \(\mu\)m, and the thickness of each petal is around 10 nm. The detailed formation mechanism can be found in our previous works [30, 31]. In this study, the Ag flower/Ni substrate was then subjected to a CSE in 0.1 M NaOH solution to convert the smooth Ag flowers into nanoporous structures. In the NaOH solution, a thin NiO layer would also be formed on the surface of the Ni substrate. Figure S1(a) is available online at stacks.iop.org/NANO/29/505501/mmedia and shows the cyclic voltammetry (CV) profiles for the Ni foil in NaOH. The anodic and cathodic peaks correspond to the reversible formation of \(\beta\)-NiOOH. In
prior to the formation of $\beta$-NiOOH, a remarkable amount of irreversible NiO was generated [32, 33]. An energy-dispersive x-ray spectroscopy (EDX) analysis verifies the formation of the NiO layer after the CSE in the NaOH solution (figure S1(b)).

The mechanism regarding the transformation from the smooth structure into the porous one was studied. A typical CV for the first cycle in 0.1 M NaOH is shown in figure 1(d). Two oxidation peaks A1 and A2, and two reduction peaks C1 and C2 are observed in the anodic scan and reversed cathodic scan, respectively (figure 1(d)). Based on previous studies, it is known that the oxidation of Ag film goes through a two-step mechanism [34, 35]. Particularly, Ag was oxidized into Ag$_2$O by two stages, and similar steps also occurred in the reversed cathodic scan. Figures 1(e) and (f) show the SEM images of the nanoporous Ag flowers after the first CSE cycle. Compared with the structures shown in figures 1(b) and (c), the smooth petals no longer existed and were changed to porous structures. The thickness of each petal increased to about 400 nm, which was 40 times larger than before. Figure S2 presents the CV profiles corresponding to the formation of nanoporous structures in repeating scans. The peak currents (both anodic and cathodic) increased after each CV scan, implying the change of morphology in 10 cycles. The largest difference of the anodic peak currents appeared between the first and second cycles. The increase of the current response is owing to the increase of surface area after the formation of the porous structure. Figure S3(a) shows the morphology of Ag flowers after the first scan, where the smooth petals became porous. After the third cycle, the difference of the peak currents between two sequential scans (e.g., scan 2 and scan 3) gradually decreased, and became negligible, which is consistent with the SEM observation in figure S3. Figures S3(b)–(d) show the morphology of the nanoporous Ag flowers after 3, 5 and 10 cycles, respectively. Compared with the morphology after the first scan, the porosity increased, and the petals became thicker. However, the change of morphology was much less, which is in accordance with the behavior of the current after the third scan (figure S2). Consequently, only the morphology change during the first cycle is considered relevant and studied further.

To investigate the morphology change in response to the applied potential, SEM was used to record the morphology of the nanoporous Ag flowers. Figure 2 shows the transformation of Ag from the smooth to nanoporous structures at different anodic and cathodic stages in NaOH. The nanostructures underwent nucleation and decomposition processes during the oxidation and reduction. The inset of figure 2(a) shows the corresponding CV profile in the voltage range of $-0.1$ to 0.3 V. In prior to the major peak A1, there is a tiny peak observed between 0.1 and 0.3 V. Compared with the morphology in figures 1(b) and (c), the Ag petals in figure 2(b) (anodic scan to 0.2 V) are covered by a thin layer, which is a thin layer of AgOH [36, 37]. The A1 peak corresponds to the formation of the primary Ag$_2$O compact layer (figure 2(c)) [38]. Figure 2(d) shows the morphology of the Ag flowers at 0.4 V. Compared to previous petals with a smooth thin layer, more nuclei appeared and the petals simultaneously became more porous and thicker. The A2 peak corresponds to the formation of Ag$_2$O secondary layer [39]. The nuclei continued to grow during the entire A2 process, which ceased at around 0.53 V. Figures S4(a) and (b) show the EDX analysis of the nanoporous Ag at 0.2 and 0.5 V,
stopped growing.

AgOH layer.

ripening and growth of the second Ag2O layer.

Ag2O layer was reduced to Ag and became more porous.

At this stage, the Ag2O became the

to Ag2O. At 0.6 V, the petals became even more porous with

0.52% and 3.16%, which was attributed to the oxidation of Ag

where the atomic percentage of elemental oxygen changed from

0.52% and 3.16%, which was attributed to the oxidation of Ag

to Ag2O. At 0.6 V, the petals became even more porous with

numerous large particles (figure 2(c)). The Ag2O was then fur-

ther oxidized into AgO. Meanwhile, the oxygen content was

increased to 6.2% at 1 V (figure S4(c)). Nevertheless, the

morphology was changed little until the end of the anodic scan

(figure 2(f)). During the reduction process, the pre-formed par-

ticles were decomposed into small particles (figures 2(g)–(i), and

figure S5). Notably, some pores were observed on the surface of

large particles, by which the surface area was further increased.

Figure 3 shows the schematic regarding the growth mechanism of nuclei, Ag2O secondary layer and the decom-

position of the solid particles, in which the nucleation and growth model was proposed. As shown in figure 3(a), a

monolayer of AgOH was formed first, on which the Ag2O grew layer by layer. This process could be depicted by Reac-

ion (1)

\[
\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{Ag} + 2\text{OH}^-; \\
E_r (0.1M \text{NaOH})/\text{versus Ag/AgCl} = 0.12 \text{ V.} 
\]  

At this stage, the Ag2O became the first basal layer in the next oxidation processes. Figure 3(b) illustrates the mechanism underlying the A2 stage. Since AgOH and Ag2O have dif-

ferent lattice parameters, a mismatch is expected to be generated between these two layers. This mismatch leads to

energy strain, which is the source of the nuclei generation. The presence of the Ag2O nuclei results in the formation of

the secondary Ag2O porous layer. Equation (2) can be used to evaluate the degree of mismatch (\(\epsilon\)) between two thin

films [40]:

\[
\epsilon = \frac{a_{\text{Ag}_2\text{O}}}{a_{\text{AgOH}}} - 1. 
\]  

In equation (2), \(a_{\text{Ag}_2\text{O}}\) and \(a_{\text{AgOH}}\) are the lattice parameters of Ag2O and AgOH, respectively. So the mismatch between Ag2O and AgOH is about 0.16. When the mismatch is larger

than 0.1, the thin film growth will transfer from layer-by-layer mode to Stranski–Krastanov mode (layer-plus-island) [41].

Therefore, when the growth of the Ag2O thin layer reached to a critical thickness, the growth finally transferred from the film mode to the island mode, leading to the formation of nuclei. Thereafter, large nuclei turned into large particles, while small nuclei were dissolved into Ag+ since the solu-

bility of small particles is higher in the electrolyte. Conse-

quently, the large hemispherical particles grew at the expense of small ones, which is commonly known as Ostwald ripen-

[42, 43] (figure 3(c)). In figure 3(d), the growth of the secondary Ag2O layer became slow and finally stopped since the surface of Ag was entirely blocked by the oxide layer, and the flux of Ag+ ions was hindered. Meanwhile, a small amount of AgO might have formed at this time.

Figure 3(e) shows the morphology change during the reduction process. When we scanned back to 0.2 V, the AgO was reduced and the morphology changed little (figure 2(g)). At a more negative potential, the Ag2O layer started to be reduced, and OH− was generated as described in equation (1). However, the Ag atoms involved in the formation of the oxide layers could not return to their original position on the petals [44], hence the porous structure was formed by con-

structing a large number of small Ag particles (figure S6(a)). Figure 3(f) shows the morphology of the nanoporous Ag flowers after reduction. The particles were covered by
abundant tiny holes, and the surface area increased significantly. However, most of the first Ag₂O layer remained unchanged due to the thick second Ag₂O layer. The mean Ag particle radius was estimated to be 10.86 nm in figures 2(h) and 20.37 nm in figure 2(i), respectively; the corresponding particle size distributions were analyzed as well (figure S7).

Figure S4(d) shows the EDX analysis of the prepared sample after cyclic scanning. The EDX results show the content of elemental oxygen decreased to 0.96%. The d-spacing of the structure in figure S6(b) confirms the final product is Ag, with a negligible amount of silver oxide.

### 3.2. Electrochemical characterization of the nanoporous Ag flower electrode

The electroactive area of the catalyst is important, and the surface area of the nanoporous Ag flowers was estimated using the Randle–Sevcik equation in a ferro/ferricyanide redox system [45]:

\[ I_p = 2.69 \times 10^5AD^{1/2}n^{1/2}ν^{1/2}C^*, \]

where \( I_p \) is the peak current, \( A \) is the electroactive area (cm²), \( n \) is the number of evolved electrons, which equals to 1 in this system. 1 mM K₃[Fe(CN)₆] in 0.05 M KCl was used, and \( D \) (diffusion coefficient) equals to 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}. C^* \) is the bulk concentration of the electroactive species and \( ν \) is the scan rate (V s⁻¹). The redox CV under different scan rates and the linear fitting of \( I_p \) versus \( ν^{1/2} \) are shown in figure S8. Two anodic peaks correspond to the adsorption and oxidation of Fe(CN)₆³⁻ (figure S8); similarly, two cathodic peaks correspond to the reduction of Fe(CN)₆³⁻ and desorption of Fe(CN)₆⁴⁻, which have been reported by Dezfuli et al and Sappia et al [46, 47]. Herein, only the second anodic peak current was used for the linear fitting, since it is related to the Fe(CN)₆⁴⁻ oxidation. The slope of the \( I_p \) versus \( ν^{1/2} \) was calculated to be 0.002 29 A sec⁻¹/² \text{ cm}⁵/² (figure S8(b)). Therefore, the equivalent surface area of the nanoporous Ag flower was estimated to be 15.44 cm² per unit geometric area.

We also investigated the electrocatalytic behaviors of the nanoporous Ag flowers. Figure 4(a) shows the CV profiles of the nanoporous Ag flowers in 0.1 M NaOH without and with 5 mM glucose. In the presence of 5 mM glucose, the oxidation current is enhanced. The increased oxidation current is attributed to the electro-oxidation of glucose into gluconic acid [48–50].

In addition, we investigated the relationship between the peak current and the scan rate. Figure 4(b) shows the CV

![Figure 4](image_url)
profiles of the as-prepared sample at different scan rates (10–100 mV s⁻¹) in a 0.1 M NaOH solution with 5 mM glucose. As the scan rate increases, the peak current also increases. The oxidation potential gradually shifts positively, and the reduction potential shifts negatively. The redox peak currents are proportional to the square root of the scan rate (figure 4(c)), indicating the reactions involved are the diffusion-controlled process.
3.3. Amperometric detection of glucose and anti-interference properties

The amperometric detection method was used to evaluate the catalytic activity of glucose detection. The applied potential in the amperometric test is very important. High potential can improve the signal to noise ratio (S/N) but is favorable for side reactions of most interferences. However, a low potential generally induces a low sensitivity. After multiple attempts, we chose 0.75 V as an optimum detection potential.

Figures 5(a) and (b) show the amperometric response to the successive addition of different concentrations of glucose. The results exhibit the electrode possesses a rapid response (less than 5 s) to the addition of glucose and the current increases with the increase of glucose concentration. The limit of detection (LOD) was estimated to be 0.1 μM (S/N = 3). Figures 5(c) and (d) show the corresponding calibration curves, which are linear in relation to the glucose concentration. The slope varies with concentration ranges, and the highest sensitivity was calculated to be 1549 μA mM⁻¹ cm⁻². The obtained LOD and sensitivity are better than or comparable to the previously reported non-enzymatic glucose sensors (table 1). These enhanced electrocatalytic activities can be attributed to the large surface to volume ratio of nanoporous Ag flowers. The three-dimensional porous petals also facilitate electron transport. In addition, based on the bridge-linker of MPS between the nanoporous Ag and the substrate, a good interfacial contact is provided and results in the efficient current collection [51].

Good selectivity is another important parameter for glucose sensors, but it is also a universal challenge for non-enzymatic glucose sensors. Species like UA and AA generally exist in the human blood and are easily oxidized, which could interfere with the result of glucose detection. The concentration of glucose in blood is about 4–7 mM [52], and the concentration of AA and UA in blood is about 0.125 mM and 0.33 mM, respectively [53]. We chose 5 mM glucose, 0.125 mM AA, and 0.33 mM UA for the selectivity test, which appropriately simulated the real situation in blood. The nanoporous Ag flowers were fabricated on Ni and FTO glass. Figure 5(e) shows the response of the nanoporous Ag flowers on Ni and FTO substrates to glucose and some interferences. The results for the FTO electrode show that adding AA or UA causes a 1.96-fold or 1.61-fold higher response, respectively, than the addition of 0.1 M NaOH base solution. Due to the inert intrinsic properties of the FTO substrate, all these responses could be regarded as the catalytic activity of the Ag nanosstructure towards AA and UA oxidation. However, when using nanoporous Ag/Ni electrode, the current responses towards AA and UA decrease to 1.39-fold and 1.03-fold higher, respectively, than 0.1 M NaOH. This result indicates the Ni substrate is helpful to suppress the oxidation of interference. To test the effect of the Ni substrate for suppressing interferences, we conducted the experiments using the solution of glucose only and mixture of glucose with the interference. By using Ni substrate, the addition of 0.125 mM AA and 0.33 mM UA in 5 mM glucose causes a 1.02-fold and 1.07-fold signal increase, respectively (figure 5(e)), while when using FTO substrate, signals increase 1.28-fold and 1.25-fold, respectively. Obviously, the selectivity of the nanoporous Ag flowers was improved by using Ni as the substrate. The enhancement against the interferences can be explained by the repelling effect [54]. During the fabrication of nanoporous Ag flowers, the top surface of Ni was oxidized into NiO, which was verified and discussed in the preceding part. The isoelectric point (IEP) of NiO is about 10–11 [55], and the pH value for 0.1 M NaOH is 13, indicating that the NiO thin layer was negatively charged in this alkaline solution. Moreover, in the 0.1 M NaOH base solution, AA and UA lost protons thus became negatively charged as well. Therefore, the negatively charged NiO layer repelled the negatively charged AA and UA molecules. The UA and AA interference molecules had less opportunity to reach the electrode surface, which improved the selectivity. The amperometric test results of different analytes are shown in figure 5(f). At the constant potential of 0.75 V, we successively injected 0.125 mM AA, 0.33 mM UA and 5 mM glucose into the 0.1 M NaOH base solution. The experiment exhibits that the response to the injection of interference is almost negligible compared to the current increase for the addition of 5 mM glucose. Notably, the nanoporous Ag flowers/Ni electrode

<table>
<thead>
<tr>
<th>Electrode composition</th>
<th>Sensitivity (μA mM⁻¹ cm⁻²)</th>
<th>LOD (μM)</th>
<th>Working potential (V)</th>
<th>Selectivity</th>
<th>Year</th>
<th>References</th>
</tr>
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<tr>
<td>Pt NPs/graphene</td>
<td>6.36</td>
<td>1</td>
<td>0.40</td>
<td>√</td>
<td>2015</td>
<td>[56]</td>
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<td>Co₃O₄/PrO₂ core–shell nanorod arrays/C</td>
<td>460.3</td>
<td>0.31</td>
<td>0.55</td>
<td>√</td>
<td>2014</td>
<td>[57]</td>
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<tr>
<td>Pd/Au cluster</td>
<td>1600</td>
<td>50</td>
<td>0.60</td>
<td>√</td>
<td>2015</td>
<td>[58]</td>
</tr>
<tr>
<td>Hollow Cu₂O nanospheres</td>
<td>2038.2</td>
<td>0.41</td>
<td>0.6</td>
<td>—</td>
<td>2015</td>
<td>[59]</td>
</tr>
<tr>
<td>Co₃O₄ nanoparticle modified GCE</td>
<td>520.7</td>
<td>0.13</td>
<td>0.59</td>
<td>—</td>
<td>2012</td>
<td>[60]</td>
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<tr>
<td>Au@Cu₂O/GCE</td>
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<td>1.83</td>
<td>0.63</td>
<td>√</td>
<td>2015</td>
<td>[61]</td>
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<tr>
<td>GO/CuO/GCE</td>
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<td>0.69</td>
<td>0.67</td>
<td>√</td>
<td>2012</td>
<td>[62]</td>
</tr>
<tr>
<td>Ag–CuO/rGO/GCE</td>
<td>214.37</td>
<td>0.76</td>
<td>0.60</td>
<td>√</td>
<td>2018</td>
<td>[63]</td>
</tr>
<tr>
<td>PVA/MnO₂@GO/CuO</td>
<td>53</td>
<td>53</td>
<td>0.4</td>
<td>—</td>
<td>2016</td>
<td>[64]</td>
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<tr>
<td>CuO-reduced graphene oxide</td>
<td>2221</td>
<td>0.1</td>
<td>0.4</td>
<td>—</td>
<td>2014</td>
<td>[65]</td>
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<tr>
<td>Ag NP/grGO</td>
<td>725.0</td>
<td>4</td>
<td>0.65</td>
<td>√</td>
<td>2017</td>
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<td>1.2</td>
<td>0.7</td>
<td>√</td>
<td>2016</td>
<td>[67]</td>
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<tr>
<td>Nanostructured Ag flower on FTO</td>
<td>4230</td>
<td>0.0001</td>
<td>0.95</td>
<td>—</td>
<td>2017</td>
<td>[68]</td>
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<tr>
<td>Nanoporous Ag flowers on Ni</td>
<td>1549</td>
<td>0.1</td>
<td>0.75</td>
<td>√</td>
<td>This work</td>
<td></td>
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</tbody>
</table>

Table 1. Performance comparison of different materials for glucose detection.
was applied to detect the glucose in wine, which is in good accordance with the commercial glucose sensor (figure S9). Compared with recently reported electrodes, the synthesized nanoporous Ag flowers/Ni electrode exhibits prominent detection performance in terms of sensitivity, LOD, and selectivity at 0.75 V.

4. Conclusion

In summary, we developed a universal method to fabricate nanoporous Ag flowers on the Ni substrate. The formation mechanism of the porous structure was explored systematically. The morphology transformation from smooth to porous is due to the oxidation and reduction processes of Ag. The S–K (layer-plus-island) mode of thin film growth is considered to be the origin of the nuclei, and this process plays a main role in the formation of the nanoporous petals. The nanoporous Ag flowers electrodes were used for non-enzymatic glucose detection at 0.75 V. Because of the excellent conductivity of Ag and the high surface to volume ratio of the three-dimensional structure, this material shows a high sensitivity for glucose detection. Besides, the material shows a significant selectivity, which is usually lacked in non-enzymatic sensors. The good selectivity was explained by the formation of a NiO thin layer on the top of the surface of the Ni substrate. Because the NiO and interferences like AA and UA were all negatively charged in the 0.1 M NaOH base solution, the NiO layer repelled the interference molecules and kept them away from the substrate surface. Consequently, the effect of interferences was suppressed, and the selectivity was improved. The nanoporous Ag flowers are a promising material for developing a new enzyme-free glucose sensor.

Acknowledgments

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ORCID iDs

Jianan Chen @ https://orcid.org/0000-0003-3869-6966

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