Electrochemical synthesis to convert a Ag film into Ag nanoflowers with high electrocatalytic activity†

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The cyclic scanning electrodeposition method was proposed to convert a thin Ag film into nanocrystals (NCs) with various shapes including nanoflowers, nanorods, dendrites, decahedrons, and icosahedrons. The flower-like Ag NCs exhibit a remarkably enhanced catalytic activity for electro-oxidation of glucose.

Metal nanocrystals (NCs) have attracted great attention due to their fascinating size- and shape-dependent properties for various applications, such as catalysis, sensing, and drug delivery.1 In particular, the development of high-performance catalysts relies on the synthesis of functional NCs with high surface-to-volume ratios (SA : V) and high-index planes for enhanced activities.2 Over the past decade, tremendous efforts have been made to search for a versatile method to precisely control the morphology of NCs. The most common synthetic methods are seed-mediated growth methods and polyl processes.3,4 However, these synthesis processes are time consuming as they include seed preparation, intermediate purification, and adsorbate removal.5 Moreover, surfactants may block the active sites and introduce hetero-

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Electrochemical glucose oxidation has been widely applied to new-generation glucose sensors for medical diagnostics. The core of this electrochemical reaction is to fabricate highly catalytic NCs to overcome a detection limit of ~ 1 μM which is normally limited in conventional enzyme-based glucose sensors.5 Considerable attention has been paid to employing noble metals, such as Pt and Au, to achieve noninvasive glucose detection in the source of tears or saliva. Nevertheless, Pt electrodes are easily poisoned by intermediates so as to suppress their activity and Au electrodes are limited by a high working potential and relatively poor sensitivity.6

This work presents a new cyclic scanning electrodeposition (CSE) method, which encompasses a combination of a potential waveform, a suitable choice of additives, and an abrupt change in adions in the electrical double layer (EDL), to convert a thin Ag film into various Ag NCs, in different shapes such as nanoflowers, nanorods, dendrites, decahedrons, and icosahedrons. The in situ current-potential response of CSE was used to systematically investigate the shape evolution of NCs corresponding to each additive. Based on this understanding, a generic design rule can be developed to precisely control the nucleation and growth of Ag NCs with different shapes. Furthermore, Ag nanoflowers are directly synthesized on the substrate from a bulk Ag film, which are constituted by hundreds of nanoplates which possess both a high SA : V and a high density of atomic steps. This is indeed the first demonstration that Ag has been turned into a super-efficient catalyst for glucose sensing, with...
one order of magnitude improvement in the detection limit and a record-high sensitivity in electrochemical glucose biosensors.

Scheme 1 shows the formation of flower-like Ag NCs on fluorine-doped tin oxide (FTO) glass. A 150 nm-thick Ag layer was electroplated on FTO pretreated with 3-mercaptopropyltrimethoxysilane (MPS) (Fig. S1, ESI†). The Ag-coated substrate was then subjected to a CSE in an electrolyte consisting of CH₃COONa, NiSO₄, and Na₂SO₄. During CSE, the Ag layer was stripped into Ag⁺ ions during the forward scan and was then re-electroplated on FTO during the reversed scan (Fig. 1). The shiny Ag surface became half transparent after CSE because the Ag layer was converted into scattered Ag NCs on FTO (Fig. S2, ESI†). The entire process can be completed within 10 min from MPS pretreatment to the formation of flower-like Ag NCs, where the CSE is effective and directly grows Ag NCs on the substrate.

Two anodic peaks (marked as A₁ at 0.69 V and A₂ at 1.1 V) on the forward scan correspond to electro-oxidation of Ag/Ag⁺ and Ni²⁺/Ni³⁺, respectively. Two cathodic peaks (marked as C₁ at 0.4 V and C₂ at 0.33 V) on the reversed scan are the seed formation and the crystal growth of flower-like Ag NCs, respectively. An instantaneous high concentration of Ag⁺ was generated near the electrode after anodic stripping, which initially forms a myriad of nuclei at the subsequent reversed cathodic scan. The concentration of Ag⁺ then decreased abruptly due to the consumption in the nucleation process and the diffusion into the bulk electrolyte. When the concentration of Ag⁺ near the electrode became extremely low, the adatoms were preferentially deposited on the relatively active area (e.g., sharp edges) of the existing nuclei. This kinetics-controlled process usually induces stacking faults and causes lattice strain. The Ag seeds with stacking faults will easily evolve into a plate-like shape, of which the top and bottom faces are [111] facets and the side surfaces are enclosed by a mixture of {100} and {111} facets. Once the Ag nanosheet reached a certain size, Ag²⁺ appeared to be reduced on its surface active sites and grew into another branched Ag nanosheet. The scanning electron microscopy (SEM) images under different end points of the reversed scan (0.35 V, 0.3 V, 0.2 V) provide evidence that the small Ag clusters with the standing intercrossed nanoplates were formed as seeds at the C₁ peak and then grew into flower-like shapes at the C₂ peak (Fig. S3, ESI†). This process was repeated to form a three-dimensional network of intercrossed Ag nanosheets (Fig. S4, ESI†), resulting in a japonica-like Ag flower. Galvanostatic Ostwald ripening plays an important role in the consumption of tiny Ag nanoplates to further grow in the diameter of the Ag flowers when the scanning potential is lower than 0.2 V (Supplementary Note 1, ESI†).

The SEM images in Fig. 1a show that the japonica-like Ag flowers are composed of intercrossed lamellar nanopetals with high SA : V (flower size, ~5.5 μm; petal thickness, ~10 nm). One of the nanopetals was examined by transmission electron microscopy (TEM), in which the basal plane of the Ag nanopetal was observed along the [111] zone axis (Fig. 1b). The six strong spots in a six-fold symmetry correspond to the (220) reflections (d-spacing, 1.4 Å) of the face-centered cubic (FCC) Ag single crystal. There are also unexpected forbidden reflection spots in a six-fold symmetry (1/3{422} reflections) which should be caused by the formation of stacking faults or twins. The [111] TEM image of the nanopetal in Fig. 1c shows the × 3{422} lattice spacing (2.5 Å) of the FCC Ag crystal, and the [110] TEM image of the nanopetal tilted at 34.8° reveals plenty of atomic steps at the edges of the petals (Fig. 1d), at which the side planes are a mixture of {100} and {111} planes (Fig. S5a and b, ESI†). The strong Ag signal shown in Fig. S5c (ESI†) confirms the high purity of Ag. The XRD measurement also shows the FCC Ag crystal for flower-like NCs (Fig. S6, ESI†).

A series of control experiments were carried out to understand the roles of MPS, Ni²⁺, CH₃COO⁻, and SO₄²⁻ based on the in situ current–potential responses and SEM observations. Fig. S7a (ESI†) shows the presence of only a small number of scattered nanoparticles after CSE when using Ag coated on bare FTO. The MPS with the hydrolysable methoxy end-group adhered to the substrate and its sulfur functional group can perform as a bridge to link the metal ions in the electrolyte, which provides a strong covalent bond to improve the interfacial contact between the electroplated metal and the substrate (Supplementary Note 2, Fig. S7a-c, ESI†). The MPS...
layer facilitates the nucleation of NCs, where usually a high overpotential is required, so that a small overpotential can be used for the nucleation and the MPS layer provides the synthetic freedom in manipulating the overpotential for the shape control of NCs. The Ni$^{2+}$ ions in the electrolyte are responsible for the etching process because the electro-oxidative product of Ni$^{3+}$ becomes an etchant in the formation of Ag NCs, leading to a reduced petal thickness (from a ~20 nm nanoplate to a ~10 nm nanosheet) and round Ag nanosheets (Supplementary Note 3 and Fig. S7d–f, S8, ESI†). SO$_4^{2−}$ and CH$_3$COO$^−$ are utilized for selective adsorption on certain crystal planes to produce high-aspect-ratio NCs. The geometric symmetry of SO$_4^{2−}$ $(C_{5v})$ prefers to adhere to the Ag {111} plane, which induces the kinetic product of two-dimensional-hexagonal Ag nanopetals. In contrast, CH$_3$COO$^−$ is a crucial ligand in this system to directly influence the final morphology of Ag NCs in a standing architecture by adsorbing on both the basal {⟨111⟩} planes and the side planes (a mixture of {100} and {⟨111⟩} planes). The capping effect of CH$_3$COO$^−$ ions causes the preferential growth on the defects of Ag nanopetals to form interlaced clusters. Our experiment shows that the optimum [CH$_3$COO$^−$]/[SO$_4^{2−}$] ratio approximates to 2 to produce japonica-like Ag flowers constructed with high-aspect-ratio Ag nanopetals (Supplementary Note 4, Table S1 and Fig. S7g–i, S9, S10, ESI†).

The CSE technique was also utilized to synthesize NCs in various morphologies and a generic rule is proposed to control the morphology of Ag NCs. Icosahedral and decahedral Ag NCs were created by CSE using a high scan rate of 50 mV s$^{-1}$ at a reversed potential (Fig. 2a and b). In this case, electrodeposition occurs entirely at a sufficient Ag$^+$ concentration and sufficient atoms can be added to the surface of the seeds for their continuous growth into thermodynamically favored shapes. Fig. 2c and d show the comb-like Ag dendrites obtained by employing a modified cathodic potential with a square waveform ($E_{on,1} = 0.3$ V, $E_{on,2} = 0$ V, 10 cycles per s), where the electroplating rate at 0 V is faster than that at 0.3 V. The fast atomic addition would cause a non-equilibrium condition between the diffusion rate and the reaction rate, and the diffusion-limited growth was invoked, resulting in dendrite-like nanostructures under favorably branching growth. TEM images and the corresponding SAED pattern reveal that most of the main stems and branches of polycrystalline Ag dendrites grow along the [211] direction and are bound with {111} surfaces. Fig. 2e and f show that the Ag nanorods with a length larger than 3 μm were produced in a high yield. By changing the working potential of the square waveform in the cathodic potential ($E_{on} = 0.3$ V, $E_{cat} = 0.9$ V, 10 cycles per s), the thermodynamically favored Ag decahedra were primarily formed, since the presence of the five-fold twinned structure can minimize the surface energy of a single Ag crystal (Fig. S11a, ESI†). However, the diminution of the surface energy cannot compensate the internal strain energy in a twinned structure as the seeds become larger than a critical size. Additionally, under the effect of the Ni$^{3+}$ etchant, the most reactive twinned structures were etched away. The decahedral Ag seeds then grew into single-crystal truncated octahedrons enclosed by four {⟨111⟩} and four { ⟨100⟩} surfaces (Fig. S11b, ESI†). In a subsequent kinetically controlled region, Ag was intermittently electroplated with a slow atomic addition when the potential was switched to 0.3 V (the reduction reaction ceases at a potential of 0.9 V). The slow atomic addition provides enough time for Ag seeds to evolve along the axial direction, where a hexagonal cross section is observed in the final product. The nanorods are enclosed by four {⟨111⟩} and two { ⟨100⟩} surfaces in their side planes, corresponding to a { ⟨111⟩}/[ ⟨100⟩] ratio approximating to 2 (Fig. S11c and d, ESI†), which is in accordance with the effective adsorption of [CH$_3$COO$^−$]/[SO$_4^{2−}$] in this system.

Fig. 2g and h describe the proposed formation mechanism of Ag NCs, which demonstrates the programmability of Ag NCs that can be achieved by CSE. The growth rate is controlled via the overpotential in the cathodic scan and the population of adions is manipulated via the dissolution of a thin metal film in the growth medium. Here, it has to be emphasized that the concentration of Ag$^+$ near the interface is dynamically correlated with the potential waveform used in CSE. Four examples are given. For the flower-like Ag NCs shown in the blue curve of Fig. 2h, the kinetic product, i.e. two-dimensional Ag nanosheets, was favorably formed when Ag$^+$ was sufficient near the equilibrium condition (at a low overpotential). When the potential was increased gradually (a slow scan rate was performed in the reduction), a continuous growth of Ag nanosheets was allowed, which then began to grow vertically as standing-type Ag NCs on the surface active sites of the preformed nanosheets due to the preferential adsorption of CH$_3$COO$^−$ as discussed before. The flower-like Ag NCs with smaller nanopetals can be effectively produced via repeated CSE cycles (Fig. S12, ESI†). In contrast, when a high scan rate was performed in the reversed potential, icosahedral and decahedral Ag NCs will be quickly formed in the thermodynamically controlled region with a sufficient Ag$^+$ concentration near the interface, as shown in the red curve of Fig. 2g. Fig. 2h shows that the Ag seeds were initially formed by using a square waveform in the reversed cathodic potential, which would evolve into nanorods through a slow atomic addition where a sufficient Ag$^+$ concentration was maintained at a low overpotential (red curve), or grow into the typical non-equilibrium product of dendrites via a fast reaction rate because of the depletion of Ag$^+$ at a high overpotential (blue curve).
To demonstrate the high electro-oxidation activity, our synthesized flower-like Ag NCs were chosen as electrodes in the application of non-enzymatic electrochemical glucose biosensors. Enzyme-based biosensors have been used to detect blood glucose based on glucose oxidase. Yet, their detection limit is not effective in other sources, such as tears and saliva.9 The current record-high sensitivity of 12.5 mA cm$^{-2}$ mM$^{-1}$ and an ultralow detection limit of 5 nM are reported based on a gold electrode that incorporates NiO, or carbon nanotubes for an ultralow detection limit of 5 nM are reported based on a gold electrode exhibiting rapid response and reaches a steady state within 2 s. The flower-like Ag NCs exhibit significantly enhanced electrocatalytic activity with a detection limit of <0.1 nM at a signal-to-noise ratio of 3 and a sensitivity of up to 4230 mA cm$^{-2}$ mM$^{-1}$ (Fig. 3b), which is the lowest detection limit and the highest sensitivity achieved to date among all reported catalysts9 (Supplementary Note 5, Video S1 and Fig. S13–S15, ESI†). The inset of Fig. 3b and Fig. S16 (ESI†) shows a good triple-linear calibration range between the current and the concentration of glucose. The superior activity of flower-like Ag NCs can be attributed to four aspects. First, the curved nanopetals with a high density of atomic steps reduce the dissociation barrier in the electrocatalytic reaction.29 Second, the flower-like Ag NCs provide a highly effective area for the Ag(OH)$_{ad}$ layer to react with glucose molecules. Third, the three-dimensional continuity of intercrossed high SA:V Ag petals facilitates electron transport. Finally, the bridge linker of MPS provides a good interfacial contact between Ag NCs and the substrate, leading to efficient current collection.30 Thus the prominent electrocatalytic ability of flower-like Ag NCs has the potential to serve as new-generation electrodes in the application of noninvasive electrochemical glucose biosensors.

In summary, a new CSE technique is developed to electrochemically convert a Ag film into functional NCs in a high yield. This technique provides great flexibility in tuning the shapes of Ag NCs by dealing with a potential waveform, population of adions and additives in a methodical manner. Significantly enhanced electro-oxidation activity to glucose was demonstrated using the flower-like Ag NCs, which turn Ag into a highly active catalyst among all of the reported catalysts used in non-enzymatic electrochemical glucose biosensors.

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References