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Facile and shape-controlled electrochemical synthesis of gold nanocrystals by changing water contents in deep eutectic solvents and their electrocatalytic activity

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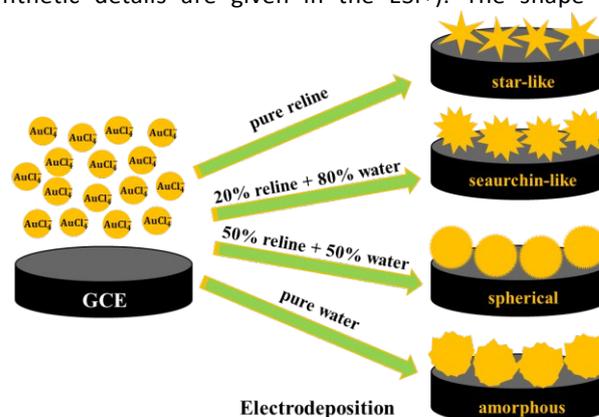
A green, facile and shape-controlled method was developed to synthesize Au nanocrystals (NCs) with different morphologies in deep eutectic solvents (DESs) with different contents of water. The shape and structure of Au NCs were tuned by using different DESs, and/or by controlling the applied potential and the content of water. The resulting Au NCs exhibited a high electrocatalytic activity and poisoning-resistance for ethanol electrooxidation in alkaline media.

Shape-controlled synthesis of gold (or other noble metals) nanocrystals (NCs) has attracted, in recent years, intense interest because of their fascinating physical and chemical properties and promising applications in various regions, such as sensors, catalysts, electronics, optics, surface-enhanced Raman scattering (SERS) and fuel cells.¹⁻⁸ It is well known that the properties and catalytic functions of Au NCs depend strongly on their size, shape, crystallinity and surface structure.⁹⁻¹⁴ Therefore, the shape-controlled synthesis and applications of Au NCs have been extensively studied and received great success during the past decade. Au NCs with different shapes (spheres, cubes, rods, wires, flowers, dendritic structures and polyhedral) have been obtained by different methods.¹⁵⁻²² For example, Qin et al. prepared single-crystalline dendritic Au nanostructures in a solution of ionic liquid ([BMIM][PF₆]).²³ Huang et al. synthesized Au dendrites using the complexes of dodecyltrimethylammonium bromide and β -cyclodextrin.²⁴ One-step electrodeposition, as an effective and convenient method, has been developed for shape-controlled syntheses of Au NCs.^{25,26}

Deep eutectic solvents (DESs) were first reported by Abbott and co-workers as a new generation of ionic liquids (ILs).²⁷⁻²⁹ DESs, simple eutectic-based ionic liquids (ILs), can be usually produced by using quaternary ammonium or phosphonium salts mixed with hydrogen-bond donors such as amides, carboxylic acids and alcohols, and thus are liquids at ambient temperature.^{28,30-32} Compared with the conventional ILs, DESs

have additional advantages of nontoxicity, biodegradation, low cost and environment-friendliness.³³⁻³⁶ Therefore, DESs have broad applications in shape-controlled synthesis of nanoparticles, electrochemistry, metal-organic frameworks, colloidal assemblies and biocatalysis.³⁷⁻⁴² In recent years, shape-controlled synthesis of nanomaterials in DESs represents an intense research interest. Sun and co-workers have contributed to this area: triambic icosahedral (TIH) Pt NCs were synthesized in DESs using a programmed square-wave potential electrodeposition method;⁸ star-shaped Au NCs bounded with (331) and vicinal high-index facets were also obtained directly by the reduction of HAuCl₄ with L-ascorbic acid in DESs at room temperature.¹⁴ However, during synthesis of nanomaterials in DESs, a major problem is the presence of water like an impurity which can affect the shape and monodispersity of the resulting nanomaterials.^{14,43} Hence, controlling the content of water in media is particularly important to shape-controlled synthesis of nanomaterials in DESs.

Herein, we report a green, facile and shape-controlled electrochemical synthesis of Au NCs by changing water contents in DESs for the first time. Au NCs with different morphologies were successfully prepared by simple one-step electrodeposition on a glassy carbon electrode (GCE) in DES with different contents of water as illustrated in Scheme 1 (synthetic details are given in the ESI†). The shape and



Scheme 1. Illustration of the electrodeposition method for preparation of Au NCs in reline with different contents of water.

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structure of Au NCs can be tuned easily by using different DESs, and/or by controlling the applied potential. Particularly, the water content was used as a key factor to control the morphology and structure of Au NCs. Furthermore, the obtained Au NCs modified electrodes exhibited a high electrocatalytic activity and good poisoning-resistance for ethanol electrooxidation in alkaline media.

The Au nanostars (NSs), Au nanodentists (NDs) and Au hierarchical nanoflowers (NFs) were obtained respectively in reline, ethaline and glyceline, and their field emission scanning electron microscopy (FESEM, ZEISS SUPRA 40) images are shown in Fig. 1. Furthermore, high-magnification FESEM images (insets of Fig. 1) and transmission electron microscopy (TEM, JEOL JEM 2100) image (Fig. S4, ESI[†]) reveal the details of the Au NCs. In the preparation process of Au NCs, DESs played a key role in shape control, and any template, surfactant, additive and seed needn't be used. Compared with water system, when DESs were used as media, no supporting electrolyte such as sulfuric acid was needed in the preparation of Au NCs, therefore the method is more environment-friendly.

As shown in Fig. 1A, well-crystallized Au NSs were synthesized in reline. The reason for star-like nanostructure of Au NCs might be due to -NH₂ groups of urea, which have an impact on crystal formation process.^{16,44} Nucleation, adsorption and formation of NCs are fast processes and the morphology adjustment is a slow process dominated by the kinetic model. The growth of Au NSs occurs at the initial tips and thorns of the star structures, which is predominated by kinetic process.^{10,26,45} Fig. 1B and Fig. 1C show that Au NDs and Au hierarchical NFs were obtained in ethaline and glyceline, respectively. In ethaline and glyceline, only the functional groups (-OH groups) of the hydrogen-bond donor are different from -NH₂ groups of reline. Therefore, the reasons for dendritic and branched nanostructures of Au NCs are likely that -OH groups of ethylene glycol and glycerol have an impact on the formation process and morphology of Au NCs. Consequently, the DESs acted as not only solvents but also shape-directing agents in preparation of Au NCs.

It is generally known that the applied potential plays a vital role in the nucleation and growth of Au NCs in the process of electrodeposition.¹⁶ The well-crystallized and uniform Au NCs couldn't be synthesized at less or more negative applied potential than the optimal potential. As shown in Fig. S1 (ESI[†]), at less negative applied potential than -0.60 V (vs. Pt), such as -0.40 V (Fig. S1A, ESI[†]), we could barely obtain Au NCs in reline, because it is difficult to reduce Au³⁺ ion to Au. When the applied potential is less negative than -0.36 V (Fig. S2, ESI[†]), no deposition of metallic Au carried out in reline. While the potential drops to -1.40 V (Fig. S1B, ESI[†]), a large amount of irregular Au NCs were obtained in reline and some of them were conglomerated. The reason is that as the applied potential negatively shifts, it becomes much easier to reduce

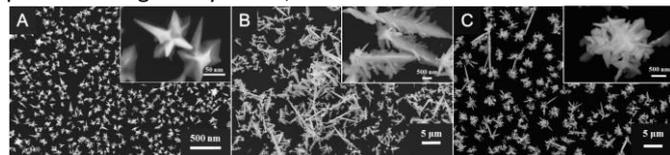


Fig. 1. FESEM images of Au NCs electrodeposited on GCEs in DESs containing 20 mM HAuCl₄ at 90 °C for 600 s with different conditions: (A) applied potential of -0.60 V (vs. Pt) in reline, (B) applied potential of -0.90 V in ethaline and (C) applied potential of -0.85 V in glyceline. The insets show high-magnification FESEM images of Au NCs.

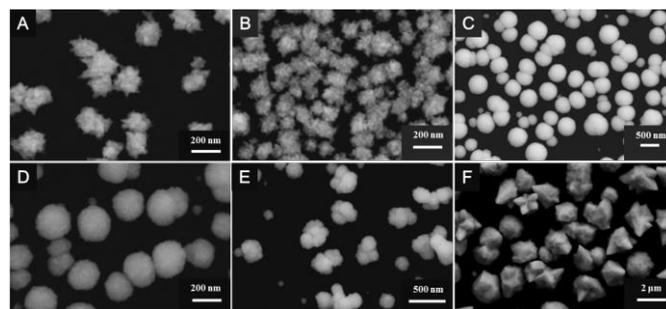


Fig. 2. FESEM images of synthesized Au NCs in reline with water content of 10% (A), 20% (B), 50% (C), 80% (D), 90% (E) and 100% (F).

Au³⁺ to Au and the reduction rate also gets fast. Therefore, the nucleation and growth of Au NCs are hard to be controlled at more negative applied potential. In addition, we also found that the nuances of the applied potential, even though a small change of 50 mV, could make a significant effect on the morphology of synthesized Au NCs in the DESs. Fig. S1C and S1D (ESI[†]) show the FESEM images of Au NCs prepared at -0.55 V and -0.65 V in reline. When the applied potential positively moved from -0.60 V (the optimal applied potential) to -0.55 V (Fig. S1C, ESI[†]), the amount of NSs were decreased and some irregular NCs were produced. When the applied potential negatively moved 50 mV to -0.65 V (Fig. S1D, ESI[†]), lots of irregular NSs and several nanorhons (NTs) were produced instead of uniform NSs structures. Results showed that Au NCs with a well-crystallized and unique morphology could be synthesized in reline only at -0.60 V (Fig. 1A). The applied potential determines the current and the reaction rate, and thus affects the eventual morphologies and structures of Au deposits.⁴⁶ Therefore, the final morphology of Au deposits depends strongly on the potential applied on the electrode. Similar cases also happened in ethaline and glyceline.

The presence of water in DESs could also influence on the morphology of synthesized Au NCs. As shown in Fig. 2 and Fig. S3 (ESI[†]), Au NCs with different morphologies were synthesized in reline, ethaline and glyceline with different contents of water. Fig. 2B shows that in reline-water mixed solvent (8:2, v/v), the prepared Au NCs were seurchin-like aggregates of numerous small nanoparticles, while thorns of NSs disappeared entirely. When the content of water increased to 50% (reline-water, 5:5), spherical Au NCs with a rough surface (Fig. 2C) were obtained and their sizes increased. Fig. 2E shows that some conglomerated spherical Au NCs were obtained in reline-water (1:9, v/v). The morphology and structure of as-obtained Au NCs became irregular with the increase of the water content. When the solvent was pure water, the prepared Au NCs were irregular polyhedron nanostructures (Fig. 2F). To sum up, the morphology and structure of Au NCs could be tuned by controlling the content of water in DESs. Meanwhile, Au NCs with different morphologies were also synthesized in two other DESs with different contents of water (Fig. S3, ESI[†]). The reasons for the morphology control of Au NCs by water content are as follows: 1) The rate of ionic migration and electrochemical reduction are slow in high viscosity DESs, and thus the nucleation and growth of NCs are slow. It is beneficial to orienting growth and shape-controlling of NCs. With the increasing of water content, the viscosity of the medium decreases, the rate of ionic migration and electrochemical reduction get fast, and the

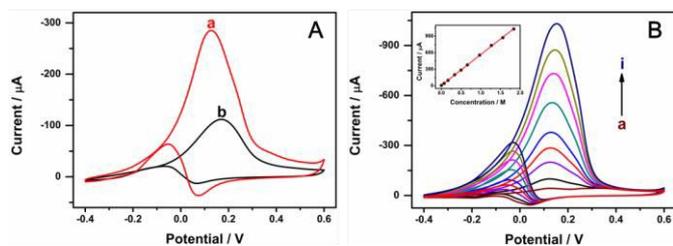


Fig. 3. (A) CVs of the Au NSs modified electrode (curve a) and commercial Au electrode (curve b) in 0.5 M NaOH solution containing 0.50 M ethanol with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, (B) the catalytic responses of the Au NSs modified electrode with different concentrations of ethanol (curve a-i): 0.07, 0.17, 0.34, 0.50, 0.66, 0.97, 1.27, 1.56 and 1.84 M in 0.5 M NaOH. Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$. Inset: The relationship of the catalytic current with ethanol concentration.

nucleation and growth of NCs get fast too. Thus, the morphology of Au NCs changes. 2) In pure DESs, the diffusion of Au^{3+} to electrode surface is hindered by a large number of choline cations (Ch^+), which means that only a few Au^{3+} take part in the electrochemical reaction and thus NCs with sharply pointed structures are formed. When the water content of medium increases, the number of Ch^+ decrease, a larger number of Au^{3+} take part in the electrochemical reaction and thus the obtained Au NCs do not have the sharply pointed structure. To further confirm the structure and composition of the Au NSs, other characterizations were carried out (detailed information are given in the ESI†, Fig. S4–S7).

Ethanol is one of the most promising fuels for alcohol based fuel cells.^{47,48} The mechanism for ethanol oxidation on catalyst is that ethanol is adsorbed on the surface of the catalyst, then the bonds in ethanol molecules are broken and the activation energy reduce.⁴⁹ There are main reaction pathways for the electrooxidation of ethanol on electrocatalyst surface: one is direct oxidation, the other is indirect oxidation. In the pathway of indirect oxidation, ethanol is oxidized by breaking the C–C bond and ultimately generates CO_2 .^{48,50} Gold nanomaterials are beneficial to improving the C–C bond cleavage and complete oxidation of ethanol to CO_2 .⁵⁰ Hence Au NCs exhibit a good electrocatalytic activity for ethanol electrooxidation as electrocatalyst. The electrocatalytic activities of the Au NSs modified electrode and commercial Au electrode toward ethanol oxidation were evaluated by cyclic voltammetry in 0.5 M NaOH solution containing 0.50 M ethanol (Fig. 3A). The Au NSs modified electrode performed much better electrocatalytic ability, and had smaller oxidation potential (0.13 V, vs. SCE) for ethanol (Fig. 3A, curve a) than the commercial Au electrode (0.17 V, Fig. 3A, curve b). Besides, the catalytic current of the Au NSs modified electrode was higher than that of the commercial Au electrode, revealing a larger electroactive surface area and more surface active sites of the Au NSs modified electrode. The higher catalytic ability may be ascribed to the star-like morphology and specific structure of Au NSs.

Multiple ethanol oxidation pathways occur simultaneously and often yield undesirable products and long-lived intermediates such as CO, acetaldehyde, and CH_x .⁴⁸ These poisoning intermediates can be adsorbed on the surface of the catalyst, and reduce the electrocatalytic activity of the catalyst.^{50,51} In general, the cathodic peaks were observed in the reverse scan for noble metallic catalysts.^{52–54} Larger ratio of the peak currents in the forward potential scan (i_f) to the reverse scan (i_r) would bring better poisoning-resistance of the

catalyst for ethanol oxidation. The oxidation peak in the backward scan corresponds to the electrochemical oxidation of CO and other adsorbed species. The value of i_f/i_r for the Au NSs is 4.47 (Fig. 3A), and is much higher than those for Pt NCs (such as Pt nanoflowers, TIH Pt NCs, and THH Pt NCs)^{8,22,38} and composite metallic NCs (such as SF-MWCNT-Pd, Pd/C, S-MWNT/Pd, and hAg@Pt-RGO),^{55–58} showing that the Au NSs modified electrode had better poisoning-resistance and steady-state behaviour for ethanol oxidation. Fig. 3B shows the typical cyclic voltammograms (CVs) of the Au NSs modified electrode with successive addition of ethanol into a blank 0.5 M NaOH solution. After injection of ethanol into the solution, the modified electrode responded quickly (less than 0.1 s) to reach 95% of the maximum current. At the same time, the corresponding catalytic currents increased linearly. As can be seen from the inset of Fig. 3B, the linear response toward ethanol oxidation was up to 1.84 M ethanol. The results indicate that the prepared Au NSs modified electrode showed a high electrocatalytic activity and good poisoning-resistance for ethanol electrooxidation. Meanwhile, other two Au NCs modified electrodes prepared in ethaline and glyceline also exhibited a high electrocatalytic activity and stability for ethanol electrooxidation in alkaline media (Fig. S8, ESI†).

In summary, a green, facile and shape-controlled electrodeposition synthesis method was developed to prepare Au NCs with different morphologies in three DESs by changing water contents. The morphologies and structures of Au NCs can be tuned easily by using different DESs, and/or by controlling the applied potential and the content of water. Furthermore, the Au NCs modified electrodes exhibit a high electrocatalytic activity and good poisoning-resistant ability for ethanol electrooxidation in alkaline media. This work would have an important instruction meaning for shape-controlled synthesis of other noble metal NCs in DESs and be of significance in some promising applications of fuel cells, electrochemical sensors and electrocatalysis.

Acknowledgements

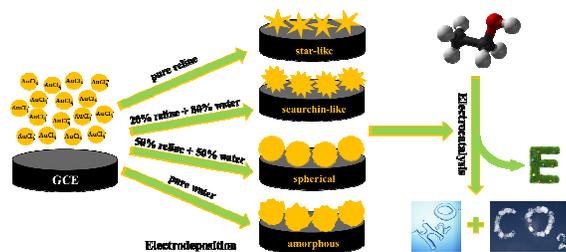
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Table of Contents



Au NCs with different morphologies were synthesized in DESs by changing water contents, and used as electrocatalyst for ethanol electrooxidation.