



Gold Aerogels: Three-Dimensional Assembly of Nanoparticles and Their Use as Electrocatalytic Interfaces

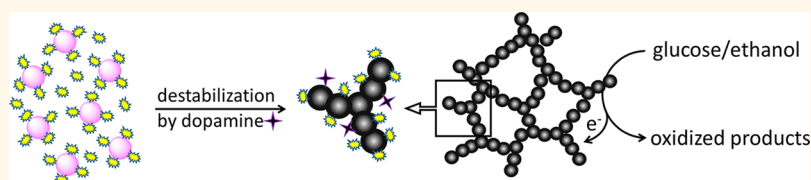
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S Supporting Information



ABSTRACT: Three-dimensional (3D) porous metal nanostructures have been a long sought-after class of materials due to their collective properties and widespread applications. In this study, we report on a facile and versatile strategy for the formation of Au hydrogel networks involving the dopamine-induced 3D assembly of Au nanoparticles. Following supercritical drying, the resulting Au aerogels exhibit high surface areas and porosity. They are all composed of porous nanowire networks reflecting in their diameters those of the original particles (5–6 nm) *via* electron microscopy. Furthermore, electrocatalytic tests were carried out in the oxidation of some small molecules with Au aerogels tailored by different functional groups. The beta-cyclodextrin-modified Au aerogel, with a host–guest effect, represents a unique class of porous metal materials of considerable interest and promising applications for electrocatalysis.

KEYWORDS: Au aerogels, nanoparticle assembly, dopamine, electrocatalysis, host–guest interaction, porous metal

Assembling of colloidal nanocrystals into nanostructured materials with macroscopic dimensions has attracted growing research interest in the last decades, since their collective properties might be superior to those of the individual nanocrystals as well as bulk samples.^{1–4} Considerable effort has been made in the self- or directed-assembly of nanoparticles (NPs) into one, two, and three dimensions. This concept provides a tailored, bottom-up approach to material design and enlarges the scope of potential applications.^{5–8} However, the merging of nanosized entities with their unique optical, electronic, and/or magnetic properties into materials with macrodimensions that can be easily manipulated and processed is still a challenge. Recently, gels and aerogels fabricated from various metal and semiconductor NPs available in colloidal solutions have been demonstrated to offer such an avenue.^{9,10}

Aerogels are highly porous materials with ultralow density, high surface area, and large open interconnected pores.^{11,12} Significant progress has been achieved among others by the Brock, Leventis, and Kanatzidis groups as well as ours, which led to a variety of aerogel components and opened up enormous opportunities for semiconductor technologies,

catalysis, optoelectronics, sorbents, and filters.^{13–16} In particular, the interest in noble metal aerogels has sparked sustained research to develop synthetic methods and potential applications because of their unique electronic, catalytic, and optical characteristics. For example, our group reported on a series of mono/multi-noble metal aerogels prepared from solutions of colloidal NPs *via* a controllable destabilization approach.^{17,18} Further research has shown that such noble metal aerogels exhibited excellent performance in electrocatalysis, used as advanced electrocatalysts or metal porous supports.^{19,20} An interesting step has been made on metal nanoshell aerogels derived from the assembly of hollow structures (Ag, Au/Ag, Pd/Ag, Pt/Ag) by Arachchige *et al.*^{21,22} As is well known, Au nanostructures have been extensively studied, driven by their fascinating properties and widespread applications in nanoelectronics, biomedicine, sensing, catalysis, *etc.*^{23–25} Various monometallic Ag, Au, Pt, and Pd and bi- or trimetallic composite aerogels were prepared

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via different approaches such as oxidation-, salt-, and temperature-induced aggregation as well as a spontaneous gelation, where the issues of gelation time and the avoidance of preaggregation have been solved for Pd and Ag.^{16,21} The only example thus far referring to monometallic Au aerogels involves strongly preaggregated original colloidal particles (larger than 100 nm) and long gelation time (1 week), thus limiting further applications.¹⁷ Considering Au NPs that have often been restricted by their tendency to sinter to large-size aggregates, to date, the fabrication of Au aerogels with nanosized metal backbones by a direct sol–gel method and especially their applications still remain largely unexplored and a great challenge.

In this contribution, we reported on a facile strategy for preparing Au aerogels composed of three-dimensional (3D) nanowire-like networks by dopamine-induced assembly of Au NPs. The primary structural units of the resulting Au aerogels match the sizes of the original particles (5–6 nm). Here, dopamine acts as an efficient destabilizing agent for the controlled assembly of Au NPs into a branched network with various capping ligands, namely, beta-cyclodextrin (β -CD), citrate, and nonstabilizers (without organic surface ligands). Compared to established methods, this synthetic procedure is distinguished by a fast, simple, and versatile gelation without preaggregation of the NPs. The as-prepared Au aerogels possess different functional groups and exhibit large surface areas and high porosity. Taking glucose and ethanol as examples, electrochemical results show that the catalytic progress is greatly promoted by the Au aerogel functionalized with β -CD.

RESULTS AND DISCUSSION

The building blocks for the β -CD-modified Au hydrogel were directly synthesized by reducing chloroauric acid with sodium borohydride in the presence of natural β -CD at room temperature, which have an average diameter of 5.0 ± 1.0 nm (β -CD–Au NPs; see Figure S1, Supporting Information). The β -CD is expected to adsorb on the surface of the Au NPs and stabilize the particles due to steric effects and the surface charge of -39.8 mV.²⁶ It is reported that dopamine can form a host–guest inclusion complex with β -CD in aqueous solution,²⁷ and it might also adsorb and interact with the Au surface due to the strong affinity between dopamine and the Au core.^{28,29} Thus, dopamine could be employed as a destabilizing agent to induce the β -CD–Au NPs to assemble into a hydrogel. Prior to the addition of the dopamine, the NP solution for each sample was wine red and stable for at least three months. The gelation of the Au hydrogels was initiated by the introduction of dopamine into this solution. Fluffy black solids settled out of the solution within 6 h at high concentrations of dopamine (*i.e.*, 100 μ M), while at 10 μ M dopamine, the gelation process was extended to 2 days (details can be seen from Table 1 and Figure 1). It is found that the gelation kinetics can be tuned by the concentration of the destabilizer. The Au hydrogel induced

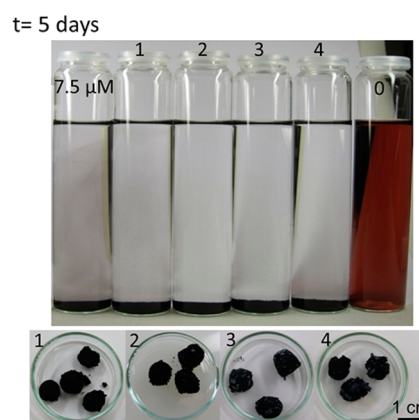


Figure 1. Photographs of Au colloids before and after the addition of dopamine with different concentrations: 7.5, 10, 20, 50, and 100 μ M, respectively. Time = 5 days (up) and the as-prepared Au aerogels (bottom).

by lower concentrations of dopamine (*i.e.*, 7.5 μ M) showed a light gray supernatant after 1 week, while 2.5 μ M dopamine would not work for Au NP gelation even after 3 months (Figure S2). Our presented method enables a rapid gelation of the β -CD–Au NPs by simple addition of the appropriate amount of dopamine. In addition to no need for concentrating the initial sols, which is generally required in the sol–gel transformation of NP colloids,^{17,18,20–22} the method is easy to scale up.

After supercritically drying with CO_2 , the four Au aerogel samples (formed with the aid of 10, 20, 50, and 100 μ M dopamine, respectively) reveal almost the same morphologies as seen in scanning and transmission electron microscopy (SEM and TEM), as shown in Figure 2 and Figure S3. The

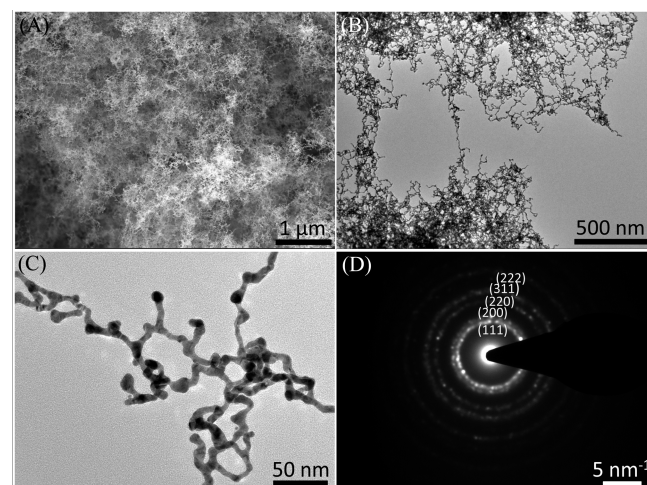


Figure 2. SEM (A), TEM (B, C), and electron diffraction (D) of the $\text{Au}_{\beta\text{-CD}}$.

Table 1. Summary of Au Gel Formation Data

Au aerogels	[dopamine]/ μ M	time for gelation/h	density/g cm^{-3}
1	10	72	0.043
2	20	24	0.040
3	50	12	0.040
4	100	6	0.042

evolving structures are highly porous and composed of interconnected networks of ultrathin wire-like structures with many bifurcations. They exhibit a very broad pore size distribution with open meso- and macropores. The average diameters of the wires are 5.8 ± 1.0 , 5.8 ± 1.0 , 5.9 ± 1.0 , and 5.7 ± 1.0 nm, respectively, which are of similar size to the starting β -CD–Au NPs, thus suggesting direct fusion of the original particles. The typical electron diffraction pattern

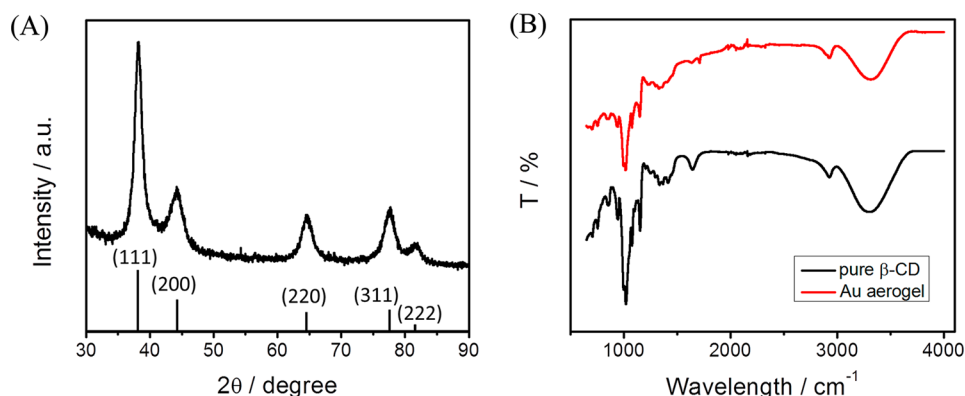


Figure 3. XRD patterns (A) and FT-IR spectrum (B) of the $\text{Au}_{\beta\text{-CD}}$.

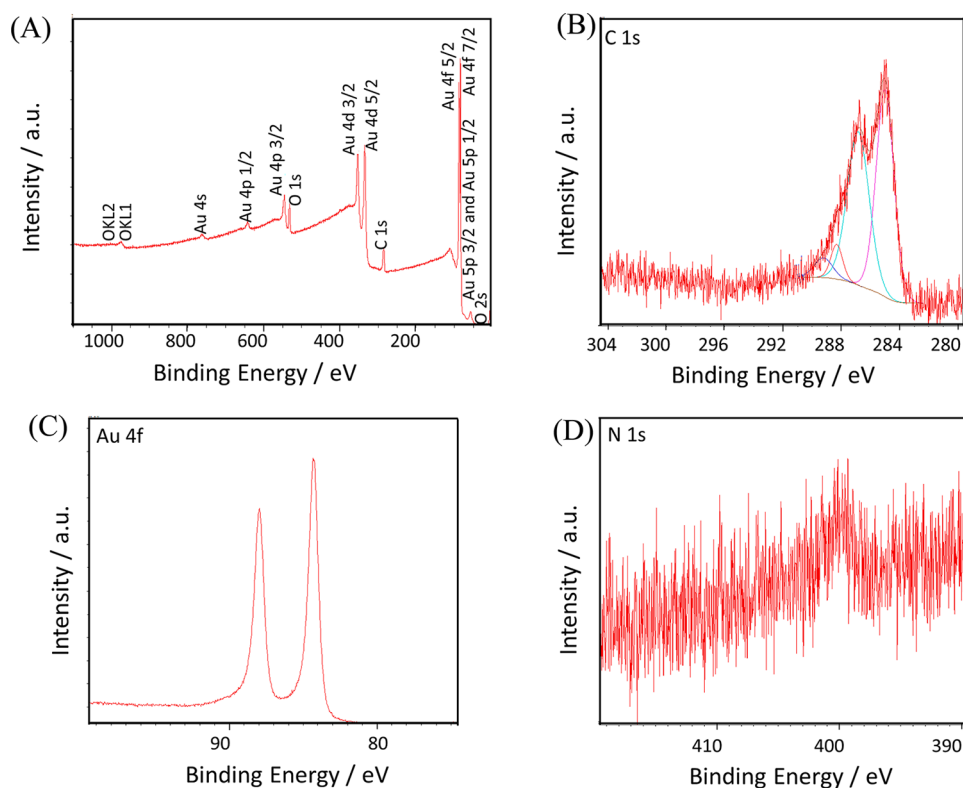


Figure 4. XPS wide scan (A) and high-resolution C 1s (B), Au 4f (C), and N 1s (D) spectra of the $\text{Au}_{\beta\text{-CD}}$.

presented in Figure 2D shows diffraction rings that prove the polycrystalline nature of the nanowires shown in the corresponding TEM image. According to a rough estimate based on volume and weight of several pieces of the black Au aerogels, the average densities of the materials are calculated to be $0.041 \pm 0.002 \text{ g cm}^{-3}$, corresponding to less than 1/500 of the bulk density of Au. This value fits into the typical range of aerogel densities ($0.004\text{--}0.500 \text{ g cm}^{-3}$), being much smaller than those of other porous Au structures.^{30–32} From the physical properties and morphologies of the Au aerogels produced by different concentrations of dopamine, we may deduce that the concentration of the destabilizer affects only the speed of the Au NP gelation, but not the final structures of the aerogels (*cf.* also ref 19). Considering the ease of the Au aerogel preparation and the consumption of the agents, a Au aerogel induced by 20 μM dopamine (noted as $\text{Au}_{\beta\text{-CD}}$) was chosen as an example for further investigations.

A representative powder X-ray diffraction (XRD) pattern of a $\text{Au}_{\beta\text{-CD}}$ aerogel sample in Figure 3A displays diffraction peaks that can be assigned to the (111), (200), (220), (311), and (220) planes of a face-centered-cubic (fcc) polycrystalline structure, which is in accordance with the electron diffraction. The broad Bragg reflections are due to the nanoparticulate nature of the as-prepared Au aerogel. The Fourier transform infrared (FT-IR) spectrum of the $\text{Au}_{\beta\text{-CD}}$ exhibits typical CD absorption features of the coupled C–O–C stretching/O–H bending vibrations at 1156 cm^{-1} , the coupled C–O/C–C stretching/O–H bending vibrations at 1030 and 1080 cm^{-1} , CH and CH_2 stretching vibrations at $2800\text{--}3000 \text{ cm}^{-1}$, and a broad hydroxyl band at $3300\text{--}3500 \text{ cm}^{-1}$ (O–H stretching) and at 1643 cm^{-1} (OH groups of the glucose moieties), respectively (Figure 3B). This suggests that the aerogel surface was capped with β -CD molecules. The amount of the surface coverage was investigated by means of thermogravimetric analysis (TGA). An about 18 wt % of β -CD was suggested in

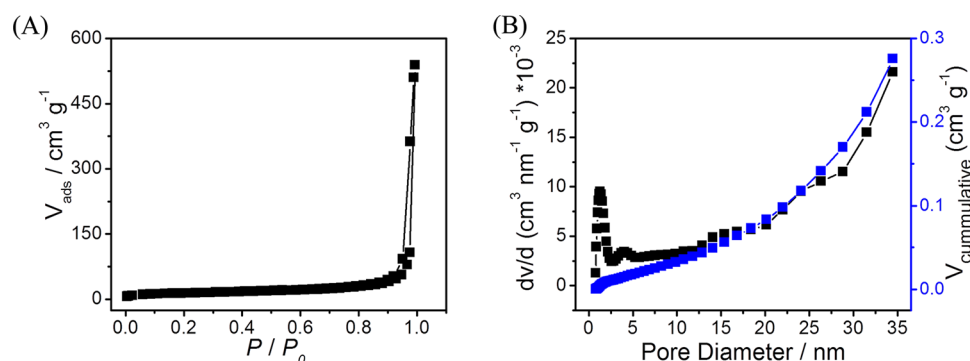


Figure 5. N_2 physisorption isotherm (A) and pore size distributions and cumulative pore volumes ($V_{\text{cumulative}}$) (B) of the $\text{Au}_{\beta\text{-CD}}$ aerogel.

the aerogel sample, which is in good agreement with the inductively coupled plasma optical emission spectroscopy (ICP-OES) results with a Au content of 81%.

The data derived from the wide-scan X-ray photoelectron spectroscopy (XPS) spectrum (Figure 4) display that the aerogel samples show as main elemental components Au, C, and O, coincident with the energy-dispersive X-ray spectroscopy (EDS) data (Figure S4A). High-resolution XPS was performed to gain more insight into the structure of the as-prepared Au aerogel sample. The C 1s spectrum was deconvoluted into four component peaks, which are assigned to the saturated hydrocarbons (C–C, 285.0 eV), C–O–(C, H) (286.7 eV), and O–C–O (288.6 eV) of the β -CD molecules and some small amount of oxidized groups (C=O). Such observations depict the presence of a large number of highly functionalized carbon-containing molecules and further confirm the presence of β -CD in the Au aerogel.³³ Additionally, the recorded Au 4f spectrum was composed of the Au 4f_{7/2} and Au 4f_{5/2} peaks with the binding energy at 84.2 and 87.9 eV, respectively, indicating mainly metallic gold of the sample. A small, but not-negligible signal for N 1s was observed at 399.6 eV via high-resolution XPS, which can be ascribed to the dopamine in the final aerogel product.

The N_2 physisorption isotherm for the $\text{Au}_{\beta\text{-CD}}$ provides information on the surface area and porosity properties. We observe a type II isotherm that is characteristic for macroporous materials. The surface area mainly reflects the adsorption on the walls of these macropores and is determined to be $50.1 \text{ m}^2 \text{ g}^{-1}$ by fitting the data to a Brunauer–Emmett–Teller (BET) equation. This is considerably larger than those of other porous Au materials.³⁴ The pore size distribution of the $\text{Au}_{\beta\text{-CD}}$ (Figure 5B) shows the presence of a broad range of pores from micro- to mesopores. The existence of micropores with a maximum at 1.4 nm can be attributed to the high content of β -CD in the Au aerogel.³⁵ The hierarchically porous structure of the Au aerogel with large surface area may offer more reaction sites and enable faster diffusion for the substrates in catalysis.

To monitor the formation process of the Au hydrogel induced by dopamine, UV–vis spectroscopy and TEM were conducted, providing evidence for a time-dependent growth (Figures 6, 7, and S5). Upon addition of $20 \mu\text{M}$ dopamine, the surface plasmon resonance (SPR) peak of the Au colloid is broadened and decreases with a slight red shift, from 513 to 524 nm, together with an obvious increase of the long-wavelength SPR band over time. These generally indicate the formation of larger nanostructures compared to nanoparticulate Au.³⁶ One may notice the gradually decreases of the long-wavelength SPR with increasing time, which is due to the

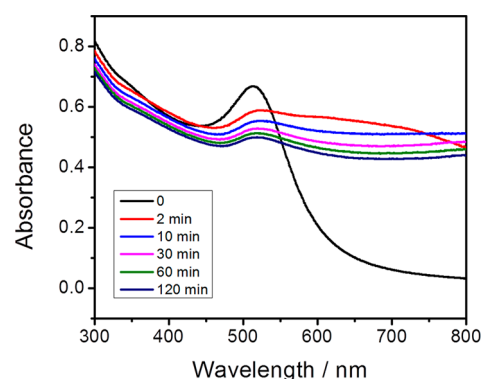


Figure 6. UV–vis spectra for the β -CD–Au NP assembly process at 0 min, 2 min, 10 min, 30 min, and 2 h, upon addition of $20 \mu\text{M}$ dopamine.

settling of the big network structures. It is clear from the corresponding TEM images that the fast growth of the Au hydrogel can be observed starting with the well-dispersed β -CD–Au NPs, via small assemblies composed of several NPs to short nanowires, small branched networks, and finally to large-scale interconnected nanowire networks within 2 h. About 2 days later, a Au hydrogel composed of highly porous nanowire networks is formed at the bottom of the bottle. Notably the dimensions of all the intermediates as well as those of the final hydrogel and aerogel are in the same size range as the original NPs (5–6 nm), and no preagglomerations occur into any kind of secondary structures.

We anticipate that the host–guest interaction between dopamine and β -CD could be one of the driving forces for the Au hydrogel formation from the β -CD–Au NPs. The XPS analysis of the $\text{Au}_{\beta\text{-CD}}$ shows, compared to β -CD–Au NPs, a significantly reduced atom ratio of C to Au (from 3.03 to 1.83), indicating a partial removal of β -CD from the Au surface during the dopamine-induced assembly. It is likely that dopamine induces the assembly of Au NPs into the fused nanowires starting from a partial loss of the β -CD surfactants, which initially stabilizes the particles against aggregation, as a consequence of the competition between dopamine and Au NPs. Driven by this host–guest interaction-induced assembly, a number of other guests for β -CD having similar complexation constants are suitable for the NP gelation. However, as seen in Figure 8A–C with increased concentration of these guests, instead of branched nanowire networks, the treatments of the β -CD–Au NPs yield different structures passing the state of fusion of several particles.

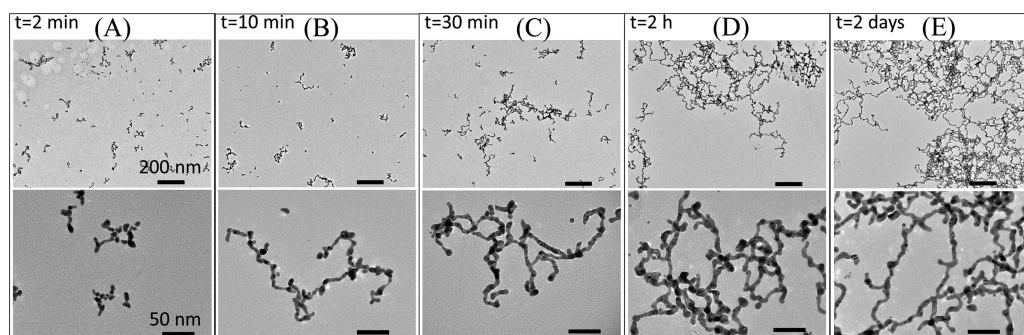


Figure 7. Corresponding TEM images of the β -CD-Au NP assembly process at 2 min (A), 10 min (B), 30 min (C), 2 h (D), and 2 days (E) upon addition of 20 μ M dopamine.

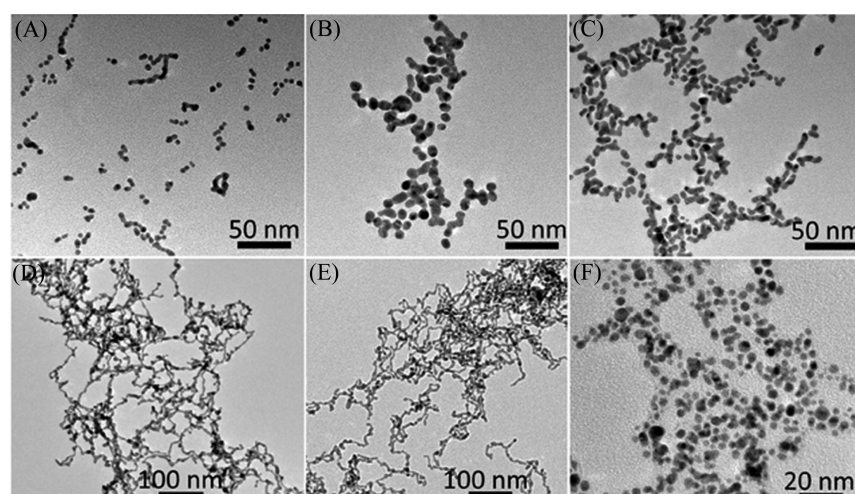


Figure 8. TEM images of Au assemblies induced by pyrocatechol (A, 500 μ M), 2-phenylethylamine hydrochloride (B, 100 μ M), and ferrocenecarboxylic acid (C, 100 μ M) from β -CD-Au NPs. TEM images of Au assemblies induced by 20 μ M dopamine from NS-Au NPs (D), Cit-Au NPs (E), and 5-HSTz-Au NPs (F).

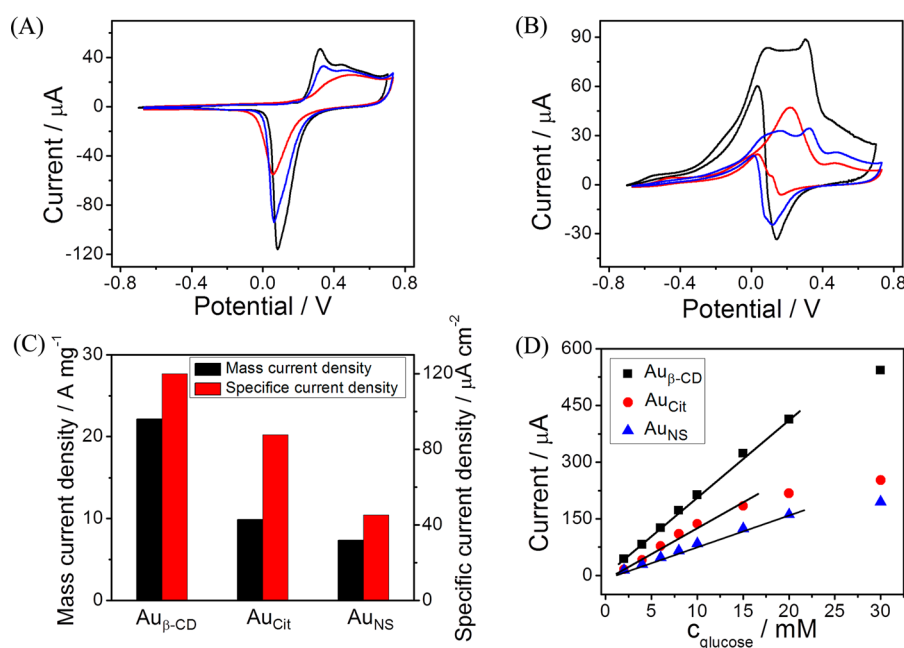


Figure 9. CVs of the $Au_{\beta-CD}$ (black line), Au_{Cit} (red line) (b), and Au_{NS} (blue line) (c) modified electrodes in the absence (A) and presence (B) of 4 mM glucose in 0.1 M NaOH at a scan rate of 50 mV s^{-1} . (C) Current densities for 4 mM glucose oxidation on three Au aerogel modified glassy carbon electrodes. (D) Plots of the electrocatalytic current of glucose vs concentration (2–30 mM) of the modified electrodes.

Three kinds of Au NPs tailored by citrate, 5-mercaptopentyltetrazole (5-HSTz), and nonstabilizers, which were designated as Cit–Au NPs, 5-HSTz–Au NPs, and NS–Au NPs, were introduced to the dopamine-induced assembly. With 20 μ M dopamine, both Au NPs with no or quite weak stabilizers (*i.e.*, citrate) gelate and form a nanowire network (noted as Au_{NS} and Au_{Cit}, respectively). The average wire diameters (6.2 ± 1.4 and 4.9 ± 1.0 nm) match well with the sizes of the original NPs, similar to the results with the β -CD–Au NPs. In contrast, Au NPs with the strong stabilizer 5-HSTz remain unaltered nanoparticulate Au sols (Figures 8 and S6). Dopamine is strongly bound to the Au NPs' surface and acts as a ligand competing with the initial "stabilizers", further interacting with the Au core.^{28,37–39} Here the existence of dopamine in the final aerogel samples is evidenced *via* XPS (Figure 4D). Hence the Au NPs with rather weak protections are easily attacked by dopamine for surface ligand exchange and subsequent interaction, resulting in branched nanowire-like hydrogels. The Au–S bond between 5-HSTz and the Au NPs is strong enough to protect the Au core from particle fusion.⁴⁰ Typically, the destabilization of a Au NP sol leads to uncontrolled aggregation; here the dopamine-induced route realized a simple, yet efficient way for 3D assembly of several kinds of Au NPs. It not only provides a novel strategy for producing high-quality Au aerogels with different functional groups but also offers opportunities for further applications in catalysis, sensing, surface-enhanced Raman spectroscopy, *etc.*

Due to the high activity and selectivity for catalytic reactions, nanostructured Au materials have gained stained and growing interest in catalysis and sensing.^{41,42} In addition, materials with multimodal or hierarchical porosity facilitate mass transport and exhibit both increased surface area and reaction sites.^{43–45} In this regard, the Au aerogels prepared in this work with high surface area and broad open porosity are first tested as advanced electrocatalysts for the oxidation of glucose, as it is of great importance for sugar sensing in human blood and their potential use in fuel cells.^{46,47}

As shown in Figure 9A, all Au aerogel modified glassy carbon electrodes (*i.e.*, Au β -CD/GCE, Au_{Cit}/GCE, and Au_{NS}/GCE) depict the electrochemical characteristics for Au in alkaline solution, where the anodic oxidation current starts at about 0.20 V due to the formation of Au oxide that is subsequently reduced, as indicated by the appearance of a reduction peak in the negative potential scan. The Au β -CD/GCE shows the smallest peak-to-peak potential separation, implying the fastest electron-transfer kinetics at the electrode surface.^{48,49} In addition, the electrochemical active surface area (ECSA) of the Au aerogels were estimated using the reduction charge of Au oxide obtained from the cyclic voltammograms (CVs), which are 18.2, 11.1, and 16.0 m² g^{−1} for Au β -CD, Au_{Cit}, and Au_{NS}, respectively. The larger ECSA for Au aerogel functionalized with β -CD provide more active sites for the further electrocatalytic reactions.

After the addition of different concentrations of glucose, two anodic peaks attributed to the oxidation of glucose are observed in the positive potential scan with all Au aerogel modified glassy carbon electrodes (GCEs). Again an anodic peak corresponding to the glucose oxidation is found in the negative potential scan once the oxide layer is reduced (Figure 9B and Figure S7). The calibration curves corresponding to the amperometric response against the glucose concentration are illustrated in Figure 9D. The Au β -CD/GCE exhibits very high activity toward glucose oxidation with a sensitivity of $332.9 \pm 7.6 \mu\text{A mM}^{-1}$

cm^{−2} ($n = 7$) in the range of 0 to 20 mM, which is superior to those reported in the literature (see Table S1). Meanwhile, the controlled experiments show that all of the three Au aerogels have much higher catalytic activities than the corresponding NPs when applied as electrocatalysts (Figure S8). This is mainly because the Au aerogels increase the conductance and electron transfer for the electrocatalysis on one hand, and on the other hand, the open porous structures of the Au aerogels not only allow fast transport of glucose through the electrolyte/electrode interface but also ensure contact with a larger reaction surface due to the high surface area. It is noted that the Au β -CD aerogel shows the highest catalytic activities regardless of the mass or specific current density. Similar electrocatalytic results (*i.e.*, best performance on a Au β -CD aerogel) are obtained when the three Au aerogels with different capping ligands are applied for the oxidation of ethanol, another important small molecule in fuel cell reactions (see Supporting Information, Figures S9 and S10). Most probably this enhancement is because of the faster electron-transfer kinetics and larger ECSA at the Au β -CD/GCE surface mentioned before and the intermolecular interaction between substrates (glucose and ethanol) and β -CD.⁵⁰ Additionally, the Au β -CD aerogel modified electrode shows little electrochemical response on 0.2 mM ascorbic acid and uric acid, two common coexisting interferences^{51,52} (see Figure S11), indicating its good selectivity for glucose. After 100 successive scans the Au aerogel modified electrode shows more than 96% of the initial catalytic current and almost no change after 4 weeks' storage at room temperature toward the oxidation of glucose. These results suggest that the Au aerogel exhibits high sensitivity, broad linear range, and good stability, demonstrating the promise of the Au β -CD/GCE as a non-enzymatic sensing electrode for analytical applications.

CONCLUSIONS

In summary, we have successfully demonstrated a new and facile synthesis of Au aerogels *via* a dopamine-induced route, where the Au aerogels are composed of 3D nanowire networks that exhibit diameters of 5–6 nm as the original particles together with very high surface area and large hierarchical porosity. Interestingly, capping the NPs with different surface ligands yields Au aerogels with the respective functional groups. Applied in electrocatalysis, Au aerogel modified electrodes offer high activities toward the nonenzymatic oxidation of glucose, which carries potential for high-performance glucose sensors and fuel cells. Our approach not only provides a template-free method for the 3D assembly of Au NPs into highly porous aerogels but also holds promise for their superior sensing and catalysis applications.

EXPERIMENTAL SECTION

Reagents and Materials. Gold(III) chloride trihydrate (HAuCl₄·3H₂O, 99.9%), sodium citrate, dopamine hydrochloride, 2-phenylethylamine hydrochloride, pyrocatechol, 5 wt % Nafion, and sodium borohydride (NaBH₄) were bought from Sigma-Aldrich. β -D-(+)-Glucose was also purchased from Sigma, and the stock solution was allowed to mutarotate at room temperature overnight before use. β -CD was received from VWR. Commercial Pd/C catalyst (Pd, 20% on activated carbon powder) was purchased from Alfa Aesar. Ferrocenecarboxylic acid (Fc) was received from Fluka. Acetone ($\geq 99.8\%$) and absolute ethanol were obtained from Merck. A 0.1 or 1 M NaOH solution was used as supporting electrolyte for the electrocatalytic experiments. Other chemicals were of analytical grade, and Milli-Q water was used throughout.

Au Nanoparticle Synthesis. First, all glassware was cleaned with freshly prepared *aqua regia* ($\text{HCl}/\text{HNO}_3 = 3:1$) and rinsed thoroughly in water. The β -CD–Au NPs was synthesized according to the reported method with modification.⁵³ In a typical synthesis, 348 μL of 10% HAuCl_4 was added into 398 mL of 10 mM β -CD under continuous stirring for 10 min, and then 2 mL of freshly prepared 180 mM NaBH_4 was quickly added into the solution. The above solution was kept stirring for about 2 h to get a wine red Au colloid. The citrate-stabilized Au NPs (Cit–Au NPs) was prepared *via* a similar strategy to that above, where 10 mM β -CD was replaced by a 0.3 wt % sodium citrate solution. For the Au NPs without capping ligands (NS–Au NPs), it was synthesized by reducing a gold precursor in the absence of any stabilizing ligands, under otherwise identical experimental conditions. The 5-HSTz-modified Au NPs were obtained according to our previous method, by first preparing Cit–Au NPs and subsequent ligand exchange.⁵⁴

Preparation of Au Hydrogels and Aerogels. Hydrogels from β -CD–Au NPs were produced by adding 80 μL of varied concentrations of dopamine solution (0.05, 0.1, 0.25, and 0.5 M) to the above β -CD-modified Au colloids to give a final concentration of 10, 20, 50, and 100 μM , respectively. After slightly shaking for 5 min, 400 mL of the above solution was divided into 100 mL and then settled at room temperature. Fluffy black solids settled out of the solution down to the bottom of the flask from 6 h to within 3 days, depending on the concentration of dopamine. After carefully washing with at least 15 times the amount of water and stepwise replacing the supernatant by acetone (10 times, twice per day), the resulting anhydrous, acetone-containing gels were transferred into a critical point dryer for supercritical CO_2 drying. The Au hydrogels and aerogels both possess a black color. The other guests, 2-phenylethylamine hydrochloride, pyrocatechol, and Fc-induced β -CD–Au NP assembly, and the Cit–Au NPs and NS–Au NPs induced by 20 μM dopamine were obtained *via* a method similar to that above.

Electrocatalytic Experiments. A GCE (3 mm in diameter) was polished with a 1.0 and 0.3 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for a few minutes, respectively. The cleaned GCE was dried with an air stream for the next modification. Au aerogels (*i.e.*, β -CD-, citrate-, and nonstabilizer-modified Au aerogels, noted as $\text{Au}_{\beta\text{-CD}}$, Au_{cit} , and Au_{NS} , respectively) derived from different NPs were dispersed in water to obtain black suspensions with a metal concentration of 1.0 mg mL^{-1} (evaluated by ICP-OES). 4 or 3 μL of the as-prepared aerogel dispersions was deposited on the clean GCEs, which were left to dry in the oven at about 40 $^\circ\text{C}$ followed by coating 2 μL of 0.5% Nafion for further electrochemical experiments.

Apparatus and Measurements. CO_2 supercritical drying was conducted on critical point dryer model 13200J-AB obtained from SPI Supplies. Since the drying process was carried out in baskets close to spherical in shape, the resulting aerogel monoliths are shaped like a sphere, and volumes were calculated accordingly. After weighing them *via* a precise balance (0.0001 g), the mass density of the as-prepared Au aerogel samples was roughly estimated by weight/volume ($n = 9$). TEM was performed on a TECNAI T20 at an accelerating voltage of 200 kV. SEM and EDS were performed on a Zeiss DSM 982 Gemini instrument. XRD was carried out in reflection mode on an X'Pert Pro multipurpose powder diffract meter operated at a voltage of 40 kV and a current of 30 mA with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The data were collected in the $5\text{--}90^\circ$ (2θ) range with a step size of $\Delta 2\theta = 0.026^\circ$. XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, England). UV–vis spectroscopy was recorded on a Cary 50 UV–vis spectrophotometer. ICP-OES was carried out on a PerkinElmer Optima 7000DV optical emission spectrometer. Nitrogen physisorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 instrument. About 50 mg of Au aerogels was transferred into the measuring cell and degassed overnight at 323 K under vacuum before measurement. The pore size distribution of the Au aerogel was assessed using the quenched solid density functional theory equilibrium model (N_2 on carbon) based on a slit-shaped pore geometry because of the surface coverage with β -CD. FT-IR

spectroscopy was performed on a Thermo Scientific Nicolet 8700 FT-IR spectrometer configured with a Smart iTR diamond accessory. TGA was measured on a Mettler Toledo TGA/DSC1 STRAe system under an argon flow of about 30 mL min^{-1} in the temperature range 25–1000 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C min}^{-1}$. Zeta-potential measurements were performed on a Delsa Nano C particle analyzer (Beckman Coulter Corporation). All electrochemical measurements were performed at an Autolab/PGSTAT 30 (Eco Chemie B. V. Utrecht, The Netherlands) in an earthed Faraday cage. The modified GC electrode was used as the working electrode. Platinum foil and Ag/AgCl (1 M KCl) were employed as the counter electrode and the reference electrode, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07505.

UV–vis absorption spectrum and TEM images of the β -CD–Au NPs, TEM images of Au assemblies induced by a low concentration of dopamine, SEM and TEM images of Au aerogels produced by 10, 50, and 100 μM dopamine, TGA and EDS of $\text{Au}_{\beta\text{-CD}}$, TEM images of the Cit–Au NPs, NS–Au NPs, and 5-HSTz–Au NPs, TEM and SEM images of the corresponding Au_{Cit} and Au_{NS} aerogels as well as the original Au NP modified electrodes corresponding to different concentrations of glucose and ethanol (PDF)

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Notes

The authors declare no competing financial interest.

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