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Electrocatalytic Oxidation of Alcohols, Tripropylamine, and DNA with Ligand-Free Gold Nanoclusters on Nitrided Carbon

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Abstract

Electrocatalytic properties of ligand-free gold nanoclusters (AuNCs, <2 nm) grown on nitrided carbon supports (denoted as AuNCs@N-C) were evaluated for the oxidation of representative organic molecules including alcohols, an amine, and deoxyguanosine in oligonucleotides. AuNCs@N-C catalysts were incorporated into films of architecture {PDDA/AuNCs@N-C}_n by using layer-by-layer assembly with oppositely charged poly(diallyldimethylammonium) (PDDA) on pyrolytic graphite (PG) electrodes. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to survey the electrocatalytic properties of these AuNCs@N-C films. Ligand-free AuNCs in these films demonstrated excellent electrocatalytic oxidation activity with maximum peak currents and the lowest potentials for oxidizing ethanol, propanol, and tripropylamine (TprA) compared to controls with Au-surface capping agents or to larger sized Au nanocrystals on the nitrided carbon supports. EIS kinetic studies showed that ligand-free AuNCs films have the smallest charge-transfer resistance, largest electrochemically active surface area, and largest apparent standard rate constants, as compared to the control films for all compounds examined. DNA films on AuNCs@N-C were oxidized at deoxyguanosine moieties with good catalytic activity that depended on charge transport within the films.

Graphical Abstract

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Good as gold: Ligand-free Au nanoclusters supported on nitrated carbon nanoparticles and assembled into layer-by-layer films of {PDDA/AuNCs@N-C}_n are found to be highly active for the electrocatalytic oxidation of alcohols, an amine, and DNA.

Keywords

alcohol; DNA; electrocatalytic oxidation; gold nanoclusters; tripropylamine

1. Introduction

Unique properties of gold nanocatalysts including size-dependent catalytic activity, high surface-to-volume ratio, and ease of chemical functionalization have led to their integration into sensors,^[1] catalysts,^[2] photocatalysts,^[3] and electrocatalysts.^[4] Monodisperse gold nanoparticles (AuNPs) display highly active catalysis related to nanoscale physicochemical properties.^[1a, 5] There is a growing body of literature documenting catalytic activity with AuNPs that generally increases with decreasing size.^[6–8]

The growth of AuNPs with ultrasmall sizes, including nanoclusters (NCs, <2 nm) that contain a few hundred or less Au atoms, has, until recently, required thiol-terminated or other ligands for their synthesis in stable forms.^[7, 9] AuNPs on high-surface-area supports have also been used effectively to electrocatalyze various heterogeneous reactions, but have also required ligands to stabilize and control their size.^[10] We recently reported the facile synthesis of ligand-free Pd, Pt, and AuNCs with diameters < 2 nm on nitrated carbon supports (hereafter denoted AuNCs@N-C) through soft nitriding, and we documented excellent electrocatalytic efficiency for the oxidation of methanol.^[11] A decrease in electrocatalytic activity was observed when surface ligands were introduced onto the noble-metal clusters.

In this contribution, we extend our studies of these novel supported AuNCs to the electrochemical oxidation of representative organic molecules including alcohols, an amine, and deoxyguanosine in oligonucleotides. To do so, negatively charged AuNCs@N-C catalysts were assembled with polycation poly-(diallyldimethylammonium) (PDDA) to make films of architecture {PDDA/AuNCs@N-C}_n through layer-by-layer (LbL) assembly on pyrolytic graphite (PG) electrodes. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize the electrocatalytic properties. Ligand-free AuNCs of < 2 nm in diameter gave maximum peak currents and the lowest potentials for the oxidation of ethanol, propanol, tripropylamine (TPrA), DNA, and polyguanylic acid (polyG) compared to controls with thiol ligands or larger sized AuNPs on

the nitrated carbon supports. This film system with ligand-free gold NC catalysts provides a novel approach for highly catalytic active films.

2. Results

2.1. Characterization of AuNCs@N-C and Fabrication of {PDDA/AuNCs@N-C}_n Films

Ligand-free AuNCs with different sizes were grown in situ onto carbon supports by “soft” nitriding,^[11] to give AuNCs@N-C. Solution pH influences the interfacial charge of the nitrated carbon supports as well as affinity interactions between supports and metal precursors. Therefore, the size of the Au particles can be simply adjusted by changing the solution pH. AuNCs of < 2 nm in diameter were grown on the supports at neutral pH, whereas AuNCs with larger sizes were grown at lower or higher pH values.^[11]

Morphological and structural features of AuNCs@N-C were characterized by using transmission electron microscopy (TEM) (Figure 1). The AuNCs are highly dispersed and homogeneously loaded onto the 50 nm N-C nanospheres. At pH 7, AuNCs@N-C has an average diameter of 1.6 nm (Figures 1A and 1E). High-resolution TEM further indicates a crystalline structure, revealing the Au(111) plane with a *d* spacing of 0.24 nm, and the graphitic layered structure of the carbon (002) plane with a *d* spacing of 0.34 nm (Figure 1B). These results showed that ligand-free AuNCs@N-C NCs were successfully synthesized and loaded onto nitrated carbon supports. In contrast, AuNCs with an average diameter 6 nm (Au-6 nm) were obtained at pH 3 (Figures 1C and 1F), whereas 10 nm AuNCs (Au-10 nm) were obtained at pH 12 (Figures 1D and 1G).

Films of negatively charged AuNCs@N-C particles and controls were made by LbL assembly, using the polycation PDDA in between NP layers. The growth of {PDDA/AuNCs@N-C}_n LbL films was monitored by using a quartz crystal microbalance (QCM) (see Figure S1). The QCM resonance frequency decreased ($-F$, Hz) with an increasing number of layers, reflecting a reproducible mass increase on QCM gold electrodes at each layer assembly step. $-F$ had an approximately linear relationship with the number of adsorption steps, confirming that the {PDDA/AuNCs@N-C}_n multilayer films were successfully assembled in a regular and reproducible manner.

The mass/area (M/A) of each deposited, dried layer of PDDA and AuNCs@N-C was obtained from the frequency change ($-F$) on the QCM resonator by using the Sauerbrey equation [Eq. (1)]:^[12]

$$M/A \text{ (g cm}^{-2}\text{)} = -\Delta F \text{ (Hz)} / (1.832 \times 10^8) \quad (1)$$

A 1 Hz frequency decrease corresponds to a 0.87 ng mass increase. Assuming that the adsorption layer was densely packed, the nominal thickness (d , cm) of each adsorption layer for films deposited on one side of the resonator was estimated according to Equation (2):^[13]

$$d = -(3.4 \times 10^{-9}) \Delta F / \rho \quad (2)$$

where ρ is the density of the layer material (g cm^{-3}). For carbon black, the density is approximately 1.85 g cm^{-3} ,^[14] whereas for polymers such as PDDA, the density is approximately 1.3 g cm^{-3} .^[15] The loading mass and thickness of layers of PDDA and AuNCs@N-C from QCM frequency differences (Table 1) show the average mass for each layer of AuNCs@N-C as $2.99 \pm 0.19 \text{ } \mu\text{g cm}^{-2}$, corresponding to the nominal thickness of each layer of $10.0 \pm 0.6 \text{ nm}$. The loading amount of AuNC in the LbL films was obtained by multiplying the AuNCs@N-C mass by 0.0234, that is, the weight fraction of Au in catalytic materials measured by atomic absorption spectroscopy.^[11]

The stable, reproducible assembly of $\{\text{PDDA}/\text{AuNCs@N-C}\}_n$ LbL films on PG electrodes was also confirmed through the direct electrochemical response of Au incorporated in the films (Figure 2A). The $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films in 0.1 M NaOH solution gave a CV oxidation peak at approximately 0.3 V versus SCE,^[16] and the gold oxides formed were reduced in a cathodic peak at 0.02 V versus SCE on the negative scan. For bare PG electrode controls, no voltammetric response was seen (Figure 2A, inset), revealing that the CV features of the AuNCs@N-C film electrode can be attributed to the AuNCs.

CVs of the electroactive probe, $\text{K}_3\text{Fe}(\text{CN})_6$, were used to further confirm the assembly of $\{\text{PDDA}/\text{AuNCs@N-C}\}_n$ films on PG electrodes (Figure 2 B). For bare PG, $\text{K}_3\text{Fe}(\text{CN})_6$ in solution at pH 7 displayed a reversible CV oxidation–reduction peak pair at 0.17 V ; whereas, for $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films on PG, the CV response of $\text{K}_3\text{Fe}(\text{CN})_6$ was three times greater at the same potential (curve b), suggesting that the $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films were successfully fabricated on PG surface to produce a larger conductive surface area. The stability of $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films was also examined by storing the electrode in phosphate buffer (pH 7) for 1 week. The voltammograms for $\text{K}_3\text{Fe}(\text{CN})_6$ were highly reproducible and the probe maintained the same potentials. The redox peak currents were within 92% of the initial value, indicating that the $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films are relatively stable when stored in solution for 1 week.

The assembled $\{\text{PDDA}/\text{AuNCs@N-C}\}_n$ films (Figure 2D) exhibited a much rougher surface than PG (Figure 2 C), according to SEM. NC-like features appear on the surface of $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films, whereas the bare PG electrode is relatively smooth. The obvious difference in morphology is consistent with the assembly of NP films and an increase in electroactive area on the PG electrode.

2.2. Electrocatalysis of Molecular Oxidations

We used the $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ electrodes and controls with larger gold NPs to examine the electrocatalytic effect toward several redox species that give either no electrooxidation or are irreversibly oxidized on bare PG. These included ethanol, propanol, and tripropylamine (TprA). As an example with biological significance, we also examined the catalytic oxidation of deoxyguanosine in intact oligonucleotides poly(deoxyguanosine) (PolyG) and double-stranded (ds) DNA in films deposited on top of the $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films. We express current density in all CVs as mass-specific current density (J , $\text{Amg}^{-1}_{\text{Au}}$), because the catalytic activity should be related to the mass of Au as electroactive components in the films. From QCM measurements (see above), the mass of AuNCs in the $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ films is $3.44 \times 10^{-5} \text{ mg}$.

2.2.1. Oxidations of Ethanol, 1-Propanol, and TPrA—The ligand-free AuNCs in the {PDDA/AuNCs@N-C}₃ film electrodes were investigated in N₂-saturated 0.1 M NaOH solutions. Figure 3Ab–g shows a CV profile typical of ethanol oxidation in alkaline media.^[17] Figure 3a on the positive scan shows a symmetric anodic peak at 0.12 V, which involves simultaneous ethanol oxidation and gold oxide formation.^[18] In the negative scans, a gradual decrease and disappearance of the small cathodic peak at approximately 0.02 V corresponds to the reduction of Au oxide with increasing concentration of ethanol in solution. This suggests that electrogenerated gold oxide is involved in the electrocatalytic oxidation of ethanol and the surface oxides function as an electron-transfer mediator in the oxidation process, as suggested for other Au electrodes.^[16, 19] The current increases again after the surface oxides are reduced (< 0.02 V), and a small anodic peak at around –0.03 V was detected. This reactivation of the electrocatalysis is attributed to the reduction of gold oxide,^[20] and is similar to the behavior observed on platinum and palladium electrocatalysts.^[21] The peaks in the negative scan are smaller than those on the positive scan. As the oxidation of the surface is avoided, these differences are not be ascribed to the oxidation of the surface.^[22] The CVs of the AuNCs@N-C film electrodes for ethanol at different scan rates (Figures 3B) reveal that the oxidation peak current density showed a linear relationship (Figure 3C) with square root of scan rate at lower scan rates (< 50 mV s^{–1}), suggesting diffusion-controlled behavior.

The mass current density ratio of the forward (J_f) to the backward scan (J_b) oxidation peaks, J_f/J_b , is an indicator of catalyst performance.^[23] The J_f/J_b ratio of ethanol electrocatalytic oxidation at the {PDDA/AuNCs@N-C}₃ film electrode was 2.25, which is larger than the highest reported value of 1.9 for ethanol oxidation,^[24] suggesting very efficient and complete electrocatalytic oxidation of ethanol to acetic acid. The oxidation peak mass current density (J_f) increased linearly with the concentration of ethanol in solution in the range of 0.02–0.45 M, and then tended to level off when the concentration of ethanol became larger (Figure 3A, inset). All of these results are characteristic of electrochemical oxidation of ethanol catalyzed by noble-metal NPs.^[17a, 21b, d] The steady state of electrocatalytic peak current at higher concentration indicates that more active sites in the AuNCs films can be occupied by the adsorbed ethanol molecules at higher ethanol concentration, and thus the current becomes limited by the number of active sites. Furthermore, according to the Langmuir–Hinshelwood (LH) mechanism, the reaction rate starts decreasing when the concentration of adsorbed species ($\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$) increases beyond a certain threshold.^[20a] A limited stability study (Figure 3D) showed that, for 0.45 M ethanol, the main oxidation peak retained 86% of the initial peak current after 100 scans. No ethanol oxidation peaks were found on PG, {PDDA/C}₃, or {PDDA/N-C}₃ electrodes in the potential window used (Figure S2), indicating that the AuNCs in the films are the source of the electrocatalysis.

CVs on {PDDA/AuNCs@N-C}₃ electrodes of 1-propanol in 0.1 M NaOH were similar to those of ethanol (Figure 4A). A large symmetric CV oxidation peak at about 0.11 V was observed during the forward scan. Again, a J_f/J_b ratio of 2.26 suggests excellent electrocatalytic performance of 1-propanol oxidation. J_f increased initially with the concentration of 1-propanol in the range of 0.05–0.40 M (Figure 4A, inset). The saturation of peak current at higher concentrations has the same cause described for Figure 3A. Propanol

did not give an oxidation peak on bare PG (data not shown). Figure 4B displays the effect of scan rate on the electrooxidation of propanol at the AuNCs@N-C electrode. In the $10 \sim 100 \text{ mVs}^{-1}$ range, the height of the oxidation peak on the negative (reverse) potential scan decreases with increasing scan rate. For $\nu > 100 \text{ mVs}^{-1}$, the oxidation peak disappears completely, and the gold reduction current peak grows with increasing scan rate. The chemical adsorption of oxygen species (such as the OH^- anion) and the formation of precursor species on the surface of the AuNCs promotes role of the surface electrochemistry of Au in alkaline media.^[18, 25, 34] Previous work suggested a considerable polar behavior of the Au— OH^- bond, and the adsorption of OH^- on Au can be expressed as a partial charge-transfer reaction, as indicated in Equation (5).^[25a, 34, 35a] The chemical adsorption of OH^- is a relatively slow process in comparison with gold oxidation, so the slow scan rates are advantageous for propanol electrooxidation.^[18, 25]

TPrA is an important trialkylamine for biosensor technology, in which it serves as an efficient co-reactant for electrochemiluminescent (ECL) dyes.^[26] In pH 7.4 phosphate-buffered saline (PBS) containing 0.01 M TPrA, {PDDA/AuNCs@N-C}₃ electrodes gave a large CV oxidation peak at about 0.68 V (Figure 4C, curve c), in comparison with much smaller peaks at 0.9 V on bare PG and 0.88 V on {PDDA/N-C}₃. The oxidation peak increased with concentration of TPrA (Figure 4D).

2.2.2. Oxidation of DNA—We also examined the oxidation of ds-DNA and single-strand (ss) poly(deoxyguanosine) (polyG) adsorbed as films on {PDDA/AuNCs@N-C}₂ electrodes. Electrooxidation of both DNA and polyG were greatly enhanced by AuNCs. Figures 5A and 5B show that their oxidation peak currents increased and the peak potentials were decreased by about 140 mV compared to {PDDA/N-C}₂/PDDA electrodes. As guanine is the most easily oxidized of the DNA bases,^[27] it is most likely that these peaks correspond to the oxidation of guanine moieties directly within the oligonucleotide strands.

DNA and polyG peaks on the {PDDA/N-C}₂/PDDA electrodes were at identical potentials as on bare PG, that is, 1.0 V (Figures 5C and 5D). This suggests that a shift of 140 mV to lower potentials on {PDDA/AuNCs@N-C}₃ electrodes can be attributed to catalysis by the AuNCs.

2.2.3. Influence of Ligands on Electrocatalytic Activity—3-Mercaptopropionic acid (MPA) and dodecanethiol (DT) were used as ligands on AuNCs in {PDDA/AuNCs@N-C}₃ film electrodes for the electrochemical oxidation of ethanol and TPrA. The ligated materials designated as AuNCs-MPA and AuNCs-DT were synthesized and assembled into LbL films on PG electrodes to form {PDDA/AuNCs-MPA}₃ and {PDDA/AuNCs-DT}₃ films, respectively. Comparing {PDDA/AuNCs-MPA}₃ electrodes in 0.1 M NaOH solution containing 0.45 M ethanol (Figure 6A, curve b) with the ligand-free {PDDA/AuNCs@N-C}₃ films containing the same amount of ethanol (Figure 6A, curve a), the oxidation peak current density decreased by 50% with a positive shift of peak potential. For {PDDA/AuNCs-DT}₃ films under the same conditions, the oxidation peak current density decreased 60% and the peak potential increased by 80 mV compare to ligand-free {PDDA/AuNCs@N-C}₃. Similarly, for the electrocatalytic oxidation of TPrA (Figure 6B), CV results demonstrated that {PDDA/AuNCs@N-C}₃ films with ligand-free AuNCs displayed the

largest oxidation peak current density of $4.7 \text{ A mg}^{-1}_{\text{Au}}$ and lowest oxidation peak potential of 0.68 V compared to the control films. The oxidation peak potential of TPrA at ligand-free {PDDA/AuNCs@N-C}₃ films was decreased by 200 mV. Thus, electrocatalytic oxidation of ethanol and TPrA became more difficult with ligation and with increased length of the ligand. The surface ligands likely create a physical barrier that blocks access for the adsorption of ethanol or TPrA onto the catalytic sites of AuNCs, thus decreasing the catalytic efficiency.

2.3. Kinetic Studies

EIS was performed for the ethanol and DNA oxidations with the aim of modeling the electrocatalytic response. The overall oxidation pathway of ethanol catalyzed by gold is complex [Eqs. (3) and (4)]:^[17a, 20a, 25b, 35a]

Intermediate steps proposed in the following generalized form include the role of —OH_{ads} [Eqs. (5)–(8)]:^[25a, 35a]

where “ads” denotes the chemisorbed species on Au and λ is a charge-transfer coefficient between 0 and 1. The adsorption of OH^- on active sites and the formation of $\text{Au}-\text{OH}_{\text{ads}}^{(1-\lambda)-}$ constitute a partial charge transfer [Eq. (5)]. The reaction mechanism of the rate-determining step is depicted in Equation (6), in which $\delta = 1-\lambda$, and the square bracket represents the surface transition state. A hydrogen bond is formed between an oxygen atom

in $\text{Au}-\text{OH}_{\text{ads}}^{\delta-}$ and a hydrogen atom in the methyl group of ethanol. Then, a hydrogen atom loses an electron and bonds with $\text{OH}_{\text{ads}}^{\delta-}$ on Au to produce water [Eq. (7)]. $\cdot\text{CH}_2\text{CH}_2\text{OH}$ is an unstable radical that converts to CH_3COO^- in alkaline media, Equation (8).

Charge-transfer resistance (R_{ct}) and the apparent heterogeneous standard rate constant (k^0) for the oxidation of ethanol on ligand-free and ligand-capped AuNC film electrodes were measured by using EIS (Figure 7 and Table 2). The best fit of the EIS spectra (Figure 7A) was achieved with a modified Randles equivalent circuit model^[28–30] (Figure 7B) with relative error = 10%. The model does not consider chemical details of the oxidation, but can be used to obtain relevant rate parameters. Several other models were tested, but fit more poorly (see the Supporting Information). The high-frequency region of the EIS plot represents the solution resistance (R_s), which describes the resistance of the electrolyte (0.1 M NaOH) as well as the internal resistance of the electrode. R_s is represented in the EIS spectra by the intercept of the semicircle in the high-frequency region. The R_s of all samples is relatively small (12–29 Ω), owing to the high electrolyte concentration and the small internal resistance of the electrodes. In the high-frequency region, the R_s of the film with the biggest AuNP size {PDDA/Au-10 nm}₃ has the lowest R_s value, whereas the film with the smallest AuNP size {PDDA/Au-10 nm}₃ shows the highest R_s value. This may be attributed to the higher conductivity and better contact of the bigger AuNPs to the bulky electrode compared to the ultrasmall Au in {PDDA/AuNCs@N-C}₃. The medium-frequency region is attributed to the charge-transfer resistance (R_{ct}) at the electrode–electrolyte interface and the associated electrical double-layer capacitance (C_{dl}). The resistance to the transfer of charged species into the film on the electrode strongly impacts the activity of the Au catalyst. The C_{dl} in the equivalent circuit most likely represents the electrical double-layer capacitance, resulting from negatively charged $\text{Au}-\text{OH}_{\text{ads}}^{\delta-}$ on the electrode surface and the formation of the oppositely charged layer of the spectator Na^+ in solution. In the low-frequency region, the impedance is attributed to the diffusion of hydroxide and Na^+ into the catalyst film. This is represented by the Warburg impedance (Z_W), and is shown in the EIS spectra in the low-frequency region as a nearly straight line. R_{sl} represents the resistance to the migration of OH^- and Na^+ , and C_{sl} represents the capacitance of the surface passivation layer, or the outermost layer of the film. The EIS Bode plot was further analyzed, taking the electrocatalytic ethanol oxidation as an example. Results of the Bode plots in Figure S3A show the increase of the corresponding peak frequency as the size of the AuNPs increase from 2 nm in {PDDA/AuNCs@N-C}₃ to 10 nm in {PDDA/Au-10 nm}₃, which indicates faster electron-transfer rates for the smaller NPs. The same behavior is noted in Figure S3 B. The longer the chain of the ligand, the lower the corresponding peak frequency and slower the electron-transfer rate.

For ligand-free {PDDA/AuNCs@N-C}₃ films, a full semicircle was observed (Figure 7A, curve a), and the fitting results showed that the R_{ct} of the ethanol oxidation system is 1420 Ω , that is, far smaller than the 34 700 and 35 080 Ω of {PDDA/AuNCs-MPA}₃ and {PDDA/AuNCs-DT}₃ films, respectively (Table 2). Thus, interfacial charge transfer at {PDDA/AuNCs@N-C}₃ films is the easiest, and it becomes more difficult for ligand-capped film electrodes. The apparent k^0 values calculated from the EIS data [Eqs. (9) and (10)] relate to

the average oxidation rate of the reactants, but do not give detailed information about the mechanism:

$$j_0 = \frac{i_0}{A} = \frac{RT}{nFAR_{ct}} \quad (9)$$

$$k^0 = \frac{i_0}{nFC} \quad (10)$$

where j_0 is the exchange current density, i_0 is the exchange current, A is the electrode surface area, R is the gas constant, T is the absolute temperature, n is the number of electrons transferred in the reaction, F is Faraday's constant, and C is the concentration of ethanol in the electrolyte. The k^0 values for ethanol oxidation at ligand-free {PDDA/AuNCs@N-C}₃ films were about 26-fold larger than those for the other two ligand-capped AuNC assembled films (Table 2), indicating that ligand-free AuNCs have faster electrolysis rates for ethanol molecules and the highest catalytic activity. In addition, k^0 also decreased significantly with increasing AuNP size (Table 2).

CV also showed that the decreasing size of AuNPs had a large influence on the electrocatalytic activity. Figure 8 displays the influence of the three different sizes of AuNCs ({PDDA/AuNCs@N-C}₃, {PDDA/Au-6 nm}₃, and {PDDA/Au-10 nm}₃) on electrooxidation ethanol and TPrA. For {PDDA/Au-6 nm}₃ film electrodes (Figure 8A, curve b), the ethanol oxidation peak decreased by 50% and the peak potential increased by 45 mV in the forward scan compared to {PDDA/AuNCs@N-C}₃ films with Au-1.6 nm. For {PDDA/Au-10 nm}₃, the oxidation peak decreased 70% and the peak potential shifted + 100 mV. Figure 8B shows that the peak current density for TPrA oxidation also decreased with the increasing of size of AuNCs, and the peak potential of TPrA at {PDDA/AuNCs@N-C}₃ films with Au-1.6 nm was decreased by 200–300 mV compared to the larger AuNPs. Overall, AuNCs have the best electrocatalytic activity, as the smaller AuNCs provide more active surface area (Table 2) and active surface sites for electrocatalytic reaction, leading to a larger CV response at a lower potential.

The form of the EIS data for ds-DNA and ss-polyG films on the catalyst-coated electrodes (Figure 9) suggested that, rather than R_{ct} , the charge-transfer diffusion coefficient (D_{ct}) was the most significant parameter controlling the charge transfer in the films. The low-frequency data (Figures S4 and S5) were used to analyze the charge-diffusion process. Calculation of D_{ct} from the EIS^[31] employed Equations (11) and (12):

$$D = R^2 T^2 \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (11)$$

$$Z_{\text{re}} = R_{\text{total}} + \sigma \omega^{-1/2} \quad (12)$$

where D is the charge-transfer diffusion coefficient, σ is the Warburg factor (which related to the real impedance Z_{re}), R_{total} is the sum of the charge-transfer resistance and the electrolyte resistance, and $\omega^{-1/2}$ is the square root of the frequency in the low-frequency region of the EIS spectra. Results show that the size of the AuNCs has a great influence on the diffusion of charge in the film in the case of DNA oxidation, as shown by the D_{ct} values listed in Table 3. In DNA oxidation, the highest diffusion coefficient is attributed to {PDDA/AuNCs@N-C}₃, which has the smallest AuNP size and largest surface area of gold. As the size of the particles increases to 6 nm in {PDDA/Au-6 nm}₃, the charge-transfer diffusion coefficient drops by a factor of 5. Increasing the size of AuNPs to 10 nm, as in {PDDA/Au-10 nm}₃, led to a drop in the D_{ct} value to 100 times lower than that of {PDDA/AuNCs@N-C}₃. Also, changing the ligand showed an influence on the D_{ct} values of the ligands, where {PDDA/AuNCs-MPA}₃ shows 40% lower D_{ct} values than {PDDA/AuNCs-DT}₃, suggesting faster charge movement in films without DT ligands. Trends are less clear from the ss-polyG films, in which the reactive guanines are much more accessible, as we discuss later.

3. Discussion

Results above show that ligand-free AuNCs (<2 nm, AuNCs@N-C) grown in situ directly on nitrided carbon NPs have excellent electrocatalytic activity for the oxidation of alcohols, TprA (in solution), DNA, and polyG (in thin films) when incorporated into LbL polyion films on electrodes (Figures 3–5). This is most likely caused by the greatly increased electrochemically active surface area ($ECSA$) (Table 2) that provides a large population of active sites compared to films of {PDDA/N-C}₃ without or with 6 and 10 nm AuNPs or bare PG (Table 2). Conductive AuNCs in the films may also act as “electron relays” to enhance the charge-transfer rates.^[32] Coating of AuNCs with 3-mercaptopropionic acid (AuNCs-MPA) and dodecanethiol (AuNCs-DT) decreased the electrocatalytic activity significantly (Figure 6). {PDDA/AuNCs@N-C}₃ films with ligand-free AuNCs have the highest peak current density, lowest oxidation peak potential, and largest k^0 values for the electroactive molecules tested (Table 2 and Figure 6). The electrocatalytic activity was in the sequence of AuNCs@N-C > AuNCs-MPA > AuNCs-DT, suggesting that activity decreased with increasing ligand length. Longer ligands on the surface of AuNCs can inhibit the electroactive molecules from reaching catalytic sites. The $ECSA$ (Table 2) of the ligand-capped AuNC films is 5–10% smaller the ligand-free AuNC films, which is consistent with this interpretation. These results also highlight the high value of the synthetic method that produces ligand-free noble-metal NCs on nitrided carbon NPs.^[11]

The size of AuNPs in the films also had considerable influence on electrocatalysis. Results demonstrated that larger AuNPs in N-C NPs had lower electrocatalytic activity in the activity sequence of AuNCs > Au-6 nm > Au-10 nm (Figure 8, Table 2 and Table 3).

Pt and Pt-based electrocatalysts have been extensively investigated for the oxidation of alcohols,^[21, 33] but practical applications may be limited by cost. Compared to Pt, Au is a more cost-effective noble metal. Moreover, the advantage of gold compared with Pt or Pd is that, during the process of alcohol electrooxidation, poisoning intermediates are not formed and the activity of Au in alkaline media remains comparatively high (Figure 3).^[20b, 34, 35] Au and Au-composite catalysts, thus, have promising applications for direct alcohol fuel cells.^[35, 36, 37] For example, AuNPs prepared through the reduction of AuCl_4^- on the surface of an activated carbon support demonstrated good catalytic activity toward methanol.^[34] Particle shape can also be manipulated to increase active sites, for example, Pt-decorated Au nanoflowers had a higher specific activity for electrocatalytic methanol and ethanol oxidations compared to Pt-decorated Au nanospheres.^[24] Ethanol and propanol may be more suitable fuels than methanol, owing to lower toxicity and higher mass energy density (8.00 and 8.58 kWh kg⁻¹, respectively) in comparison with methanol (6.09 kWh kg⁻¹).^[37a]

{PDDA/AuNCs@N-C}_n films are relative easy to synthesize, and gave excellent electrocatalysis for the oxidation of ethanol and 1-propanol. The J_f/J_b ratio was 2.25 for ethanol (2.26 for propanol), which is higher than the best previous value of 1.9 for electrocatalytic oxidation of ethanol on a nanocatalyst.^[24] The mass activity was 3560 mA mg⁻¹, about 25% lower than the best reported value (Table S1). Nonetheless, these results are consistent with very high quality catalysis. Earlier we found that J_f/J_b for methanol electrocatalytic oxidation on the AuNCs is 2.1, which is similar to the largest value of 2.3 for methanol.^[24] Tripropylamine (TPrA) electrocatalytic oxidation was also greatly enhanced. Although a limited stability study showed that 86% of catalytic activity was retained after 100 CV scans (Figure 3D), there is still room for improving AuNC stability, which may be related to NC aggregation. This issue is currently under further study.

Control experiments at {PDDA/C}₃ and {PDDA/N-C}₃ film electrodes in the absence of AuNCs (Figure S2) for NaOH in 0.45 M ethanol gave no electrocatalytic peaks for ethanol oxidation, suggesting that {PDDA/C}₃ and {PDDA/C-N}₃ films have no electrocatalytic activity for ethanol oxidation. This confirms that AuNCs were responsible for the catalytic effects.

The mechanism of the TPrA oxidation was proposed, as shown in Equation (13):^[38]

In control experiments, bare PG and {PDDA/N-C}₃ film electrodes showed dramatically suppressed CV peak currents and a large positive shift of oxidation peak potentials to 0.9 V for TPrA (Figure 4C, curves a and b). The lowest oxidation peak potential and highest peak current density of TPrA for {PDDA/AuNCs@N-C}₃ confirmed again that the ligand-free AuNCs greatly enhanced the electrochemical oxidation of TPrA.

DNA constitutes the genetic material of living organisms, and is of great importance in biomedical research. Electrochemical DNA sensors have traditionally employed planar Au

or carbon electrodes. However, voltammetric peaks of DNA on these electrodes can present difficulties,^[39] and feature high overpotentials that cause peaks to partly merge with background discharge currents. Nanostructured electrodes can enable significant enhancement in sensor response.^[40] In the present work, the oxidation potential of DNA films on the {PDDA/AuNCs@N-C}₃ electrodes gave decreased oxidation potentials by about 140 mV and peaks were increased compared to controls (Figures 5A and 5C), indicating a strong catalytic effect of AuNCs on DNA oxidation. This peak is most likely caused by oxidation of guanine moieties that are the most easily oxidized among DNA bases.^[27] The peak for polyG is larger than that of DNA, owing to the larger number of guanines in polyG (Figure 5).

EIS experiments (Figure 7 and Table 2) confirmed the large influence of ligands and AuNPs on the electrocatalytic activity. By comparative experiments with different ligand-capped AuNC films, ligand-free {PDDA/AuNCs@N-C}₃ film electrodes showed the smallest charge-transfer resistance and the largest standard rate constant. The electrocatalytic activity of the different gold NCs in film electrodes showed the following sequence: AuNCs > AuNCs-MPA > AuNCs-DT, consistent with CV results. For different sized AuNC film electrodes, the k^0 value derived from R_{ct} displayed the same trend: the smallest size (1.6 nm) of AuNCs films had a higher electron-transfer rate than the 6 nm and 10 nm AuNCs.

For the DNA and polyG films, CVs exhibited the lowest peak potentials (0.86 V vs. SCE) and largest peak currents for {PDDA/AuNCs@N-C}₃ compared to controls (Figure 5). EIS results showed a strong dependence on the charge-transfer diffusion coefficient D_{ct} in the films (Table 3). For ds-DNA, D_{ct} clearly increases with decreasing AuNP size, but not for ss-polyG. This is probably because electrooxidizable guanines are partially shielded inside the DNA double helix, and this structure may inhibit charge transport involving ions or electrons.^[41] PolyG is a single, random, coil-like strand with no shielding ability, and may have a lower ability to limit charge transport within the films. Further studies are underway to elucidate this effect.

4. Conclusions

Ligand-free Au nanocluster catalysts supported on nitrated carbon NPs and assembled into {PDDA/AuNCs@N-C}_n LbL films exhibited high activity for electrooxidation of ethanol, propanol, TPrA, DNA, and polyG. Ligand-free AuNC catalysts had the best electrocatalytic activity, which correlates with large *EC*SA providing a large number of active sites. This supported gold NC system may also greatly facilitate the electron transfer for other molecules and biomolecules, improve performance of sensors and biosensors, and facilitate new approaches and applications for other nanocatalysts.

Experimental Section

Reagents and Materials

Poly(diallyldimethylammonium) (PDDA, 20 %, M_w 200 000–350 000), gold (III) chloride hydrate (HAuCl₄), 3-mercaptopropionic acid (MPA), NaBH₄, urea, ethanol, 1-propanol, dodecanethiol (DT), tripropylamine (TPrA), polyguanylic acid potassium salt (polyG),

salmon testes (ST) ds-DNA (2000 base pairs av, 41.2% G/C), potassium ferricyanide, hydrochloric acid, and sodium hydroxide were purchased from Sigma–Aldrich. Printex G activated carbon (AC; primary particle diameter of 50 nm) was obtained from Orion. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of $>10.0\text{ M}\Omega$ was used in all experiments.

Synthesis of AuNCs onto Nitrided Carbon Supports

Synthetic procedures of ligand-free AuNC catalysts onto nitrided carbon (AuNCs@N-C) have previously been reported.^[11] In brief, AC was mixed with excess urea, sealed, and annealed at 150°C for 2 h and then at 300°C for 2 h (details in the Supporting Information). After washing, the synthesized nitrided carbon and HAuCl_4 were dispersed in water under neutral conditions. Chemical reduction of the metal precursor was performed by using NaBH_4 .

AuNC Films on Electrodes

AuNCs@N-C NPs were immobilized onto basal plane pyrolytic graphite (PG; Advanced Ceramics, 0.16 cm^2) disk electrodes by using LbL film assembly.^[42] First, PG disk electrodes were abraded on 600-grit metallographic SiC paper while flushing with water, and then ultrasonicated in water for 30 s before being dried in air. Electrodes were alternately immersed into positively charged PDDA solution (3 mg mL^{-1}) and negatively charged aqueous AuNCs@N-C suspension (2 mg mL^{-1}) for 20 min each with intermediate water washing and drying in nitrogen. This sequence was repeated three times to form $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ multilayer films on the PG electrodes.

Apparatus and Procedures

A CHI 660 A electrochemical workstation (CH Instruments) was used for electrochemical measurements, using a three-electrode cell with a saturated calomel electrode (SCE) as the reference, platinum wire as the counter electrode, and the coated PG disk as the working electrode. The solution was purged with high-purity nitrogen for 10 min before electrochemical measurements, with nitrogen kept above the solution for the entire experiment, at ambient temperature, $20 \pm 2^{\circ}\text{C}$.

Film deposition was monitored at the formation of each layer by using a QCM (USI Japan). The 9 MHz quartz crystal resonator (ATcut, International Crystal Mfg. Company) was covered by thin gold films on both sides ($0.16 \pm 0.01\text{ cm}^2$). Gold-coated quartz crystal resonators (9 MHz) were first covered with a few drops of freshly prepared “piranha” solution: (Caution: piranha solution should be handled with extreme care) on each side for 10 min, and then washed successively and thoroughly with water and ethanol. The QCM gold resonators were then immersed in 5 mM MPA ethanol solutions for 24 h to chemisorb an MPA monolayer onto the gold surface by formation of Au—S bonds between Au and MPA, introducing negative carboxylate groups onto the outer surface. $\{\text{PDDA}/\text{AuNCs@N-C}\}_3$ LbL films were then assembled on the Au/MPA surface in the same way as on the PG electrodes. After each adsorption step, the QCM gold electrodes were washed with water and dried under nitrogen, and the frequency change was then measured in air by using a

QCM. The mass and nominal thickness were obtained from the decrease in QCM frequency by using appropriate equations.^[12]

SEM was performed by using an FEI Nova NanoSEM 450. TEM and high-resolution TEM studies were done on a JEOL 2010 FasTEM microscope at 200 kV.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Structural characterizations of electrocatalytic AuNPs. TEM images and corresponding diameter distributions of AuNCs@N-C (A, B, E), Au-6 nm (C, F), and Au-10 nm (D, G). The average diameter of carbon nanospheres is 50 nm. Diameter distributions were measured from TEM images of AuNCs (E), Au-6 nm (F) and Au-10 (G) by averaging >300 particles.

Figure 2.

A) CVs in 0.1 M NaOH at 0.01 Vs^{-1} for {PDDA/AuNCs@N-C}₃ films assembled on a PG electrode. Inset: CVs for bare PG electrode under the same conditions. B) CVs of 1 mM $K_3Fe(CN)_6$ at 0.1 Vs^{-1} in pH 7.0 buffers for a) bare PG and b) {PDDA/AuNCs@N-C}₃ films. SEM top views of C) bare PG electrode surface and D) {PDDA/AuNCs@N-C}₃ films fabricated on the PG disk electrode.

Figure 3.

A) CVs for {PDDA/AuNCs@N-C}₃ films at 0.01 Vs⁻¹ in N₂-saturated 0.1 M NaOH containing a) 0, b) 0.02, c) 0.05, d) 0.10, e) 0.20, f) 0.30, and g) 0.45 M ethanol. Inset: dependence of CV peak current density (*J*) on concentration of ethanol. B) CVs of 0.10 M ethanol in N₂-saturated 0.1 M NaOH solution for {PDDA/AuNCs@N-C}₃ films at different scan rates: a) 0.01, b) 0.02, c) 0.03 and d) 0.05 Vs⁻¹. C) Effect of scan rate (*v*) on electrocatalytic oxidation peak current density of ethanol for {PDDA/AuNCs@N-C}₃ films. D) The forward scan peaks of the a) 1st, b) 50th, and c) 100th repetitive CV scans for PG/{PDDA/AuNC}₃ films at 0.01 Vs⁻¹ in N₂-saturated 0.1 M NaOH solution containing 0.45 M ethanol.

Figure 4.

A) CVs for {PDDA/AuNCs@N-C}₃ films at 0.01 Vs⁻¹ in a 0.1 M NaOH solution containing a) 0, b) 0.05, c) 0.12, d) 0.25, e) 0.35, and f) 0.40 M 1-propanol. Inset: dependence of CV peak current density on concentration of 1-propanol. B) CVs of 0.35 M 1-propanol in 0.1 M NaOH solution for {PDDA/AuNCs@N-C}₃ films at different scan rates: a) 0.01, b) 0.05, c) 0.1, d) 0.2, e) 0.3 Vs⁻¹. C) CVs at 0.05 Vs⁻¹ in 0.01 M pH 7.4 phosphate buffers at a) bare PG electrode, b) {PDDA/N-C}₃ films, c) {PDDA/AuNCs@N-C}₃ films for 0.01 M TPrA, and d) {PDDA/AuNCs@N-C}₃ films in the absence of 0.01 M TPrA. D) CVs of {PDDA/AuNCs@N-C}₃ films at 0.05 Vs⁻¹ in pH 7.4 PBS containing a) 0.005, b) 0.010, and c) 0.015 M TPrA.

Figure 5.

CVs at 0.05 Vs^{-1} in 0.01 M pH 7.4 PBS for A) $\{\text{PDDA}/\text{AuNCs}@N\text{-C}\}_2/\text{PDDA}/\text{DNA}$ (a), $\{\text{PDDA}/N\text{-C}\}_2/\text{PDDA}/\text{DNA}$ (b), and $\{\text{PDDA}/\text{AuNCs}@N\text{-C}\}_2$ (c); B) $\{\text{PDDA}/\text{AuNCs}@N\text{-C}\}_2/\text{PDDA}/\text{polyG}$ (a), $\{\text{PDDA}/N\text{-C}\}_2/\text{PDDA}/\text{polyG}$ (b), and $\{\text{PDDA}/\text{AuNCs}@N\text{-C}\}_2$ (c); C) $\text{PG}/\text{PDDA}/\text{DNA}$; and D) $\text{PG}/\text{PDDA}/\text{PolyG}$.

Figure 6.

CVs showing the influence of ligands on the AuNCs: A) 0.45 M ethanol at 0.01 V s^{-1} in 0.1 M NaOH solution and B) 0.01 M TPrA at 0.05 V s^{-1} in 0.01 M pH 7.4 PBS at {PDDA/AuNCs@N-C}₃ (a), {PDDA/AuNCs-MPA}₃ films (b), and {PDDA/AuNCs-DT}₃ film (c) electrodes.

Figure 7.

A) EIS behavior of different films for 0.45 M ethanol in 0.1 M NaOH: a) {PDDA/AuNCs@N-C}₃, b) {PDDA/Au-6 nm}₃, c) {PDDA/Au-10 nm}₃, d) {PDDA/AuNCs-MPA}₃, and e) {PDDA/AuNCs-DT}₃ multilayer film electrodes for ethanol oxidation reaction at 0.1 V and a frequency range of 0.1 to 100 000 Hz. The inset shows the magnification of curve (a). B) The best fit equivalent circuit model for the complex impedance.

Figure 8.

CVs of A) 0.45 M ethanol at 0.01 Vs^{-1} in 0.1 M NaOH solution and B) 0.01 M TPrA at 0.05 Vs^{-1} in 0.01 M pH 7.4 PBS at a) {PDDA/AuNCs@N-C}₃, b) {PDDA/Au-6 nm}₃, and c) {PDDA/Au-10 nm}₃ film electrodes.

Figure 9.

EIS behavior and corresponding relationship between Z_{real} and $\omega^{-0.5}$ of the different nanocatalysts assembled into a) {PDDA/AuNCs@N-C}₃, b) {PDDA/Au-6 nm}₃, c) {PDDA/Au-10 nm}₃, d) {PDDA/AuNCs-MPA}₃, and e) {PDDA/AuNCs-DT}₃ multilayer film electrodes for A) DNA and B) polyG oxidation reaction at 0.9 V versus SCE and a frequency of 0.1–100 000 Hz.

Table 1

QCM results for adsorption layers of {PDDA/AuNCs@N-C}_n films on Au/MPS surface (*n* = 3).

Layer	$-F$ [Hz]	$m[a]$ [ng]	d [nm]
PDDA	163 ± 30	143 ± 26	4.3 ± 0.7
AuNCs@N-C	545 ± 35	478 ± 31	10.0 ± 0.6

[a] Amount adsorbed.

Table 2

The electrochemically active surface area and the best-fit equivalent circuit parameters of ethanol oxidation for the different materials in the films.^[a]

Catalyst	C_{dl} [μF]	$ECSA$ [cm^2]	R_{ct} [$\text{K } \Omega$]	k^0 [cm s^{-1}]
AuNCs	20.1 ± 1.5	0.34 ± 0.03	1.4 ± 0.1	0.0158
AuNCs-MPA	19.1 ± 1.9	0.32 ± 0.03	34.7 ± 3.5	0.0006
AuNCs-DT	18.5 ± 1.9	0.31 ± 0.03	35.1 ± 3.5	0.0006
Au-6 nm	14.9 ± 1.2	0.25 ± 0.02	6.0 ± 0.5	0.0037
Au-10 nm	12.4 ± 0.9	0.21 ± 0.01	16.2 ± 1.1	0.0014

^[a]The capacitance was calculated from the fitted equivalent circuit (assuming a specific capacitance of $60 \mu\text{F cm}^{-2}$).

Table 3

Charge-transfer diffusion coefficient (D_{ct}) for oxidation of DNA and polyG films from EIS of different film assemblies.

Sample	$D_{\text{ct}} (\times 10^{-22})$ ds-DNA [cm ² s ⁻¹]	$D_{\text{ct}} (\times 10^{-22})$ ss-polyG [cm ² s ⁻¹]
AuNCs@N-C	2.100	1.40
Au-6 nm	0.490	2.20
Au-10 nm	0.024	0.05
AuNCs-MPA	0.440	1.20
AuNCs-DT	0.750	1.10