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Catalytic Au “nano wool-balls”

Xiuxiu Yin[a], Nagappa Teradal[b], Ahiud Morag[a,b], and Raz Jelinek*[a,b]

Abstract: New gold nanoparticles mimicking “wool-balls” were synthesized through simple, spontaneous crystallization / reduction of gold thiocyanate [Au(SCN)₂] in water, without co-addition of neither nucleating seeds, templating compounds, nor reducing agents. The Au nano wool-balls were highly uniform in size and displayed remarkable nanoribbon surface morphology. Size- and structural-modulation of the particles were accomplished through both tuning the concentration of the gold complex, as well as upon adding small quantities of organic solvents. The unique corrugated morphology and high surface area of the Au nano wool-balls enabled their use as effective catalytic substrates for methanol oxidation and nitrophenol reduction.

Introduction

Gold nanostructures, particularly Au nanoparticles (NPs) have attracted significant scientific and technological interest due to their physical properties and applications in electronics, optics, catalysis, biology, and sensing.[1] The sizes, shapes, and surface features of Au NPs constitute the fundamental parameters affecting their properties and applications. Accordingly, broad research efforts have focused on development of synthetic routes aimed at tailoring Au NPs’ structures and surface properties.[2] While most Au NPs reported thus far exhibit spherical shapes and smooth surface architectures, gold particles exhibiting rough or corrugated surfaces have been sought for important applications such as sensing and catalysis, which benefit from extended surface areas. Varied wrinkled/branched Au NP morphologies have been reported, including polyhedral NPs,[3] dendritic nanostructures,[4] star-shaped,[5] flowery NPs,[6] “urchin”-like,[7] and others. The challenges, however, for fabricating irregularly-shaped and non-smooth Au NPs in controlled and practical ways are significant. Most reported strategies are relatively complex, consisting of multistep processes, and requiring addition of reducing agents, seeds, and/or template substances.[8] Furthermore, uniformity and structural reproducibility have been generally limited in many published reports.

Au NPs have been employed as catalytic substrates in varied reactions, including aerobic oxidation of alcohols,[9] carbon monoxide oxidation,[10] degradation of nitro-aromatic compounds,[11] and others. Importantly, the catalytic efficiency of Au NPs has been linked to their sizes, shapes, and surface properties.[12] In particular, wrinkled/branched Au NP morphologies are of interest for catalysis applications, as such particles exhibit high specific surface areas and abundant edges and crevices presumed to contribute to catalytic activity. Porosity is considered another important determinant for the catalytic activity of Au NPs; recent studies have demonstrated, for example, 50% enhanced electrocatalysis attained in nanoporous Au NPs compared to porous gold sheets.[13] Au “nanoflowers” which combine nanoporosity and wrinkled surface morphology have similarly displayed good catalytic properties for degradation of nitroaromatic compounds.[14] Here, we describe generation of unique Au “nano wool-balls” and their application as broad-based catalytic substrates. The Au nano wool balls were prepared through a simple process comprising self-assembly and reduction Au(SCN)₂ in water without co-addition of nucleation seeds, templates, nor reducing agents. The nano wool-balls were highly uniform in size and shape, which could be tuned by modulating the reaction conditions. We demonstrate that the Au nano wool-balls exhibited excellent catalytic activity for methanol oxidation and 4-nitrophenol degradation, ascribed to the intricate surface nanoribbon morphology.

Results and Discussion

Figure 1 depicts the synthesis scheme of the Au nano wool-balls, and analytical characterization of the particles. The spontaneous self-assembly process is outlined in Figure 1A. Following dissolution of KAu(SCN)₂ in the aqueous solution, Au nanoparticles exhibiting intertwined sheet morphology gradually grew, forming within few hours spherical particles mimicking wool-balls. The scanning electron microscopy (SEM) analysis in Figure 1B highlights the particle growth process and morphology. Small Au nanoparticles exhibiting sizes of 30±3 nm appeared within 2 hours after dissolving KAu(SCN)₂ in water (Figure 1B, left image). NPs exhibiting diameters of around 300 nm were observed after 8 hours, adopting interweaved nanosheet structures (Figure 1B, middle). The Au nano wool-balls reached maximal growth 16 hours after dissolution of the gold complex in water, and the SEM image in Figure 1B, right reveals abundant spherical particles exhibiting diameters of 650±50 nm, displaying remarkable “nanoribbon” morphology. Transmission electron microscopy (TEM) data presented in Figure S1, A-B indicate that that while the inner cores of the Au nano wool balls are not hollow, the corrugated “nanoribbon” morphology is extended deep within the Au nanoparticle. The Au nano wool-balls were fairly uniform in size (see inset in Figure S1,C for size distribution analysis).

[b] Ahiud Morag and Prof. R. Jelinek
Ilse Katz Institute for Nanotechnology,
Ben-Gurion University of the Negev
Beer Sheva 84105 (Israel)

Supporting information for this article is given via a link at the end of the document.

[a] X. Yin, Dr. N. Teradal, Ahiud Morag and Prof. R. Jelinek
Department of Chemistry,
Ben-Gurion University of the Negev
Beer Sheva 84105 (Israel)
E-mail: raz@bgu.ac.il

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The electrons produced in the plasma chamber react with the constituent intermediate species in the spontaneous reduction (approximately 15% abundance as compared to the Au(111) and Au(200) crystal planes, respectively (Figure 2B,i)). The low intensity XRD signals at 5.12 Å and 2.6 Å are attributed to partially organized crystalline structures of KAu(SCN)₂.[15] The presence of the Au(11) thiocyanate complex is also supported by the XPS results in Figure 2A,i. The Au⁺ ions are intermediate species in the reduction of the Au(III) species in Au(SCN)₂ by the thiocyanate ligands.[16] An additional prominent peak at around 30° corresponds to 3.0 Å inter-planar distance and is ascribed to crystalline assembly comprising KAu(SCN)₂ units bonded through aurophilic interactions.[15]

Aurophilic interactions between Au⁺ atoms have been reported in varied gold assemblies, generating anisotropic metallic gold nanostructures.[20] In the system presented here, the mechanism responsible for the wool-ball-like crystal growth is likely based upon aurophilic interactions between the Au⁺ in Au(SCN)₂⁺ complexes. The linear configuration of aurophilic-bonded Au(SCN)₂⁺ complexes facilitates planar crystalline growth, giving rise to the nanoribbon morphology. The anisotropic ribbon-like structures (Figure 1B), as well as the diffraction parameters in the XRD analysis (Figure 2B) both point to the prominent role of aurophilic interactions in the assembly of the nano-wool balls. Echoing the XPS analysis, virtually all the gold in the colloid sample was converted into Au in after plasma treatment, as only the Au(111) and Au(200) crystal planes are apparent (Figure 2B,ii).

Figure 1C depicts kinetic analysis the nano wool ball growth carried out through application of dynamic light scattering (DLS). The DLS experiment in Figure 1C complements the SEM study (Figure 1B) and highlights the gradual particle growth. Notably, similar to the SEM image in Figure 1B, left, distinguishable particles appeared only after approximately 1.5 hours, consistent with initial assembly of nucleation seeds in the aqueous solution, which subsequently enlarged into nano wool balls. Figure 1C also points to a particle diameter plateau of around 650 nm, consistent with the SEM data in Figure 1B. The polydispersity index of the DLS analysis presented in Figure S2 yielded values of 0.035–0.158, confirming a relatively low particle size distribution.

To elucidate the structural features and assembly mechanism of the Au nano "wool-balls" we carried out x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) analyses (Figure 2). The XPS spectrum of the particles in features superimposed peaks of Au₃ at 84.2 eV and 87.9 eV, and low area signals at 85.4 eV and 88.8 eV corresponding to Au⁺ ions (approximately 15% abundance as compared to the Au(111) peaks).[15] confirming that the "nano-wool-balls" structures comprise of predominantly metallic gold, and additional Au⁺ (Figure 2A,i). Previous studies have reported that Au⁺ ions constitute intermediate species in the spontaneous reduction process of Au(SCN)₂ in aqueous solutions.[16] Plasma treatment of Au films is known to induce efficient reduction of the metal.[17] The electrons produced in the plasma chamber react with the residual Au⁺ ions, reducing them to crystalline gold. Indeed, treating the Au colloids with air plasma eliminated the Au⁺ XPS peaks, yield purely metallic gold particles (Figure 2A,ii).

Powder XRD data presented in Figure 2B corroborates the XPS experiments, providing evidence for the crystalline nature of the Au nano-wool-balls. The powder XRD pattern of the as-synthesized colloids reveals two diffraction peaks at 38° and 45° corresponding to the Au(111) and Au(200) crystal planes, respectively (Figure 2B,i). The polydispersity XRD peaks at 5.12 Å and 2.6 Å are attributed to partially organized crystalline structures of KAu(SCN)₂.[15] The presence of the Au(11) thiocyanate complex is also supported by the XPS results in Figure 2A,i. The Au⁺ ions are intermediate species in the reduction of the Au(III) species in Au(SCN)₂ by the thiocyanate ligands.[16] An additional prominent peak at around 30° corresponds to 3.0 Å inter-planar distance and is ascribed to crystalline assembly comprising KAu(SCN)₂ units bonded through aurophilic interactions.[15]

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The effect of organic solvents co-added to the aqueous KAu(SCN)₄ solution was also examined (Figure 3B). The SEM images presented in Figure 3B reveal that addition of small concentrations of organic solvents (10% v/v) had noticeable effects upon the size and morphologies of the Au colloids. Acetone appears to have induced the most pronounced structural effect, giving rise to small gold particles (~300 nm diameter, Figure 3B,i) comprising disk-like morphologies rather than curved nanoribbons. Addition of ethanol produced Au nanoparticles that were slightly bigger, although the particles’ surface exhibited more abundant nanoribbons (Figure 3B,ii). The SEM image of Au particles grown in a dimethylformamide (DMF)/water solution (Figure 3B,iii) depicts larger Au colloids (diameters of ~500 nm) displaying relatively abundant intertwined nanoribbons.

Interestingly, co-addition of dimethylsulfoxide (DMSO) and Au(SCN)₄ generated similarly sizeable nanoparticles, although their surface morphology featured very dense curved nanoribbons (Figure 3B,iv) that closely resemble the nano-wool-balls assembled in pure water (i.e. Figure 1B). The effects of the organic solvents upon assembly and structures of the Au colloids are ascribed to the intimate relationship between crystallization processes and solvent properties. In particular, we observe that the polarity of the solvent was correlated to the structural impacts, as the polarity indexes of acetone and ethanol were close to each other (5.4 and 5.2, respectively), and considerably smaller than DMF and DMSO (6.4 and 6.5, respectively.) Elevated temperature had also a dramatic effect of elevated upon the Au nanoparticles (Figure 3C). Specifically, increasing the temperature of the aqueous KAu(SCN)₄ solution from 25°C to 50°C completely eliminated the intertwined nanoribbon morphology, instead generating particles comprising roughly-shaped surface morphology displaying irregularly-shaped protruding domains (Figure 3C,ii). Similar particle morphologies were recorded in samples incubated at higher temperatures (Figure 3S).

Figures 4 and 5 demonstrate applications of the new Au nano wool-balls as effective substrates for electrocatalysis and heterogeneous catalysis. Figure 4A presents the electrochemically-active surface area analysis of the Au wool-balls, carried out through electrochemical gold oxide stripping in 0.5 M H₂SO₄ at a scan rate of 5 mV s⁻¹. To determine the significance of the unique surface morphology of the Au nano-wool-balls, we also measured the electrochemically-active surface areas of the Au NPs grown through incubation of KAu(SCN)₄ at 50°C – a temperature in which the particles formed did not exhibit the surface nanoribbon morphology (e.g. SEM images in Figure 3C,ii). We also examined solid ~100 nm-diameter Au NPs displaying smooth surface (SEM image in Figure S4).

Figure 4A shows that the Au nano wool-balls exhibit a lower oxidation peak, at 1.06 V, compared to both the Au particles synthesized at 50°C (1.12 V) and conventional 100-nm Au NPs (1.18 V), indicating that surface atoms on the nano wool-balls were more readily oxidized. The electrochemically-active surface areas were quantified by integrating the areas of the gold oxide reduction curves near 0.9 V and assuming a specific charge of
450 μC cm⁻² for the gold oxide reduction. Electroactive surface areas of 10.34 m² g⁻¹, 1.10 m² g⁻¹, and 2.69 m² g⁻¹ were calculated for the Au nano wool-balls, Au colloids prepared at 50°C, and 100-nm Au NPs, respectively. These data clearly show that the nano wool-balls exhibited substantial electroactive surface area available for catalysis (comparison of the electrochemical parameters obtained from Figure 4A is provided Table S1).

Furthermore, the Au nano wool-balls exhibited much lower onset potential (-0.212 V) than the high-temperature prepared Au wool balls (-0.136 V) and smooth-surfaced 100-nm Au NPs (-0.087 V). Figure S5 compares the peak current determined according to the electroactive surface area and peak current calculated for Au mass. Notably, while the current-per-surface-area obtained for the Au nano wool balls was smaller than the Au particles prepared at 50C, the total electroactive surface area of the nano wool balls was significantly higher than the corresponding area of the Au colloids prepared at 50C. Overall, these results underscore excellent catalytic activity for methanol oxidation of the Au nano wool balls that is on par or better than previous catalytic gold systems.[14, 24] Moreover, the significantly more pronounced catalytic performance of the Au nano wool-balls compared to the two other Au NPs examined (Figure 4B) points to the crucial role of the corrugated surface morphology of the particles in promoting the catalytic activity.

Figure 4C examines the long-term electrocatalytic performance and tolerance of the Au nano wool-balls, in comparison with Au wool-balls prepared at 50°C and the 100-nm conventionally-prepared Au NPs. The chronoamperogrammetric curves in Figure 4C were recorded at 0.24 V (for the Au nano wool-balls), 0.26 V (Au particles prepared at 50°C), and 0.26 V (conventional Au NPs), corresponding to the respective oxidative peak potentials for the Au NP samples (e.g. Figure 4B). Figure 4C reveals that the Au nano wool-balls exhibited a gradual decrease in current, reaching steady state at 6.2 μA μg⁻¹ after 60 min. In comparison, the currents of the Au particles prepared at 50°C and conventional Au NPs decreased more significantly, diminishing to 2.7 μA μg⁻¹ and 0 μA μg⁻¹ after 60 min; the rapid current decrease reflects greater accumulation of carbonaceous intermediates upon the Au NPs’ surfaces, which consequently deactivate catalytic sites.[14] This performance is on par or better than previously reported gold-based methanol oxidation catalysts [Table S2].

To adhere to practical requirements in actual fuel cell applications, the stability of the nano Au wool-ball catalytic platform was evaluated by performing multiple electrocatalytic cycles of methanol oxidation (Figure 4D; the actual CV data are presented in Figure S6,A). Figure 4D shows that the Au nano wool-balls exhibited stable currents over 100 (~12.5 µA µg⁻¹) and 400 cycles (~10.1 µA µg⁻¹) with the retention of peak current at least 70% and 50%, respectively.

We also calculated the tolerance ratios for methanol oxidation (I₁/I₂, in which I₁ corresponds to forward oxidation peak current, and I₂ corresponds to backward oxidation peak current), which reflect the extent of adsorption of “poisoning” intermediate carbonaceous species which deactivate the catalysts’ surface (Figure S6,B).[25] Specifically, a high tolerance ratio was determined for the Au nano wool-balls (I₁/I₂=2.6) that was significantly higher than both the Au particles prepared at an elevated temperature (I₁/I₂=1.6), and conventional Au NPs (I₁/I₂=1.1). These results indicate greater tolerance of the Au nano wool balls towards surface accumulation of carbonaceous species and further attest to the superior catalytic performance of these Au NPs.

Figure 5 depicts the catalytic activity of the Au nano wool balls...
towards reduction of 4-nitrophenol, demonstrating their broad-based catalytic properties. Reduction of 4-nitrophenol has been studied as a representative reaction catalysed by Au nanoparticles.\cite{26} Figure 5A depicts time-dependent ultraviolet-visible (uv-vis) absorbance spectra of 4-nitrophenol added (together with NaBH₄) to a solution of Au nano wool-balls that was prepared through incubation of gold thiocyanate at 25°C with a regular time interval of 1 min. The reaction progress was monitored by the UV-vis spectroscopy at the characteristic peak of 4-nitrophenol (400 nm). The progressively suppressed intensities at 400 nm in Figure 5A reflect that 4-nitrophenol was reduced to 4-aminophenol, catalysed by the Au NPs. Furthermore, the yellow colour of 4-nitrophenol solution gradually faded upon progression of the reaction (Figure 5A). Importantly, no 4-nitrophenol reduction was observed without the Au nano wool balls, attesting to the crucial catalytic role of the Au particles in the reaction.

![Figure 5A](image1.png)

Figure 5A shows the time-dependent ultraviolet-visible absorbance spectra of 4-nitrophenol. The absorbance at 400 nm decreases over time, indicating the reduction of 4-nitrophenol to 4-aminophenol.

![Figure 5B](image2.png)

Figure 5B compares the catalytic activity of the Au nano wool-balls, Au colloids prepared at 50°C, and 100-nm Au NPs. With excess NaBH₄ and sufficient catalyst, the catalytic reduction of 4-nitrophenol is pseudo-first-order and dependent only on the concentration of 4-nitrophenol. We studied the correlation between the natural log of absorbance at 400 nm and reaction time, linearity is observed for all reaction on these catalysts. The slope of the lines reflect the apparent rate constant (kₚₑₗ) of the reaction for these three catalysts at same reaction conditions. Importantly, the calculated kₚₑₗ values were 5.92 × 10⁻³ s⁻¹ (nano wool balls), 4.04 × 10⁻³ s⁻¹ (Au wool-balls prepared at 50°C) and 2.64 × 10⁻³ s⁻¹ (conventional Au NPs). Indeed, the most pronounced kₚₑₗ recorded for the reaction catalysed by the Au nano wool-balls attests to the greater catalytic capabilities of these unique gold nanoparticles.

Conclusions

We report construction of unique Au “nano wool-balls” through a simple synthetic route comprising dissolution of KAu(SCN)₂ in water, without co-addition of nucleating seeds, reducing-, nor templating-agents. The generated nano wool-balls exhibited narrow size distribution that could be tuned by external parameters such as complex concentration or co-addition of organic solvents. The Au nano wool-balls adopted a striking interwoven nanoribbon surface morphology that was dependent upon the solution temperature and small concentrations of organic solvents. The Au particles exhibited excellent broad-based catalytic properties, both for methanol oxidation as well as 4-nitrophenol reduction. The corrugated, high surface area morphology was likely the key factor contributing to the catalytic performance of the Au nano wool-balls; indeed, the surface morphology also gave rise to interesting SERS properties (Figure S7). Overall, this study expands the universe of Au nanoparticle morphologies, demonstrating fabrication of catalytically-active size-tunable Au nanoparticles in water through an extremely simple assembly process employing a readily-available gold complex.

Experimental Section

Materials: HAuCl₄·3H₂O, KSCN, NaBH₄, 4-nitrophenol and p-aminobenzoic acid (PAB) were purchased from Sigma-Aldrich. Methanol, acetone, ethanol, dimethylformamide, dimethyl sulfoxide and H₂SO₄ were purchased from Bio Lab (Israel). All above listed reagents were used as received. Water used in the experiments was doubly purified by a Barnstead D7382 water purification system (Barnstead Thermo, Dubuque, IA), at 18.3 MΩ cm resistivity.

Synthesis of the KAu(SCN)₂ Complex: 1 mL of an aqueous solution of HAuCl₄·3H₂O (24 mg/mL) was added to 1 mL of a solution of KSCN in water (60 mg/mL). The precipitate formed was separated by centrifugation at 4000 g for 10 min. The supernatant was decanted, and the residue was dried at room temperature.
Synthesis of Au nano woolballs: 5 mL of freshly prepared KAu(ClO4)2 aqueous solution (5 mM) was placed in a glass vial. The solution was incubated at 25°C for 16 hrs, subsequently centrifuged at 1500 rpm for 5 min, and the precipitate was collected and washed with ultrapure deionized water three times and re-dispersed in acetone.

Synthesis of solid 100-nm gold nanoparticles. 100-nm gold nanoparticles was prepared according to a published procedure. A quantity of 50 ml of HAuCl4(10−5 M) by heating to boiling and 0.2 ml of trisodium citrate (1% by weight) is added. Reduction of gold chloride is practically complete after 5 min of boiling.

Electrochemical measurements: Electrochemical measurements of various samples were performed in 0.5 M KOH and 0.5 M H2SO4 solution using the standard three-electrode configuration. The working electrode used was gold nanostructure (Au wool-balls, control and solid 100) modified glassy carbon electrode (GCE), a saturated Ag/AgCl electrode as reference and the counter electrode was a Pt wire. The as prepared gold nanostructure dispersion was loaded onto a glassy carbon electrode (3 mm in diameter) by drop casting 2 µl, gold nanostructure dispersion. The methanol oxidation activity evaluated by cyclic voltammetric and chronoaamperometric techniques.

Electrochemical active surface area: The electrochemical active surface area (EASA) of gold nanostructure was explored using cyclic voltammetric technique. The surface redox behavior of the gold nanostructures were characterized in 0.5 M H2SO4 at a scan rate of 5 mV/s−1. EASA was evaluated by using the equation of Qc=2eNAΓ, where Qc is the charge passed during reduction of gold oxide was calculated by integration of the gold oxide reduction peak. The specific charge equivalent of 450 µC/cm² was used for converting the charge passed during the gold oxide reduction to a total surface area (A=Qc/450), which was then divided by the mass of the Au nano wool-ball to obtain a specific surface area per unit mass.

Catalytic reduction of 4-nitrophenolon: Sodium borohydride solution (1.5 ml, 0.3 M) was added to 4-nitrophenol solution (2 ml, 0.65 mM) within an optical cell. 0.5 ml of sample containing 39 mg/L of Au NPs was added to the NaBH4 / 4-nitrophenol solution(nano wool-balls is previous treated for 5 min by air plasma, PDC=32G, Harrick plasma). The catalytic performance of the samples was monitored using a JASCO V-550 UV/vis spectrophotometer.

Dynamic light scattering (DLS) measurements: DLS data was collected at 25 °C on an ALV-CGS-8F instrument (ALV-GmbH, Germany) at 90deg (unless otherwise indicated), and the CONTIN method was used to obtain hydrodynamic radii (Rh). Prior to measurement, solutions were filtered through 0.45 and/or 0.22 µm polycrylinidene fluoride (PVDF) Millipore filters.

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References
New gold “nano wool-balls” exhibit remarkable structural and catalytic properties

Xiuxiu Yin[a], Nagappa Teradal[b], Ahiud Morag[a], and Raz Jelinek*[a,b]

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