Transformation of Freestanding Carbon-Containing Gold Nanosheets into Au Nanoparticles Encapsulated within Amorphous Carbon: Implications for Surface Modification of Complex-Shaped Materials and Structures

Qing Yu, Jingyang Zhang, Tianyu Wang, Minhyuk Park, Hongliang Dong, Songyi Chen, Xin Zhang, Songhao Guo, Yang Yang Li, Qiaoshi Zeng,* and Yong Yang*

ABSTRACT: Freestanding metallic nanosheets (or 2D metals) have been attracting tremendous research interest because of their potential applications in numerous important fields, such as green energy, biomedical imaging, and nanodevices. However, thermal stability of 2D metals received much less attention and remains as an open issue to resolve. Here, we report the first synthesis of large-area freestanding carbon-containing gold nanosheets by polymer surface buckling-enabled exfoliation (PSBEE). Through a systematic study based on flash differential scanning calorimetry, we find that such 2D nanosheets tend to fragment upon heating, which are eventually transformed into nanoparticles of different sizes. Inspired by this interesting finding, we develop a facile method that enables scalable production of crystalline Au nanoparticles encapsulated with amorphous C by isothermally annealing the carbon-containing gold nanosheets. Compared to the traditional methods for the synthesis and deployment of nanoparticles, our nanosheet-based fabrication method is flexible and highly efficient, which can simultaneously synthesize and deploy nanoparticles on different materials regardless of their surface topologies, therefore appealing to various surface-related applications, especially the surface modification of complex-shaped electrodes and biosensors.

KEYWORDS: 2D metal, carbon-containing gold membranes, freestanding nanosheet, thermal stability, amorphous carbon-encapsulated Au nanoparticle

1. INTRODUCTION

Freestanding Au nanosheets with a nanoscale thickness, also termed as 2D Au in the literature of 2D metals, have attracted considerable research interest for their applications in catalysis, photoelectronics, and biomedicine. As a result of the high surface-to-volume ratio, Au nanosheets contain much more low-coordinated surface atoms than their bulk counterpart. Consequently, the active sites offered by Au nanosheets are abundant in various electrochemical reactions, which can lead to exceptionally high catalytic activities in CO oxidation or selective oxidation of C–H bonds. Meanwhile, the high surface-to-volume ratio also endows Au nanosheets with unique shape-dependent optical properties due to the collective oscillations of conduction electrons on their surface, a phenomenon known as surface plasmon resonance, which can result in high absorptions that can be extended to the near-infrared (NIR) region and hence suitable for applications in biomedical diagnostics and biosensors.

Although Au nanosheets are useful, a fundamental issue that remains open is how stable these freestanding Au nanosheets are. In theory, metallic nanosheets with excessive surface atoms are thermodynamically unfavorable, which can reduce their free energy by minimizing their surface area. Consequently, the properties of Au nanosheets can be readily "degraded", such as after thermal heating or irradiation by electron beams. For instance, Kan et al. reported that Au nanosheets with a thickness of ~70 nm fragmented into pieces at the temperature of 450 °C. It appeared that the thinner was the nanosheet, the lower was the fragmentation temperature. On the other hand, it was discovered that thermal stability of metallic nanostructures, such as 0D nanoparticles and 1D nanorods, could be enhanced via encapsulation with an appropriate "shell" material, such as carbon, silica, and metal oxide. The presence of the shell can hinder the diffusion...
of surface atoms even at elevated temperatures, therefore isolating the “core” material for protection. For example, Khalavka et al. reported in 2007 that a thin amorphous carbon shell could effectively stabilize Au nanorods even at temperatures close to the melting point of bulk Au. Similarly, Galeano et al. demonstrated in 2011 that carbon-encapsulated Au nanoparticles showed enhanced thermal stability and were able to retain their catalytic properties in high-temperature reactions. However, fabrication of encapsulated nanoparticles was not straightforward, which usually involved multistep chemical reactions following physical deposition or electron beam irradiation. Today, the challenge is as follows: how can one find an easy and scalable method to fabricate Au nanoparticles encapsulated with a protection layer?

With the polymer surface buckling-enabled exfoliation method (PSBEE) we previously developed, we are able to synthesize freestanding ultrathin carbon-containing gold (hereafter referred to as Au-C) nanosheets in this work, which has a centimeter in-plane size and thickness down to about 10 nm. This enables a systematic study of the thermal stability of the Au-C nanosheets, leading to an intriguing finding that the 2D Au-C nanosheets can be easily transformed into amorphous carbon-encapsulated Au nanoparticles after thermal annealing. As a result, we develop a facile and scalable method for the synthesis of amorphous carbon-encapsulated Au nanoparticles with a controlled size. More importantly, the freestanding nanosheets can be easily transferred to various planar or nonplanar substrates, which facilitates the fabrication of nanoparticles by decomposing the nanosheets for surface modification of complex-shaped electrode and biosensor materials.

2. EXPERIMENTAL SECTION

2.1. Fabrication of Au-C Nanosheets via Polymer Surface Buckling-Enabled Exfoliation. Following the method detailed in ref , we first spin-coated a polyvinyl alcohol (PVA) hydrogel layer at 1000 rpm for 30 s on a square or circular glass plate with the lateral size of 100 mm. Subsequently, the PVA–glass system was placed in a drying oven for dehydration at 80 °C for 1 h and air-cooled to room temperature. After that, we deposited Au onto the PVA–glass system with ion beam sputtering at the working pressure of 0.1 Pa and ion beam current of 10 mA. We found that the nanosheets so obtained were comprised of two phases, i.e., the Au-rich FCC phase and carbon-rich amorphous phase, which will be discussed in the later text.

2.2. Differential Scanning Calorimetry. We performed thermal analysis on the Au-C nanosheets with flash differential scanning calorimetry (DSC) (Flash-DSC 2, Mettler-Toledo, Switzerland). The Au-C nanosheets were first collected in a small plastic tube with DI water. After drying for 8 h at 60 °C, the nanosheets were transferred to glass slides or sapphire substrates for later use. The flash DSC specimens were prepared using the nanosheets, which were transferred from the glass slides onto temperature-controlled sensors (MultiSTAR UFS1, Mettler-Toledo, Switzerland) under a stereo microscope. During flash DSC, silicone oil was applied on the chip surface to facilitate heat transfer between the nanosheets and the chip. To further study the thermal stability of the nanosheets, we also heated the nanosheets on the sapphire substrates in the Netzsch DSC system in an Ar environment at a heating rate of 1 °C/s.

2.3. Scalable Production of Au-C Nanoparticles. The Au-C nanosheets were transferred to the sapphire substrates following the method detailed in ref . After that, the Au-C nanosheets were dried and heated up in a muffle furnace to a target temperature between 300 and 800 °C at the rate of 10 °C/min. Isothermal annealing was performed for 0.5 to 10 h in air to produce Au-C nanoparticles.

2.4. Structural and Property Characterizations of Au-C Nanosheets and Nanoparticles. Structural characterization was carried out for the Au-C nanosheets and nanoparticles by using scanning electron microscopy (SEM) (FEI-Versa 3D Dual Beam) equipped with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) (Tecnai F20), and atomic force microscopy (AFM) (MFP-3D Origin, Oxford Instruments). The surface morphology and thickness of the Au-C nanosheets were examined with AFM at a noncontact mode. The Raman spectra were obtained using the Renishaw inVia Raman microscope excited with a laser of a wavelength of 532 nm. The Fourier transform infrared spectra (FTIR) were measured using the Nicolet iN10 MX infrared imaging microscope.

3. RESULTS AND DISCUSSION

Figure 1 illustrates how Au-C nanosheets can be synthesized via PSBEE. First, a PVA layer was spin-coated on a glass plate and dried at 80 °C for 1 h. Subsequently, Au was deposited on the PVA layer, and heated up in a muffle furnace to a target temperature between 300 and 800 °C at the rate of 10 °C/min. Isothermal annealing was performed for 0.5 to 10 h in air to produce Au-C nanoparticles.

Figure 1. Schematic illustration of the synthesis of carbon-containing gold nanosheet. (a) Spin-coating a PVA layer on a glass plate, (b) drying at 80 °C for 1 h, (c) deposition of Au onto PVA via ion beam sputtering, (d) immersion of the Au–PVA–glass system into DI water, (e) exfoliation of Au-C nanosheets, (f) photograph of the deposited Au on the PVA layer, (g) peel-off of the Au-C nanosheet in DI water, and (h) 1 cm-wide Au-C nanosheet floating on the water surface.
Following Wang et al., these nanosheets can be easily transferred to other substrates, such as Si (Figure 2a) or Al₂O₃, for further examination. According to the AFM height image, the collected Au-C nanosheet has a uniform thickness of about 25 nm (Figure 2b). Subsequently, structural analyses of the nanosheets were conducted by TEM. As seen in Figure 2c–d, it is evident that the Au-C nanosheet consists of two phases. The dark phases are interconnected and of an FCC polycrystalline structure, as revealed by selected area electron diffraction (SAED) in the inset of Figure 2d, while the bright phases are amorphous. This two-phase structure becomes more evident in the thinner nanosheet according to the high-resolution TEM images and corresponding FFT patterns (Figure S1). Further high-resolution TEM imaging also reveals that the lattice spacing values of such an FCC phase are 0.227 and 0.207 nm for the \{111\} and \{200\} atomic planes, respectively (Figure 2e).

According to the very recent work of Schwartzkopf et al., when a polymer is irradiated by high-energy particles, such as atoms and ions, the kinetic energy of the incoming particles and the resultant stress waves will be absorbed by the molecular chains of the polymer, which could result in the breakage of chemical bonds and the formation of amorphous carbon. On the other hand, according to the elemental mapping (Figure 2f–h), Au is mainly distributed in the interconnected FCC phase, while C is seemingly distributed all over the nanosheet in a uniform manner. A quantitative energy dispersive spectroscopy (EDS) analysis indicates that Au and C are the most abundant components of the nanosheets with an atomic ratio of ~35:65 (Figure 2i). We also obtained the Raman spectra of the Au-C nanosheets in the range of 550–3200 cm⁻¹. As shown in Figure 2j, apart from the second-order Raman peak at ~970 cm⁻¹ that can be keyed to the Si substrate, we observed two Raman peaks at ~1358 and 1560 cm⁻¹, respectively. According to refs 30 and 31, these two peaks correspond to the characteristic D and G peaks of amorphous carbon, respectively. Further FTIR measurements (Figure S2) showed that the Au-C nanosheets contain some O–H and C–H bonds that originated from the broken PVA molecular structure.

The origin of the carbon-rich amorphous phase in the nanosheet is not completely clear yet at this moment. According to refs 32–35, when a polymer is irradiated by high-energy particles, such as atoms and ions, the kinetic energy of the incoming particles and the resultant stress waves will be absorbed by the molecular chains of the polymer, which could result in the breakage of chemical bonds and the formation of amorphous carbon. On the other hand, according to the very recent work of Schwartzkopf et al., sputter...
According to our EDS results (Figure S3), the atomic fraction of carbon increases with the decreasing thickness ($t$) of the nanosheet, from $\sim$44 at. % for $t = 50$ nm and $\sim$70 at. % for $t = 17$ nm to $\sim$82 at. % for $t = 11$ nm. The topology of the Au FCC phase also changes with the thickness of the nanosheet, from being interconnected for $t = 50$ and 17 nm to being isolated for $t = 11$ nm (Figure 2k–m). Next, we studied the thermal stability of the Au-C nanosheets with flash DSC. Note that a few nanosheets with the same thickness were stacked together to enhance the heat flow signals collected via flash DSC. Figure S4a shows a typical heat flow curve for the 25 nm-thick Au-C nanosheets obtained from 0 to 900 °C at the heating rate of 1 °C/s. Interestingly, one can observe two endothermic and one exothermic peaks on this curve. The first endothermic event is weak and occurs around 300 °C, which might be attributed to the elimination of hydroxyl groups or the degradation of the residual PVA as discussed in ref 37. To understand the second endothermic event, a series of non-isothermal experiments was carried out at the heating rate ranging from 1 to 20 °C/s after the nanosheets were preheated at 300 °C for 5 min. Evidently, all heat flow curves exhibit an endothermic peak followed by a sharp exothermic process (Figure 3a). With the increasing heating rate, the endothermic peak shifts from 700 to 900 °C, suggesting that the observed endothermic reaction is thermally activated. In such a case, we fit the peak temperature ($T_{\text{peak}}$) and the heating rate ($\varphi$) to the well-established Kissinger equation:

$$\ln\left(\frac{\varphi}{T_{\text{peak}}^2}\right) = C + \frac{E_a}{k_B T_{\text{peak}}}$$

(1)

where $C$ is the fitting constant, $E_a$ is the activation energy, and $k_B$ is the Boltzmann constant. As seen in Figure 3b, the experimental data can be fitted very well to eq 1. Based on the data fitting, we extracted the activation energy $E_a = 6.32$ eV. Notably, this activation energy (6.32 eV) is about 10 times of that against surface diffusion of Au atoms39 but almost equals the cohesive energy of C=≡C (6.3 eV).40 This behavior implies that the breakage of carbon bonds acts against the endothermic reaction. A similar behavior can be observed on the DSC curves of the 11 and 80 nm-thick nanosheets (Figure S4b). Furthermore, we note that at the same heating rate, the endothermic peak temperature increases with the atomic fraction of carbon.

To reveal the underlying mechanisms for the observed endothermic and exothermic reactions (Figure 3a), we further heated the 25 nm-thick nanosheets up to the temperatures of 820 and 950 °C. The SEM results clearly show that compared to the intact nanosheet before heating (Figure 3c), there are voids and pores in the Au-C nanosheet after it was heated up to 820 °C (Figure 3d), resembling the porous structure produced by carbonization of polymers.41 Since 820 °C is close to the endothermic peak temperature (Figure 3a), this finding indicates that the endothermic reaction could be attributed to voiding or disintegration of the Au-C nanosheet, in which the breakage of carbon–carbon bonds is the main energy barrier (Figure 3b). As seen in Figure 3e, the nanosheets fractured into tiny pieces after heating to 950 °C and formed particles of different sizes. According to ref 42 and our later theoretical analysis, formation of nanoparticles out of nanosheets can release their internal energy, which is supportive of the exothermal process seen in Figure 3a.

To further understand the formation of nanoparticles, isothermal annealing was performed on the 25 nm-thick Au-C nanosheets at a variety of temperatures ranging from 300 to
800 °C. As seen in Figure 4a (or Figure S5a), the nanosheet broke up into tiny fragments after annealing for 2 h at 300 °C (or ~400 °C) and was subsequently transformed into nanoparticles after 10 h of annealing (Figure 4c and Figure S5c). A similar behavior was observed for other annealing temperatures and durations, as shown in Figure 4b,d (or Figure S5b,d). The general trend is that the longer is the annealing time, the larger is the formed nanoparticle. Interestingly, we note that the particle size grew at the expense of their number density (Figure 4e,f), which is similar to a typical Ostwald ripening process.\(^{43-45}\)

Furthermore, we studied how the nanosheet thickness could affect the size of nanoparticles at the annealing temperature of 600 °C and the annealing time of 0.5 h. As seen in Figure 5a and Figure S6a–d, the particle size increases, while the particle density decreases with the nanosheet thickness. After these thermal annealing experiments, we examined the structure of the nanoparticles with transmission electron microscopy (TEM). Interestingly, we observed that the nanoparticle had a core–shell-like nanostructure, as clearly shown in Figure 5b. According to the high-resolution TEM images in Figure 5c,d and EDS spectra obtained from the nanoparticles (Figure S7), the 2 nm-thin shell is a carbon-rich amorphous layer, while the core is a Au-rich FCC nanocrystal.

Based on the above discussions, it is clear that the formation of the nanoparticles is thermodynamically favored after the Au-
C nanosheet is decomposed upon heating. Assuming that the Au-C nanosheet with a thickness $t$ is transformed into $N$ equisized spherical core–shell particles with radius $R$ (Figure 6), the free-energy change $\Delta G$ can be written as $\Delta G = N(S_\gamma C - S_\gamma + S_\gamma A_u - c) - (Nn_\gamma^0 - n_\gamma)\mu_A$ where $S_\gamma$ is the surface area of amorphous carbon in a nanoparticle, $S_\gamma A_u - c$ is the gold/carbon interface area in a nanoparticle, $S_\gamma$ is the surface area of gold, $S_\gamma A_u - c$ is the area of the gold–carbon interface, $S_\gamma$ is the surface area of carbon, $\gamma_C$ is the surface energy of carbon, $\gamma_A$ is the surface energy of gold, $\gamma_A - c$ is the interfacial energy of gold/carbon, $n_\gamma$ is the number of gold atoms within the nanosheet, $n_\gamma^0$ is the number of gold atoms within a particle, and $\mu_\gamma$ is the energy released due to the formation of gold–gold metallic bonds. Since the volume and number of gold atoms are fixed, we have $S(t - t_c) = \frac{4\pi t_c^3}{3} R(t - t_c)^3$ and $n_\gamma = N\left(\frac{4\pi t_c^3 R(t - t_c)^3}{\Omega} + n_\gamma^0\right)$, where $t_c$ and $t_c'$ denote the thickness of the carbon shell of the nanosheet and the carbon shell of the nanoparticle, respectively, while $\Omega$ and $R_A$ denote the atomic volume and radius of gold, respectively. Combining the above derivations yields

$$\frac{\Delta G}{N} = 4\pi R_A \gamma_C + 4\pi(R - t_c)^2 \gamma_A - 4\pi(R - t_c')^3$$

$$\left(\gamma_A + \gamma_A - c + \gamma_C\right) - 4\pi R_A (R - t_c')^3$$

$$\left(3(t - t_c) - 1\right)\mu_\gamma$$

Therefore, the critical particle radius $R_c$ that initiates stable growth (i.e., $\frac{d\Delta G}{dR} = 0$) is

$$R_c \approx \frac{2\Omega(\gamma_C + \gamma_A - c) + R_A \mu_\gamma}{\Omega(\gamma_A + \gamma_A - c + \gamma_C) + 2R_A \mu_\gamma} + t_c'$$

According to the literature, $\gamma_A \approx 1.4$ J/m$^2$ and $\gamma_C \approx 0.04$ J/m$^2$. Since there is no available data for the interfacial energy between amorphous carbon and gold, we take the interfacial energy between gold and graphite as an approximation, and hence, $\gamma_A - c \approx 0.89$ J/m$^2$ according to ref 48. On the other hand, $\Omega = 1.69 \times 10^{-29}$ m$^3$, $R_A = 1.44 \times 10^{-10}$ m, and $\mu_\gamma \approx \frac{\Delta H_{\text{Avogadro’s number}}}{6.022 \times 10^{27} / \text{mol}} = 6.41 \times 10^{-19}$ J. As a result, we obtain $R_c \approx 0.9(t - t_c) + t_c' \approx 0.9t + 0.1t_c$, given that $t_c' \approx t_c \approx 2$ nm (Figure 5c). Based on eq 2, we estimate that the critical particle size $R_c \approx 22.7$ nm for the 25 nm-thick nanosheet, which is close to the smallest nanoparticles we can detect in present experiments (the average particle size is 42.5 ± 17.8 nm and the smallest particle size is ~20 nm, as shown in Figure 5a and Figure S6b).

Inspired by the above findings, we here propose a facile and novel method to synthesize and deploy Au-C nanoparticles on various planar or nonplanar substrates by simply thermally annealing freestanding Au-C nanosheets in air. As a proof of concept, we transferred a few 20 nm-thick Au-C nanosheets onto the surfaces of various materials, including the flat and smooth surfaces of silicon (Figure 7a), the rough surface of the porous Mo grid (Figure 7b), and the wavy surface of the anodized alumina oxide (AAO) plate with periodic holes (Figure 7c). After the isothermal annealing at 600 °C in air for 0.5 h, we found that Au-C nanoparticles with an average size ranging from 85 to 245 nm were formed and dispersed on the surfaces of these materials in a uniform manner regardless of their surface topologies (Figure 7d–f). It is worth noting that the classic solid-dewetting method also produces nanoparticles by “dewetting” metallic films deposited on a carefully selected smooth substrate. In contrast, our nanosheet-based fabrication method is substrate-insensitive and easy to implement and control, which makes it appealing in surface modification of nonplanar complex-shaped materials and structures, such as electrodes in energy-related applications.

4. CONCLUSIONS

In summary, we first report the fabrication of large-sized freestanding carbon-containing gold nanosheets by PSBEE. Through a systematic thermal stability study, we found the decohesion of the freestanding Au-C nanosheets under thermal annealing, followed by their transformation into Au nanoparticles encapsulated by amorphous carbon. Based on these findings, we developed a simple yet efficient method to synthesize Au nanoparticles, whose sizes can be easily adjusted...
by altering the nanosheet thickness and annealing temperature and time. Moreover, owing to the flexibility of the freestanding nanosheets, our new fabrication method can deploy nanoparticles on various materials regardless of their surface topologies (e.g., planar, rough, or porous surfaces), which should be useful for the surface modification of complex-shaped materials and structures.

**ASSOCIATED CONTENT**

- Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c00565.
  High-resolution TEM images and corresponding FFT analysis of the Au-C nanosheets, FTIR spectrum of the Au-C nanosheet, flash DSC heat flow curves and EDS spectra of the Au-C nanosheets with varying thicknesses, SEM images of the Au-C nanosheets after annealing at different temperatures and thicknesses, and EDS spectra of Au-C nanoparticles (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**
Qiaoshi Zeng — Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China; orcid.org/0000-0001-5960-1378; Email: zengqs@hpstar.ac.cn
Yong Yang — Department of Mechanical Engineering, College of Engineering and Department of Material Science and Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China; orcid.org/0000-0002-0491-8295; Email: yongyang@cityu.edu.hk

**Authors**
Qing Yu — Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China; Department of Engineering Mechanics, Zhejiang University, Hangzhou 310027, China; orcid.org/0000-0002-2322-2875
Jingyang Zhang — Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China
Tianyu Wang — Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China
Minhyuk Park — Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China
Hongliang Dong — Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China
Songyi Chen — Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China
Xin Zhang — Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China
Songhao Guo — Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China; orcid.org/0000-0003-0570-0164
Yang Yang Li — Department of Material Science and Engineering, College of Engineering, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China; orcid.org/0000-0003-4153-9558

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsanm.1c00565

**Author Contributions**
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**Notes**
The authors declare the following competing financial interest(s): QY, JYZ, TYW, MP and YY are listed as the inventors on the filed patent application related to the technology described in this work. The rest of the authors declare no competing interest.

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