

## Article

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# Total Structure Determination of the Largest Alkynyl-Protected FCC Gold Nanocluster Au<sub>110</sub> and the Study on its Ultrafast Excited-State Dynamics

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Supporting Information Placeholder

### ABSTRACT:

Great attention has been paid to nanoclusters having face-centered-cubic (FCC) metal kernels, because of the similarity of metal packing to bulk gold. So far, there is no precedent example of an all-alkynyl-protected fcc gold nanocluster with gold atom number more than 100. We report the synthesis and total structure determination of an alkynyl- protected gold nanocluster [NEt<sub>3</sub>H]<sub>2</sub>[Au<sub>110</sub>(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C)<sub>48</sub>] (Au<sub>110</sub>). It has a fcc Au<sub>86</sub> kernel with 24 peripheral Au(C=CR)<sub>2</sub> staples. The Au<sub>86</sub> kernel consists of six close packing layers in the pattern of Au<sub>6</sub>: Au<sub>16</sub>: Au<sub>21</sub>: Au<sub>21</sub>: Au<sub>6</sub>. Electronic absorption spectroscopy shows Au<sub>110</sub> has a molecular-like discrete electronic structure, and transient absorption experiments reveal its nonmetallic nature.

#### INTRODUCTION

Ligand-protected gold nanoclusters with atomic precision have recently attracted wide research attention in nanoscience research because of their molecular-like behavior and unique physicochemical properties.<sup>1-7</sup> Surface ligand choice plays an important role in dictating the sizes, compositions and properties of nanoclusters.<sup>8-10</sup> Recently, alkynyl ligands have been employed in the preparation of gold clusters and a series of goldalkynyl nanoclusters have been reported.11-14 Recently all-al- $\begin{array}{l} \mbox{kynyl-protected} & \mbox{gold} & \mbox{nanoclusters}, & \mbox{Au}_{22}(\mbox{ArC}{\equiv}C)_{18}]^{.5} \\ [\mbox{Au}_{25}(\mbox{ArC}{\equiv}C)_{18}]^{.7}, & \mbox{Au}_{36}(\mbox{PhC}{\equiv}C)_{24}, & \mbox{Au}_{44}(\mbox{PhC}{\equiv}C)_{28}^{17} & \mbox{and} \end{array}$ Au<sub>144</sub>(ArC=C)<sub>60</sub><sup>18</sup> have been structurally characterized. Ligand effects are observed between alkynyl- and thiolate-protected clusters, i.e. their properties are different from their thiolated  $Au_{22}(SR)_{18}$ ,<sup>19</sup>  $Au_{25}(SR)_{18}$ ,<sup>20</sup> counterparts  $Au_{36}(SR)_{24}$ ,<sup>21</sup>  $Au_{44}(SR)_{28}^{22}$  and  $Au_{144}(SR)_{60}^{23}$ , even though they have very similar metal cores and identical metal-to-ligand ratios. Owning to the direct interaction between a conjugated system and gold atoms, the coordination of alkynyls makes the electronic structures of Au<sub>x</sub>(C=CR)<sub>y</sub> different from Au<sub>x</sub>(SR)<sub>v</sub>.<sup>24,25</sup>

Recent experimental and theoretical works have highlighted the effect of size and structure on the optical/electronic properties of gold nanoparticles and nanoclusters.<sup>3,26,27</sup> Great attention has been paid to nanoclusters having face-centered-cubic (FCC) metal kernels, because of the similarity of metal packing to bulk gold. Gold nanoclusters of fcc type display unique features compared with non-fcc clusters of similar sizes. Zeng and Pei et al. performed theoretical calculations on a set of fcc-structured gold nanoclusters and envisioned that fcc gold nanoclusters show high chemical stability.<sup>28,29</sup> Wu et al. observed that fcc-type structures have a larger HOMO-LUMO gap than non-fcc-type structures of comparable sizes.<sup>30</sup> Wu et al. also found that the fcc structure shows more enhanced emission than its non-fcc isomer.<sup>31</sup> Most of these studies are limited to small fcc gold nanoclusters (< 50 Au atoms). It is important to investigate fcc-structured large-sized gold nanoclusters (> 100 Au atoms), which may address some critical issues such as the growth patterns of lattice or interfacial structures of gold nanoparticles.<sup>32</sup> Furthermore, fcc-structured gold nanoclusters with more than 100 gold atoms are ideal models for studying the transitional state in core sizes from small gold nanoclusters to gold nanoparticles.<sup>27,33</sup> For example, plasmonic behavior was observed with fcc-type Au<sub>279</sub>(SR)<sub>84</sub>, but there is a short of welldefined fcc type gold nanoclusters with the number of metal atoms in the range of 100~200. Therefore, the critical size region in which the nature of clusters evolves from molecular to metallic has not been determined.

Nevertheless, it is still a daunting challenge to achieve isolation and structural determination of such large fcc gold nanoclusters. Among thiolate-gold nanoclusters, Dass et al. reported a large fcc gold cluster Au<sub>279</sub>(SR)<sub>84</sub>, unfortunately only the core structure was resolved.<sup>34</sup> To our surprise, the largest known fcc-type gold nanocluster in alkynyl family is Au<sub>44</sub>(C=CPh)<sub>28</sub>. It is of great interest to investigate larger fcctype alkynyl-gold nanoclusters in terms of the isolation, total structure determination and properties correlation. Herein, we report an all-alkynyl-protected large nanoclusters with a fcc Au<sub>86</sub> kernel, namely [HNEt<sub>3</sub>]<sub>2</sub>[Au<sub>110</sub>(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=C)<sub>48</sub>] (Au<sub>110</sub>), and the study on its excited-state dynamics.

## **RESULT AND DISCUSSION**

Synthesis and Characterization. The synthesis of Au<sub>110</sub> involves the direct reduction of gold alkynyl precursor p- $CF_3C_6H_4C \equiv CAu$  with NaBH<sub>4</sub> in a mixed methanol/chloroform solvent. The solution was stirred vigorously for 20 h and then was evaporated to dryness to give a black solid. Single crystal growth of Au<sub>110</sub> was performed by diffusion n-hexane : ether (V : V=1 : 1) into a  $CH_2Cl_2$  solution of this solid (see synthetic details in Supporting Information). The composition and structure of Au110 was verified by mass spectrometry and X-ray single crystal diffraction.<sup>35</sup> As shown in Figure S1a, Au<sub>110</sub> has two prominent peaks in ESI-TOF-MS in negative mode. The peak at m/z = 9927.87 is corresponding to  $[Au_{110}(p CF_{3}C_{6}H_{4}C \equiv C)_{48}$ <sup>3-</sup>, and the other one at m/z = 14891.80 corresponds to  $[Au_{110}(p-CF_3C_6H_4C\equiv C)_{48}]^2$ . The countercation [NEt<sub>3</sub>H]<sup>+</sup> in Au<sub>110</sub> was confirmed by ESI-TOF-MS in positive mode (Figure S1b). To verify which signal in Figure S1a is the molecular ion, <sup>1</sup>H NMR was measured (Figure S2) to determine the ratio of the cation and anion. The integration ratio of phenyl H in the alkynyl ligand and ethyl H in [HNEt<sub>3</sub>]<sup>+</sup> is calculated to be 6.0 : 1, supporting that the formula of  $Au_{110}$  is  $[HNEt_3]_2[Au_{110}(p-CF_3C_6H_4C=C)_{48}]$ , in which the ratio is 6.4 : 1. Thus, the formal number of valence electrons of Au110 is calculated to be 64 (110-48+2), which is more than that of  $[Au_{80}Ag_{30}(C \equiv CPh)_{42}X_9]^{+36}$  or  $Au_{57}Ag_{53}(C \equiv CPh)_{40}Br_{12}^{37}$  (58 e) and less than that of Au<sub>144</sub>(ArC=C)<sub>60</sub> (84 e).<sup>18</sup> The metal core size Au<sub>110</sub> was measured to be ~1.5 nm by STEM (Figure S3). It is noted that Au<sub>110</sub> is stable under ambient conditions (Figure S4). No decomposition was observed after a CH<sub>2</sub>Cl<sub>2</sub> solution of Au<sub>110</sub> had been stored under ambient light for a month.

gold atoms in Au<sub>110</sub> are of typical fcc packing (Figure 1). It is noted that the fcc structure in  $Au_{110}$  is guite different from the arrangements in previously reported gold-silver clusters containing 110 metal atoms,  $([Au_{80}Ag_{30}(C \equiv CPh)_{42}X_9]^{+36}$  with  $D_3$ symmetry and Au<sub>57</sub>Ag<sub>53</sub>(C=CPh)<sub>40</sub>Br<sub>12</sub><sup>37</sup> with  $C_1$  symmetry. It is notable that Tsukuda et al. determined a composition of Au<sub>110</sub>(C=CPh)<sub>40</sub> by MALDI mass spectra in 2011,<sup>24</sup> but comparison could not be made due to the lack of structural information. So far,  $Au_{144}(ArC \equiv C)_{60}$  is the only structurally characterized all-alkynyl protected gold nanocluster consisting of more than 100 gold atoms.<sup>18</sup> While Au<sub>110</sub> has a fcc Au<sub>86</sub> kernel,  $Au_{144}(ArC \equiv C)_{60}$  has a multishelled structure of  $I_h$  symmetry. The overall framework of Au<sub>110</sub> has  $C_i$  symmetry, and the Au<sub>86</sub> kernel adopts  $S_6$  symmetry (Figure 1). The Au<sub>86</sub> core has an ideal ABCABC packing as illustrated in Figure 2. Six close packing layers of gold atoms are stacked in the pattern of Au<sub>6</sub>: Au<sub>16</sub>: Au<sub>21</sub>: Au<sub>21</sub>: Au<sub>16</sub>: Au<sub>6</sub>.

Total structure determination revealed that 86 of the 110



Figure 2. (a) Side view and top view of Au<sub>86</sub> kernel. (b) Anatomy of Au<sub>86</sub> fcc kernel structure in Au<sub>110</sub>.

As portrayed in Figure S5, the  $Au_{86}$  kernel in the  $Au_{110}$ cluster is surrounded by 24 RC=C-Au-C=CR monomeric staple motifs, i.e. 18 linear and 6 L-shaped staples. The linear and Lshaped coordination modes were previously observed in gold(I) alkynyl clusters.<sup>38-40</sup> Small-sized gold nanoclusters<sup>15-17</sup> require longer staples to fit the larger surface curvature. Larger nanoclusters such as  $Au_{144}(ArC=C)_{60}^{18}$  and  $Au_{110}$  are found to be exclusively protected by monomeric staples due to smaller surface curvature. Such a pattern is also observed in thiolated nanoclusters.<sup>19-23</sup> Due to the centrosymmetric nature of Au<sub>110</sub>, the coordination patterns of the upper and lower Au<sub>43</sub> of the Au<sub>86</sub> kernel are identical. For the upper Au<sub>43</sub>, six linear staples connect Au<sub>6</sub> and Au<sub>16</sub> layers (Staple I), and another 3 linear staples link Au<sub>16</sub> and Au<sub>21</sub> layers (Staple II). Three L-shaped staples are located at the edges of the  $Au_{21}$  layer (Staple III), i.e. no bridging motifs are presented in between the two Au<sub>21</sub> layers. In <sup>19</sup>F NMR (Figure S6), four peaks at -62.44, -62.74, -63.00 and -63.36 ppm are observed, indicative of four types of F. Their integration ratio of 1 (Staple III) : 2 (Staple II) : 4 (Staple I) : 1 (Staple III) is consistent with the number of alkynyls of each staple type. Ligand shell adopts a propeller blade type arrangement (Figure S5). The neighboring (111) planes are firmly anchored by the monomeric linear staples that are parallel to each other to stabilize the fcc structure. The Au<sub>86</sub> kernel is in



**Figure 1.** (a) Molecular structure of **Au**<sub>110</sub>. (b) Shell and core structures of **Au**<sub>110</sub>. Au, orange; F, green; C, grey. All hydrogen atoms are omitted for clarity.

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roughly regular fcc packing. A summary of bond lengths is shown in Figure S7 and Table S1. The Au-Au bond lengths in the Au<sub>86</sub> kernel lie in the range of 2.7219(19)-3.0654(19) Å, and the Au-Au distances between kernel and shell range from 2.889(2) to 3.364(2) Å. The average Au-Au bond length in Au<sub>86</sub> kernel is 2.858 Å, and the average Au-Au distance between the fcc kernel and the surface staples is 3.126 Å. These two different sets of average Au-Au bond lengths support the clear classification of Au<sub>86</sub> core and (RC=C-Au-C=CR)<sub>24</sub> shell.

UV-Vis-NIR Absorption and HOMO-LUMO Gap. Au<sub>110</sub> shows two broad absorptions at 480 nm and 560 nm (Figure 3a), which indicates that it has discrete electronic states and may show molecular-like behavior, differing from plasmonic nanoparticles.<sup>41</sup> The molecular absorbance coefficient ( $\varepsilon$ ) of Au<sub>110</sub> is  $1.2 \times 10^5$  M<sup>-1</sup>cm<sup>-1</sup> at 480 nm and  $8.6 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> at 560 nm. The cross section  $\sigma$  ( $\sigma = \varepsilon / N_A$ ) values of Au<sub>110</sub> and related gold nanoclusters<sup>16,17,42,43,44</sup> are listed in Table S2. The  $\sigma$  value increases as the size getting larger, and Au<sub>110</sub> shows a lower  $\sigma$ than thiolated nanoclusters with comparable size. The optical energy gap was determined to be 1.75 eV (Figure 3b). Differential pulse voltammetry (DPV) was used to determine the HOMO-LUMO energy gap (Figure S8). The DPV of Au110 exhibits oxidation peak at 0.29 V (O1) and reduction peak at -0.13 V (R1), and the difference between O1 and R1 is determined to be 0.42 eV, which is smaller than 0.6 eV in  $Au_{92}(SR)_{44}$ <sup>45</sup>0.59  $eV \text{ in } Au_{103}(SR)_{50}^{46} \text{ and } 0.50 eV \text{ in } Au_{130}(SR)_{50}^{47}$ , but larger than 0.39 eV of  $Au_{144}(SR)_{52}^{48}$  The electrochemically HOMO-LUMO gap is determined to be 0.26 eV for Au<sub>110</sub> after subtraction of 0.16 eV charging energy.



**Figure 3.** (a) Absorption spectrum of  $Au_{110}$ . Samples were diluted to  $2.8 \times 10^{-6}$  mol/L. Inset: Photographs of  $Au_{110}$  in dichloromethane. (b) The spectrum on the energy scale (eV) of  $Au_{110}$ .

**Ultrafast Electron Dynamics.** Apart from steady-state absorption and stimulated emission,<sup>49-57</sup> transient absorption is a powerful tool to study electronic structure.<sup>58</sup> Extensive studies on ultrafast excited-state dynamics of thiolate-protected gold nanoclusters have been carried out.<sup>45,48,59-63</sup> In order to study the excited state dynamics, we measured the transient absorption spectra of **Au**<sub>110</sub>. Upon photoexcitation at 400 nm in CH<sub>2</sub>Cl<sub>2</sub>, excited state absorption (ESA) of **Au**<sub>110</sub> occurs at 518 nm and 630 nm in the transient absorption spectrum (Figure 4a). The ground state bleaching (GSB) is overlapped with the broad ESA in the visible range, so no negative signal can be observed, and

the GSB displays dips as marked with black arrows in Figure 4a. The positions of GSB are associated with bands in the steady-state UV-vis absorption. Broad ESA bands are indicative of dense excited states in  $Au_{110}$ . The red shift of GSB valley from 543 nm to 565 nm was observed in Figure 4a. The 22-nm red shift differs from blue shift observed for transient bleach signals in Au<sub>25</sub>(SC<sub>8</sub>H<sub>9</sub>)<sub>18</sub><sup>-, 59,61</sup> For Au<sub>110</sub>, the GSB around 565 nm is overlapped with the broad ESA, and some vanishing ESA signals account for uncovering the GSB signal at 565 nm. The kinetic traces probed at 518 nm and 630 nm show both signals begin to decay after time delay of 0.6 ps and diminish to about 10% within 30 ps (Figure 4b). The biexponential fitting of primary signals measured at 630 nm is shown in Figure S9 and Table 3, and the decay time constants are determined to be 1 ps and 11 ps. The GSB center energy was plotted versus time delay in Figure S10, and the energy red shift was fitted to a first-order time constant of 1.2  $\pm$  0.1 ps, which is close to 1 ps time constant in Table S3. To further probe the electron dynamics of Au<sub>110</sub>, the singular value decomposition (SVD) method and the global fitting were used to extract the transient components. According to decay associated spectra (DAS) of  $Au_{110}$  in Figure 4c, decay components are determined to be 1 ps and 10 ps, which is almost identical to the time constants obtained from the fitted kinetic (Table S3). In DAS, 1 ps component exhibits a prominent positive amplitude absorption signals at 630 nm, along with weak negative signals at 495 nm and 545 nm, whereas 10 ps component includes broad positive band centered at 518 nm and 630 nm.

Fcc-structured clusters like Au<sub>36</sub>(PhC≡C)<sub>24</sub>, Au<sub>44</sub>(PhC≡C)<sub>28</sub><sup>17</sup> and Au<sub>92</sub>(SR)<sub>44</sub><sup>45</sup> exhibit molecular like transitions, and Au<sub>279</sub>(SR)<sub>84</sub> was found in plasmonic state.<sup>33</sup> Since the size of Au<sub>110</sub> falls in between Au<sub>92</sub> and Au<sub>279</sub>, it will present valuable information to study its metallic or nonmetallic state in terms of understanding the transition size of clusters from molecular state to plasmonic state. We conducted excitation-pulse-energydependent measurements for Au<sub>110</sub>, and the pump laser power was varied from 100 to 500 nJ per pulse. The superimposition of kinetic traces exists in Au<sub>110</sub> probed at 630 nm, which is preliminarily indicative of power-independent electron relaxation dynamics (Figure 4d). Global-fitting analyses on Au110 with different excitation pulse energy revealed two constant relaxation time: the faster process (1 ps) and the slower process (10 ps) in Table S4. The relaxation time were plotted as a function of laser pulse energy in Figure 5. The 1 ps and 10 ps decay constants in Au<sub>110</sub> is comparable to time scale of electron–phonon coupling time and phonon-phonon coupling time in plasmonic gold nanoparticles,<sup>41,58</sup> respectively. As is illustrated in Figure 5a, the 1 ps relaxation times of Au<sub>110</sub> are independent of the pump laser power, which is not consistent with the two-temperature model in carrier cooling of traditional metallic-state nanoparticles.41,60 In addition, the 10 ps relaxation in Au<sub>110</sub> shows a laser powerindependent dynamics (Figure 5b), which is different from the phonon-phonon coupling in gold nanoparticles.<sup>41,64</sup> Therefore, Au<sub>110</sub> is a nonmetallic nanocluster.



**Figure 4.** (a) Transient absorption spectra as a function of delay time between 0.5 and 50 ps. (b) Kinetics traces probed at selected wavelengths. (c) Decay associated spectra obtained from global fitting of  $Au_{110}$ . (d) Normalized decay kinetics as a function of the laser excitation pulse energy pumped at 400 nm for  $Au_{110}$ .



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Figure 5. Relaxation time constants by global fitting plotted versus the laser excitation pulse energy for (a) 1 ps decay and (b) 10 ps decay of  $Au_{110}$ .

To further study the relaxation process, TA measurements on **Au**<sub>110</sub> were performed with pump at 700 nm (Figure 6a). It is found that strong ESA fades down and the intensity of GSB around 560 nm increases accordingly compared to transient absorption with excitation at 400 nm (Figure 6b). Global analysis for excitation at 700 nm gave 0.2 ps and 9.5 ps decay constants (Figure 6c). The 9.5 ps decay constant is almost the same as the long-lived component with 400-nm excitation, but 0.2 ps decay (700 nm pump) is faster than 1 ps relaxation time (400 nm pump). The subpicosecond process in **Au**<sub>110</sub> is assigned to IC (internal conversion), which occurs very fast since the excitation (400 nm, 3.10 eV) is far above the energy gap. The lowerenergy pumping (700 nm, 1.77 eV) results in electron promotion into lower initial excited state, leading to a reduced ESA intensity and faster IC process. The 10 ps relaxation process in Au<sub>110</sub> should be ascribed to the relaxation from  $S_1$  (the lowest excited-state) to  $S_0$  (the ground state) process. A kinetic model depicting the observed electronic relaxation is given in Figure S11. The carrier lifetime of fcc-typed Au<sub>92</sub>(SR)<sub>44</sub><sup>45</sup> was determined to be 1 ns, which is significantly longer than 10 ps of Au110. In Table S5, gold nanoclusters with comparable sizes also show slower  $S_1 \rightarrow S_0$  relaxation process: 420 ps for  $Au_{103}S_2(SR)_{41}^{46}$  and 180 ps for  $Au_{130}(SR)_{50}^{47}$  The UV-vis spectra and DFT calculations in our previous work demonstrated that the electronic structure of  $Au_x(C \equiv CR)_y$  is different from  $Au_x(SR)_y$ , which is attributed to the active participation of C=CR in the frontier orbitals.<sup>13,16,17</sup> It is difficult to tell the difference of the excited-state dynamics between  $Au_x(C \equiv CR)_y$  and  $Au_x(SR)_y$  at this time, because of the lack of isostructural thiolated Au<sub>110</sub>. Size effect was thought to play an important role on the excited-state lifetime for large-sized nanoclusters,<sup>45</sup> we guess accordingly the carrier lifetime of  $[Au_{110}(SR)_{48}]^{2}$  would lie in between 420 ps  $(Au_{103}(SR)_{50})$  and 180 ps ( $Au_{130}(SR)_{50}$ ), which is distinctly longer than  $Au_{110}$  in this work. In Figure S12, the average rate of nonradiative decay  $k_{\rm nr} (k_{\rm nr} = 1/\tau - k_{\rm r})$  of gold clusters increase as HOMO-LUMO gaps decrease. The plot of  $ln(k_{nr})$  values of  $Au_{103}S_2(SR)_{41}$ , Au<sub>130</sub>(SR)<sub>50</sub> and Au<sub>144</sub>(SR)<sub>52</sub> against HOMO–LUMO gaps was fitted to a linear function, which agrees with the energy gap law  $(\ln(k_{nr}) = -\gamma E_g/\hbar\omega_M + \ln A)$  ( $\gamma$ , molecular parameter;  $\omega_M$ , the highest vibrational frequency).<sup>45,48</sup> However, Au110 is off the trend line, which may be attributed to ligand effects. The coordination of alkynyls could influence the vibrational modes or molecular parameter of the cluster, leading to faster energy dissipation to the surroundings.

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**Figure 6.** (a) 2D data map transient absorption between 0 ps and 10 ps with pump at 400 nm and 700 nm, respectively. (b) Transient absorption spectra of  $Au_{110}$  with excitation at 400 nm and 700 nm, respectively. (c) The global fitting results with excitation at 700 nm. The scatterings around 700 nm due to the laser were cut off.

# CONCLUSION

In summary, we managed to prepare an alkynyl-gold nanocluster Au110 having fcc Au86 kernel. Au110 is a novel fcctype gold nanocluster with more than 100 metal atoms. No surface plasmon resonance absorption was observed in the steadystate optical absorption spectrum of Au110. Transient absorption spectra and power-independent electron dynamics reveal that Au<sub>110</sub> exhibits nonmetallic behavior. It is noteworthy that Au<sub>110</sub> is the largest fcc-structured nonmetallic gold nanocluster so far. It will be interesting to see the nature of fcc nanoclusters with the number of gold atoms falling in 110 and 279, which still need more synthetic effort. Moreover, Au<sub>110</sub> shows a significantly faster band-edge carrier recombination than thiolated gold nanoclusters of comparable sizes, indicating the coordination of alkynyls can trigger perturbation in the excitedstate dynamics. This work will stimulate more studies on the alkynyl-gold nanoclusters with a fcc kernel in order to find the critical size in terms of nonmetallic to metallic transition of gold nanoclusters.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI

Physical measurements, synthesis, characterization data and carrier dynamics of Au<sub>110</sub>, supporting Figures S1–S12, and supporting Tables S1-S4 (PDF)

Detailed crystallographic structure and data for Au<sub>110</sub> (CIF)

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#### Notes

The authors declare no competing financial interests.

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 $\alpha = 67.082(4), \beta = 85.207(4), \gamma = 84.085(4)$ °, V = 15219.0(13)Å<sup>3</sup>, Z = 1, T = 100 K, 96916 reflections measured, 46469 unique ( $R_{int} = 0.0907$ ) final  $R_1 = 0.0836, wR_2 = 0.2392$  for 16379 observed reflections [I >2 $\sigma$ (I)]. CCDC 2015300.

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