Supporting Information for

Chemical Characterization of an Alkali-Like Superatom Consisting of a Ta-Encapsulating Si₁₆ Cage

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S1. XPS measurement

All XPS measurements were performed in an ultrahigh vacuum (UHV) chamber where the base pressure was better than 2×10^{-8} Pa. In the XPS measurement, an X-ray (MgK α , photon energy ($h\nu$) = 1253.6 eV) was irradiated onto the sample surface, and photoelectrons were detected by a hemispherical electron analyzer (VGSCIENTA: R-3000) with a detection angle of 45° from surface normal. The binding energy of core electrons was calibrated by the XPS peak of the Au 4*f* core level.¹ It was carefully verified that there were no effects of X-ray irradiation on the XPS spectra for all samples.

S2. Nanocluster synthesis and deposition

In advance of the nanocluster deposition, the HOPG substrate is cleaved in air and heated to 750 K for at least 50 h in UHV to obtain an atomically clean and flat surface. The cationic Ta@Si₁₆ nanoclusters were synthesized in a gas phase aggregation cell with direct current magnetron sputtering source (Angstrom Sciences),^{2,3} where a Ta-Si mixed target was sputtered by Ar⁺ ion (~0.3 kV, ~150

mA). The nanocluster beam was guided with octopole ion guide (650 kHz, 100 V amplitude) and introduced to an ion deflector to discriminate the cationic species of nanoclusters. The targeted Ta@Si₁₆⁺ clusters are then mass-selected by a commercial quadrupole mass (Q-MS) filter (Extrel CMS LCC, MAX-16000) and deposited onto the HOPG substrate with a mass resolution of m/ $\Delta m \sim 50$, where the mass resolution of m/ $\Delta m \sim 200$ for mass analysis was optimized to enhance the ion current without any contamination from other compositions. Figure S1 shows a typical mass spectrum of Ta_mSi_n nanoclusters taken while sweeping the Q-MS filter before/after the deposition of Ta@Si₁₆⁺ clusters. The spectrum clearly shows that Ta@Si₁₆⁺ clusters (m/z = 630) were predominantly produced as "magic numbers" and were separated well from neighboring sizes of nanocluster, which ensures a high purity of deposited nanoclusters using our nanocluster-synthesis/deposition apparatus.

A sample voltage is applied during the deposition to collect the cluster ion but it was kept to be close to zero as possible, to typically more than -5 V. The applied voltage makes it possible to soft land the Ta@Si₁₆ nanoclusters on the HOPG with a low kinetic energy of < 0.5 eV per atom. The typical deposition amount is 5×10^{13} ions, which is estimated by the ion current measured from the sample and the deposition time. The diameter of the nanocluster-deposited area is about 8.5 mm. The nanocluster-deposited sample was transferred to the XPS system connected to the deposition system while maintaining vacuum conditions (~10⁻⁸ Pa).



Figure S1. Typical mass spectrum of Ta_mSi_n nanocluster cations with a mass resolution of m/ Δ m ~ 200, which is optimized to be around m/ Δ m ~ 50 during the deposition.

S3. XPS fitting procedure

For the chemical analysis of the Ta 4*f* and Si 2*p* core levels, Shirley backgrounds were subtracted from the raw data, while XPS of bare HOPG is also subtracted in advance for the Ta 4*f*. After these treatments, both core levels were fitted with a Voigt function having a full width at half maximum (FWHM) of 1.11 eV, the whose Gaussian and Lorentzian contribution are 0.75 eV and 0.56 eV, respectively,¹ which is the instrumental broadening determined based on the measurement of the Au 4*f* core level for Au(111) surface. The energy separation and branching ratio for the spin-orbit splitting of Si 2*p* and Ta 4*f* are taken from literature values.^{4,5} The parameters used in the above analysis are summarized in Table S1.

Table S1. Parameters of fixed peak shape in the fitting procedure, fitted energy and area.⁴⁻⁶

	Ta 4f	Si 2p
Gaussian width (eV)	0.75	0.75
Lorentzian width (eV)	0.56	0.56
FWHM (eV)	1.11	1.11
Spin-orbit splitting (eV)	1.915	0.608
Branching ratio	3:4	1:2
Energy (eV)	22.26 $(4f_{7/2})^5$	99.08 $(2p_{3/2})^4$
Fitted peak area	1	1.58
Expected peak area	1	1.536

S4. Ta@Si₁₆ monodispersed on C₆₀/HOPG substrate: Charge state of Ta@Si₁₆

In the main text, the charge state of Ta@Si₁₆ on HOPG has been discussed based on the energy positions of Ta 4*f* and Si 2*p* core levels observed in Fig. 1. The chemical conditions of alkali-like superatom deposited surface can be discussed by comparison with a study of alkali-metal adsorbed system. For the adsorption of alkali metals on graphite,⁷ the amount of charge transfer between alkali-metal atoms and graphite surface has been a subject of debate for many years. Theoretical calculations have suggested that the alkali-metal adatoms donate a charge of ~0.4–0.5 *e* to graphite, and the corresponding values for the alkali-metal monolayers are the orders of 0.1 *e* per atom, indicating that increased coverage weakens the adsorbate–substrate interaction as a metallic film is formed.⁸ For alkali-

like superatoms, it has been reported that Ta@Si16 deposited on a C₆₀ film is stabilized by forming a one-to-one charge-transfer complex of Ta@Si16⁺ and C_{60⁻}.^{9,10} By analogy with alkali-metal atoms, Ta@Si16 deposited on HOPG surface would be charged positive, but much less so than on C₆₀, since the clusters could interact with each other by forming small islands. In fact, our XPS results consistently indicate that isolated Ta@Si16 on C₆₀ is charged more positively than those accumulated on HOPG as shown in Figure S2. Figure S2 shows XPS spectra (circles) for Ta@Si16 monodispersed on a C₆₀/HOPG substrate measured around the (a) Si 2*p* and (b) Ta 4*f* core levels, that are almost the same with those in Fig. 1. The ratio between the integrated intensity of Ta 4*f* and Si 2*p* is evaluated to be 1:1.59. The result agrees well with the ratio calculated for Ta@Si16 (1:1.53) by using photoemission cross sections of Si 2*p* and Ta 4*f* core levels,⁶ indicating the successful deposition of targeted nanoclusters with precise mass selection. Parameters used to deconvolute the peaks are noted above in S3. The energy positions of Si 2*p*_{3/2} and Ta 4*f*_{7/2} are 99.42 eV and 22.52 eV, respectively. When the XPS data of Ta 4*f* and Si 2*p* were compared between Ta@Si16/C₆₀ and Ta@Si16/HOPG, it is found that both core levels in Ta@Si16/C₆₀ have 0.2–0.3 eV higher binding energy than those in Ta@Si16/HOPG. The result indicates that isolated Ta@Si16 on C₆₀ is charged more positively than those accumulated on HOPG.



Figure S2. XPS spectra of (a) Si 2p and (b) Ta 4f for Ta@Si₁₆ monodispersed on C₆₀/HOPG.

S5. STM images of Ta@Si16 on HOPG at 300 K and 400 K

Figure S3 shows STM images of Ta@Si16 on HOPG at (a) 300 K and (b) 400 K. After heating at 400 K, the STM image was measured around 300K. After heating, the size of the aggregated islands wasenlarged, but the individual Ta@Si16 nanoclusters are still discernable in the STM images.



Figure S3. STM images of Ta@Si16 on HOPG at (a) 300 K and (b) 400 K.

S6. XPS spectra around the O1s core level

Figure S4 shows a XPS spectrum of O 1*s* core levels for Ta@Si₁₆ on C₆₀/HOPG, which was measured after 1×10^5 Pa oxygen exposure for 40 h. The peak position is very similar to that of Si 2*p* (532-533 eV) in SiO₂ in the literature.¹¹



Figure S4. XPS spectrum of O 1*s* core levels for Ta@Si₁₆ on C₆₀/HOPG after 1×10^5 Pa oxygen exposure for 40 h.

Figure S5 shows XPS spectra of O 1*s* core levels for bare HOPG, Ta@Si₁₆, and TaSi₃ deposited films, which are taken just after preparation. The O 1*s* signal is hardly observed on the bare HOPG and Ta@Si₁₆ deposited samples, whereas it can be recognized in TaSi₃ deposited one, suggesting that the TaSi₃ deposited sample partially oxidized during the deposition process.



Figure S5. XPS spectra of O 1s core level for bare HOPG, Ta@Si16, and TaSi3 deposited films.

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