Supporting Information

Structural Characterization of Unprecedented $Al_{14}O^-$ and $Al_{15}O_2^-$: Photoelectron Spectroscopy and Density Functional Calculations

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1. Experimental results

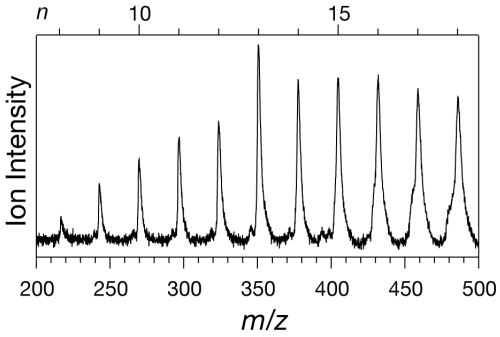

Figure S1. Mass spectra of Al_n^- with O_2 with a channel length of 7mm.

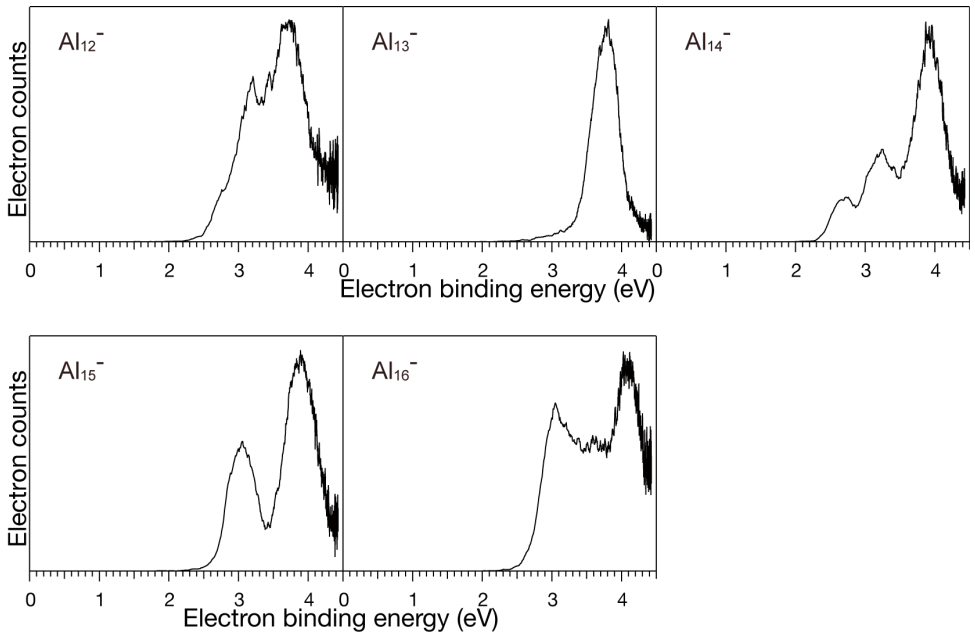

Figure S2. Photoelectron spectra of Al_n^- (n = 12–16) with the same kinetic energies as $Al_{14}O^-$ and $Al_{15}O_2^-$.

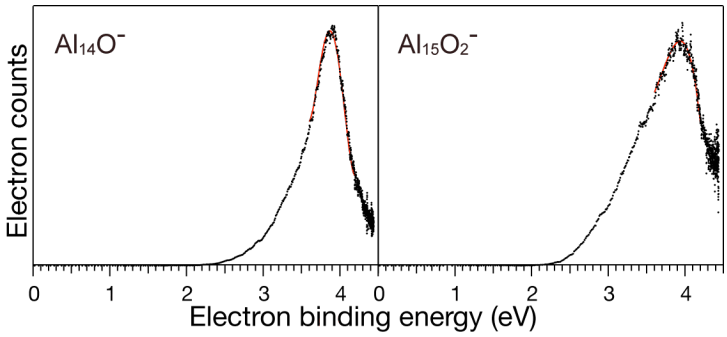

Figure S3. Fitting results of photoelectron spectra of $Al_{14}O^-$ and $Al_{15}O_2^-$. Red curves were obtained by the least square fit of the data in the energy range of 3.6–4.2 eV with fourth–degree polynomials.

2. Computational results

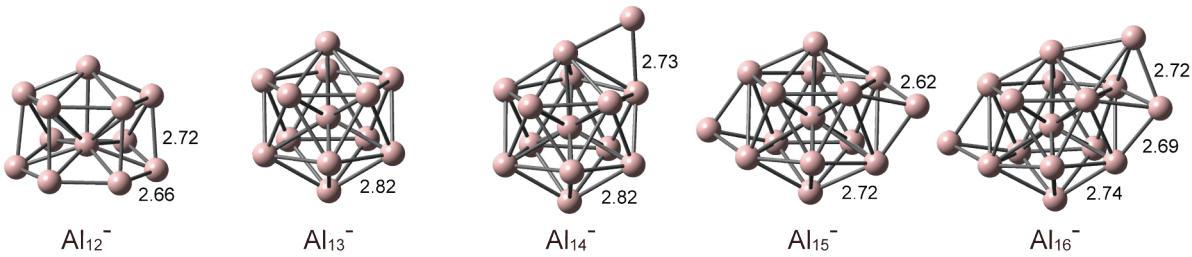

Figure S4. Optimized structures of Al_n^- (n = 12–16) obtained at the B3LYP/6–31G(d) level. The numbers are selected bond lengths (Å).

Table S1. VDE of Al_n^- (n = 12–16).

n	VDE_{cal} (eV)[a]	VDE_{exp} (eV)[b]
12	2.43	2.80 ± 0.1
13	3.45	3.75 ± 0.1
14	2.59	2.65 ± 0.1
15	2.81	2.95 ± 0.1
16	2.80	

[a] calculated for the structures shown in Figure S4 at the B3LYP/6–31G(d) level. [b] from ref 1.

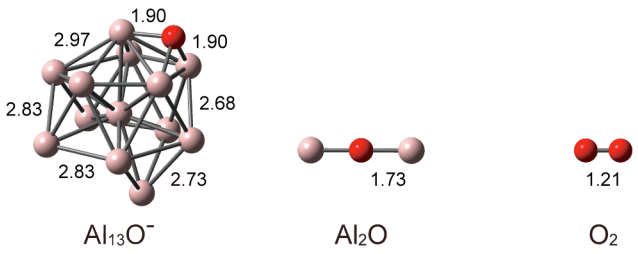

Figure S5. Optimized structures of $Al_{13}O^-$, Al_2O and O_2 obtained at the B3LYP/6–31G(d) level. The numbers are selected bond lengths (Å).

Table S2. Total energy of O_2 and $Al_nO_m^-$.

	E (Hartree)[a]
O_2	−150.3200421
Al_2O	−560.1798515
Al_{12}^-	−2909.3725651
$Al_{13}O^-$	−3227.1492532
$Al_{14}O^-$	−3469.6178843
Al_{15}^-	−3636.7520577
$Al_{15}O_2^-$	−3787.3998384
Al_{16}^-	−3879.2035060

[a] calculated for the structures shown in Figure 4, 5, S4 and S5 at the B3LYP/6–31G(d) level.

References

1. Cha, C. Y.; Ganteför, G.; Eberhardt, W. The Development of the 3p and 4p Valence Band of Small Aluminum and Gallium Clusters. *J. Chem. Phys.* **1994**, *100*, 995.