Electronic Supplementary Information for

Detection of Pb²⁺ Traces in Dispersion of Cs₄PbBr₆ Nanocrystals by In-Situ Liquid Cell Transmission Electron Microscopy

Zhiya Dang[1,*], Liberato Manna[2], Dmitry Baranov[2,*]

¹School of Materials, Sun Yat-Sen University, Shenzhen, China, 518107

²Department of Nanochemistry, Italian Institute of Technology, Genova, Italy, 16163

*Corresponding authors: dangzhy3@mail.sysu.edu.cn, dmitry.baranov@iit.it

Experimental Details of UV-Vis experiments

Materials

Lead (II) bromide ($\geqslant$98%), cesium carbonate (99%), oleic acid (tech. grade, 90%), oleylamine (tech. grade, 70%), octadecene-1 (tech. grade, 90%), cyclohexane (anhydrous) were purchased from Sigma Aldrich, lead (II) oxide (99.999%) was purchased from STREM. All chemicals were used as received.

Sample preparation and UV-Vis spectra

Cs_4PbBr_6 nanocrystals were synthesized as described previously in detail. [1] Briefly, a solution of cesium oleate precursor was injected into the mixture of lead (II) bromide dissolved in octadecene-1, oleic acid, and oleylamine at ~80 ^{o}C and kept at that temperature for 10 minutes. Upon cooling to room temperature, the transparent mixture turned cloudy white and was centrifuged to separate the solid (precipitate) from the liquid (supernatant). Small amounts of each were diluted in cyclohexane in 10 mm quartz cuvette for the UV-Vis spectra (Figure 4a, b in the main text).

A sample of lead (II) bromide-oleylamine was prepared by heating 72 mg ($\approx$0.2 mmol) of lead (II) bromide with 1.5 ml ($\approx$4.5 mmol) of oleylamine in a 4 ml glass vial under stirring at ~130 ^{o}C for 5 minutes. Upon cooling to room temperature, the mixture turned cloudy white. A small amount of the mixture was dissolved in cyclohexane to record the UV-Vis spectrum ($PbBr_2$-OLAm in Figure 4c, dark yellow curve).

A sample of lead (II) oleate was prepared by heating 56.2 mg ($\approx$0.25 mmol) of lead (II) oxide with 0.3 ml ($\approx$1 mmol) of oleic acid in an 8 ml glass vial under stirring at ~150 ^{o}C until all lead (II) oxide was dissolved. A small amount of the resulting mixture was diluted in cyclohexane to record the UV-Vis spectrum [Pb(II) oleate in Figure 4c, magenta curve].

A sample of lead (II) bromide precursor for Cs_4PbBr_6 nanocrystals was prepared by heating 76 mg ($\approx$0.2 mmol) of lead (II) bromide in 5 ml of octadecene-1, 1.5 ml of oleylamine ($\approx$4.5 mmol), 0.2 ml ($\approx$0.63 mmol) of oleic acid under stirring at ~120-130 ^{o}C until all lead (II) bromide was dissolved (< 5 minutes). The small amount of the resulting mixture was diluted in cyclohexane to record the UV-Vis spectrum [$PbBr_2$-(ODE, OLAm, OAcid) in Figure 4d, burgundy curve].

The UV-Vis spectra were recorded on Cary 300 and Cary 5000 (only $PbBr_2$-OLAm) spectrophotometers using 10 mm pathlength quartz cuvettes.
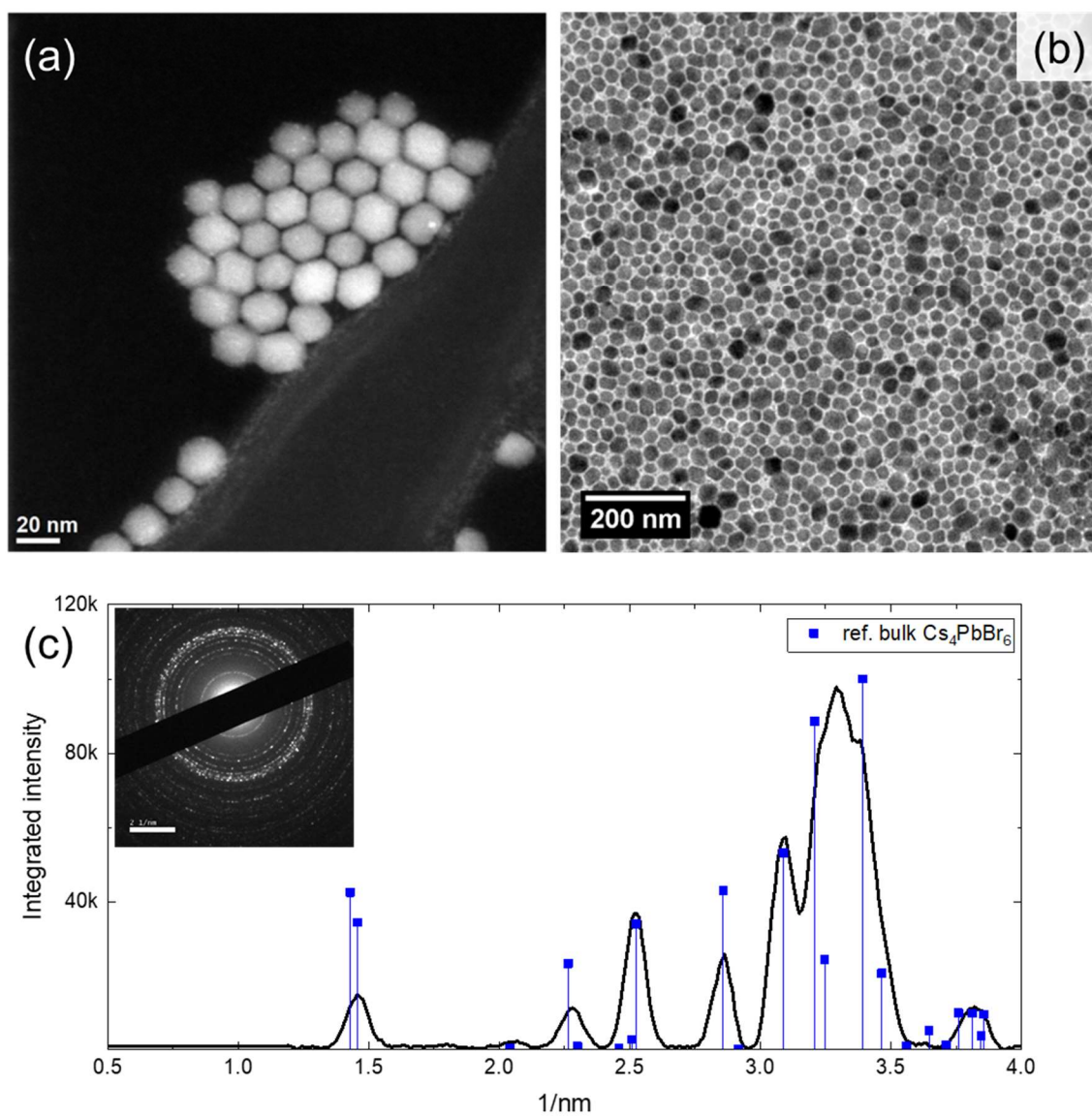
Figure S1. HAADF-STEM (a) and bright-field TEM (b) images of ~20 nm Cs_4PbBr_6 nanocrystals on top of the carbon-coated grid. STEM image shows smaller domains of Pb^0 (bright spots) formed as a result of electron beam damage.[2] Integrated selected area diffraction pattern (solid black line in c, diffractogram shown in the inset) of the sample with reference patterns for bulk Cs_4PbBr_6 (ICSD: 162158) are shown for comparison.
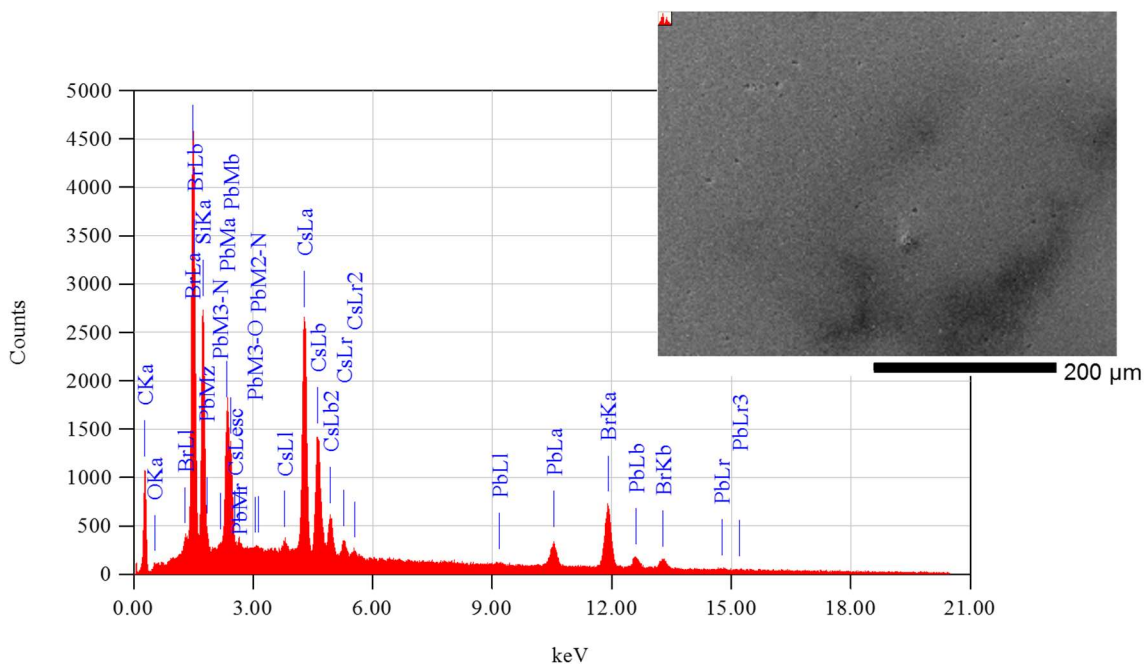
Figure S2. Representative energy dispersive spectroscopy (EDS) spectrum and a scanning electron microscopy (SEM) image (inset) of the area from a thick Cs_4PbBr_6 NC film prepared by drop-casting.

The EDS-SEM analysis was performed using a JEOL 6490LA electron microscope at 25 kV accelerating voltage. The analysis of the spectrum and elemental identification and quantification were performed using Analysis Station software ver. 3.8.0.59 (JEOL Engineering Co., Ltd), JED Series AnalysisProgram ver. 3.8.0.37. Cs, Br, and Pb were chosen as the only elements for quantification (C Ka and Si Kb lines are visible in the EDS spectra at 0.28 keV and 1.74 keV, respectively, coming from the substrate). Cs L, Br K, and Pb L lines were used for the quantification. Quantification of the EDS spectra was performed using a built-in standardless ZAF quantification method. The resulting sample composition was determined to be: **Cs**, 33.4±0.9 at.%, **Pb**, 12.3±0.2 at.%, **Br**, 54.3±0.8 at.%.

The average sample stoichiometry could be expressed as $Cs_{334\pm9} Pb_{123\pm2} Br_{543\pm8}$ (just multiplying % fractions by 10 to get integer numbers of atoms), that can be separated into a number of formula units $(Cs_4PbBr_6)_{83}$ plus excess species $(Pb^{2+})_{40}$ and $(Br^-)_{45}$, assumed to be ions in their standard oxidation states. That composition can be further normalized by the number of Cs_4PbBr_6 formula units to yield $(Cs_4PbBr_6)_1$ plus $(Pb^{2+})_{0.48}$ and $(Br^-)_{0.54}$, as mentioned in the main text.
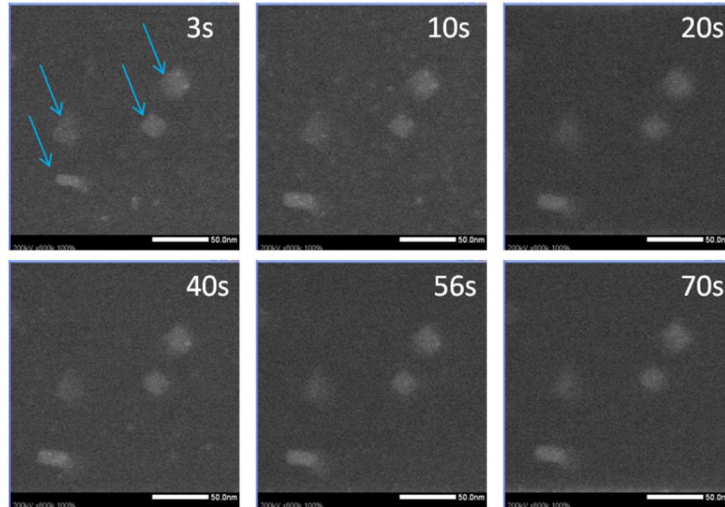
Figure S3. Cs$_4$PbBr$_6$ NCs in solution observed for a total of 70 seconds show no significant changes under the electron beam irradiation (the blue arrows point towards 0D NCs). At the beginning of the irradiation, a nucleation burst is noticeable among the NCs, which disappeared and did not grow into larger particles under further irradiation. The smaller bright spots scattered around might be small metastable Pb^0 nanoparticles.
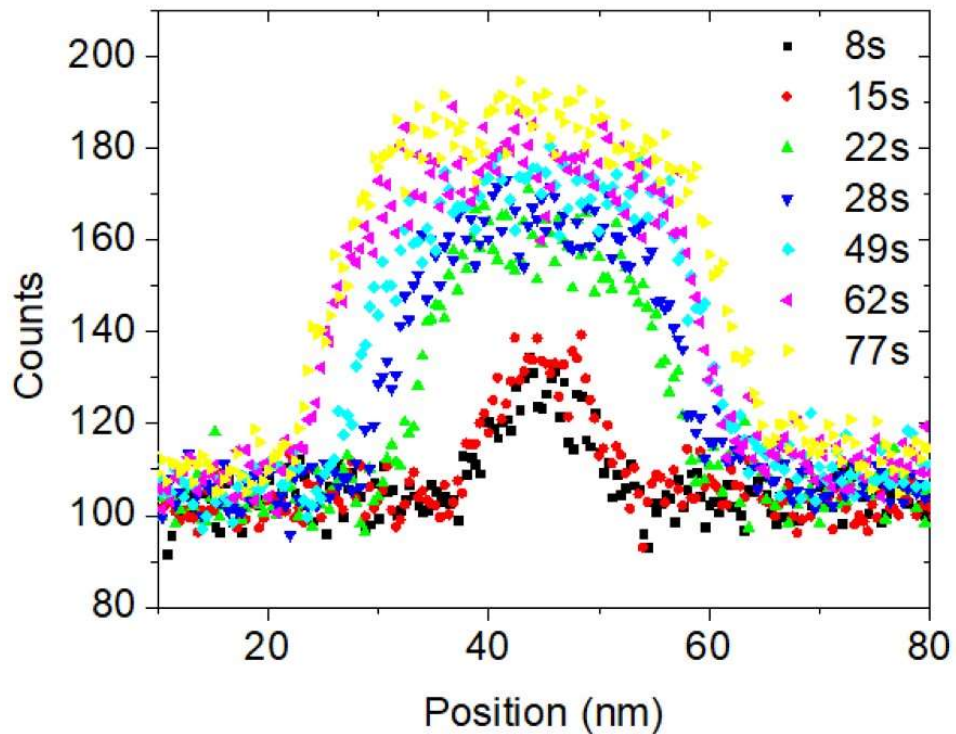

Figure S4. Intensity profile across particle 1 of **Figure 2a**, indicating a plate-like shape with increasing thicknesses and increasing area over imaging time.
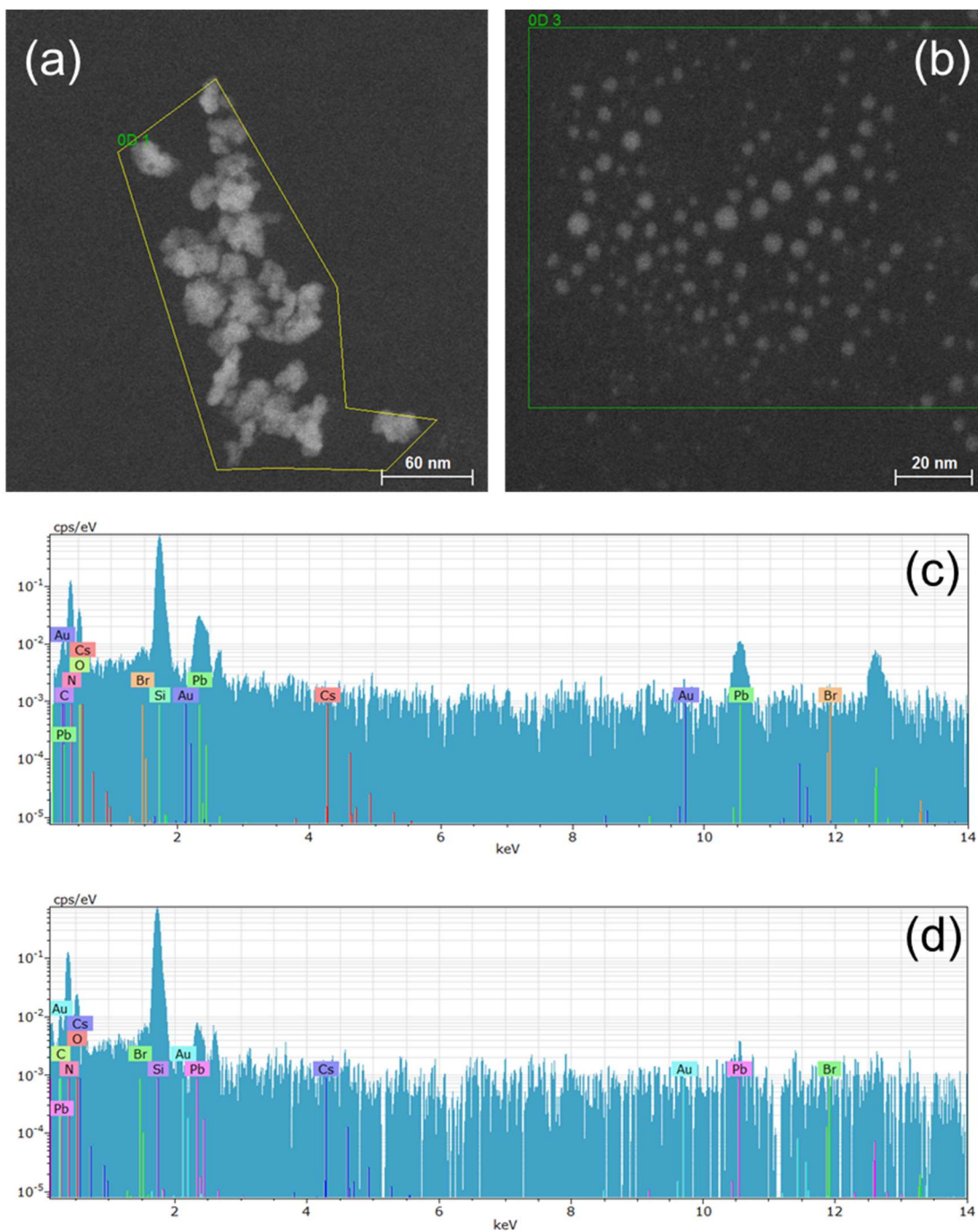
Figure S5. HAADF-STEM images (a, b) and corresponding EDS analysis (c, d) of two regions with Pb^0 particles after breaking the cell. The yellow and green regions of interest in a and b indicated the areas from which the EDS spectra in c and d were collected, respectively.
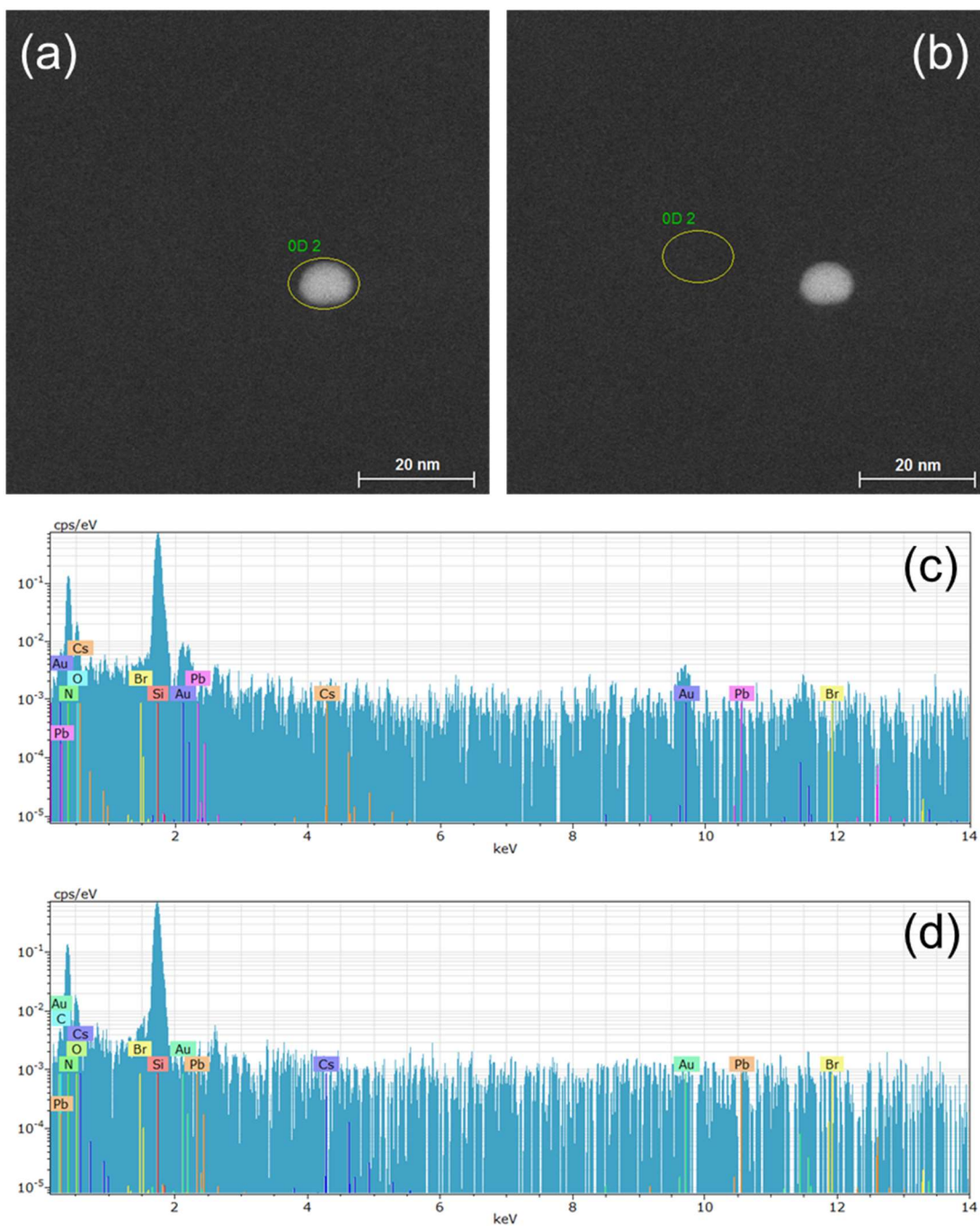
Figure S6. HAADF-STEM image (a, b) and an EDS analysis (c, d) of the sample region containing Au^0 particle after breaking the cell. The yellow region of interest circle indicates the area where EDS spectra were collected from (nanoparticle in a, and background in b).