Supplementary Information

Tunable Plasmon Resonance of Molybdenum Oxide Nanoparticles Synthesized in Non-aqueous Media

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Experimental

Materials.

Molybdenum dioxide bis(acetylacetonate) ($MoO_2(acac)_2$, Sigma-Aldrich) was used as a source of molybdenum oxide. 1-Octadecene (ODE, 90%, Wako Pure Chemical Industries), oleic acid ($C_{18}A$, 90%, Sigma-Aldrich), decanoic acid ($C_{10}A$, 99%, Wako) and octanoic acid (C_8A, 98%, Wako) were used as solvents for synthesis and capping agents for the nanoparticles (NPs). Methanol (99.8%, Wako) was used in purification processes. Hexane (96%, Wako), toluene (99%, Wako) and cyclohexane (99.7%, Wako) were used as solvents for the synthesized NPs.

Synthesis of molybdenum oxide nanoparticles.

MoO_2 and MoO_{3-x} NPs were synthesized as follows. $MoO_2(acac)_2$ (0.03 mmol) was added to a fatty acid (FA; $C_{18}A$, $C_{10}A$ or C_8A) or its mixture with ODE in a test tube. The total amount of the liquid was fixed as 2 mL. The compositions are listed in the table in Fig. 1b. The gas phase in the sealed test tube was replaced with nitrogen using the Schlenk technique. Then, the sealed test tube was heated to 50 °C for 5 min and stirred for 1 h at 200 °C to grow molybdenum oxide NPs. For the optical spectrum measurements for Fig. 1, the obtained solution was transferred to a centrifuge tube and 6 mL of toluene was added to the solution for centrifugation at 5500*g* for 1 min. The precipitates were removed by filtration. A 50-μL aliquot of the solution was diluted with 1 mL of toluene and was subjected to the measurement. For analyses in Fig. 2, as-prepared solution (3 mL) was transferred to a centrifuge tube and 6 mL of methanol and 100 uL of toluene were added for centrifugation at 8500*g* for 10-15 min. The synthesized NPs in the precipitate were further purified by repeating the procedure two more times. The product thus obtained was vacuum dried for 1 h before re-dispersion in desired solvent (typically toluene, 2 mL).

Characterization.

X-ray diffraction (XRD) patterns were collected using a Rigaku RINT-2100 instrument. The morphology of MoO_2 and MoO_{3-x} NPs were observed by transmission electron microscopy (TEM) performed on a JEOL JEM-2010F microscope with an acceleration voltage at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Phi Quantera SXM. LSPR optical spectra was measured using a Jasco V-670 absorption spectrophotometer.

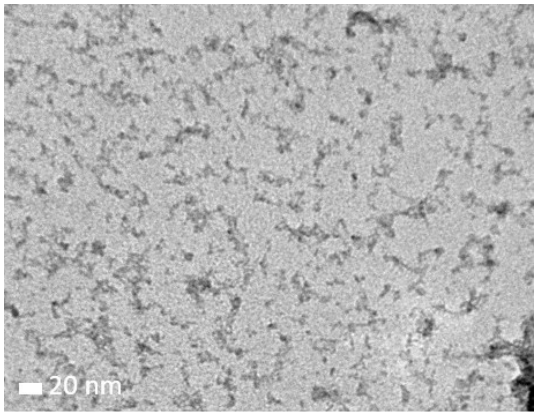

Fig. S1 TEM image of NP #7.

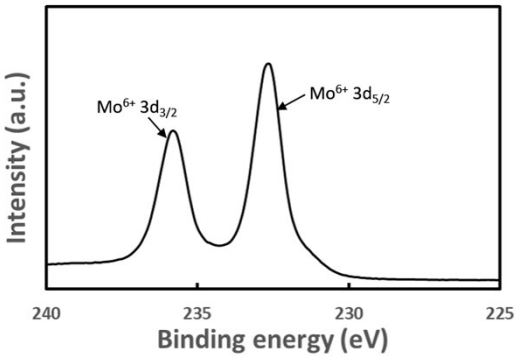

Fig. S2 Mo 3d XPS spectrum of MoO_2 NPs (NP #4) after annealing at 300 °C in air for 3 h.