

Electronic Supplementary Information

Low-temperature Benchtop-synthesis of All-inorganic Perovskite Nanowires

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Chemicals:

All reagents were of relatively high-purity. The PbBr₂ (trace metals basis, 99.999%), CsBr (anhydrous, 99.999%), oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH, technical grade, 90%) and toluene (anhydrous, 99.8%) were purchased from Aldrich. The N,N-Dimethylformamide (DMF, anhydrous, 99.8%) was purchased from Alfa- Aesar and the oleylamine (CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂, approximate C18-content 80-90%) from ACROS Organics. The oleic acid has been degassed for 1 hour under vacuum at 100°C and stored in the GloveBox. All the reagents were stored and handled under argon atmosphere in a glove box (MBRAUN, UNILab).

Low-temperature synthesis of the all-inorganic perovskite nanowires:

In a typical synthesis, a stock solution of PbBr₂ (0.4mmoles) and CsBr (0.4 mmoles) in 10 ml of anhydrous DMF was prepared in a sealed vial closed under Ar in protective atmosphere of a GloveBox. The solution let under stirring until the dissolution of the precursors. Then 1 ml oleic acid (OA) and 0.5 ml oleylamine (OLAm) were added in the above solution. 0.9 ml of this solution was added rapidly in 10 ml of anhydrous toluene (10ml) in a sealed vial under vigorous stirring (1000 RPM). This vial was placed in ice before the addition of the stock solution. Then, 40 ml of cooled anhydrous toluene added to the solution for quenching. All the syntheses were carried out on the bench, at 0°C without using Schlenk line and continuous Ar flow. The colloidal toluene-based solution removed from the ice and let at room temperature without stirring. A white precipitated product is observed after one day. The NWs colloidal solution is the supernatant. No further treatment or purification process is required for the characterization experiments.

Characterization methods:

Structural characterization:

Transmission Electron Microscopy (TEM): Low magnification and high-resolution TEM images were recorded on a LaB6 JEOL 2100 transmission electron microscope operating at an accelerating voltage of 200 kV. All the images were recorded by the GatanORIOUS TM SC 1000 CCD camera. For the purposes of the TEM analysis, a drop of the as-prepared toluene-based solution was deposited onto a carbon-coated copper TEM grid and then the solution let to evaporate. Statistical analysis was carries on several HRTEM images, with the help of dedicated software (Gatan Digital Micrograph). For each sample, about 150 individual NWs were counted up. The structural features of the NWs were studied FFT patterns obtained from the HRTEM images.

X-ray Diffraction (XRD). Powder X-ray diffraction (XRD) studies were performed on a Rigaku D/MAX-2000H rotating anode diffractometer with Cu K α radiation, equipped with a secondary graphite monochromator. The XRD data at room temperature were collected over a 2 θ scattering range of 10–40°, with a step of 0.02° and a counting time of 10 s per step. Many drops of the as-prepared toluene-based solution was deposited onto a glassy sample holder and then the solution let to evaporate.

Optical properties characterization:

Optical Absorption Spectroscopy: The colloidal solutions after quenching with the cooled toluene were placed in quartz cuvettes without further dilution. The UV-Vis absorption spectra were collected at room temperature on a Perkin Elmer, LAMBDA 950 UV/VIS/NIR spectrophotometer.

Laser-Induced Fluorescence (LIF) spectroscopy: The colloidal solutions after quenching with the cooled toluene were placed in quartz cuvettes without further dilution. They were placed on a X-Y stage and the PL spectra were recorded at room temperature upon laser irradiation for the excitation of the samples. For sample excitation, a KrF excimer nanosecond laser, operating at 248 nm has been utilized. The pulse duration was about 20 ns, the excitation energy ~ 0.5 mJ and the laser beam diameter 3.6 mm (Fluence ~ 5 mJ/cm²). The fluorescence measurements were performed at room temperature and recorded by an Andor Technology Mechelle 5000 spectrograph which is connected with an Andor iStar 734 Series, time resolved, cooled and Intensified Charge Coupled Device (ICCD). The fluorescence signal of the samples was collected and guided to the spectrograph by an optical fiber.

Crystal structures Visualization: The crystal structure in the Figure S6 is prepared using *Diamond 3.0* software.¹

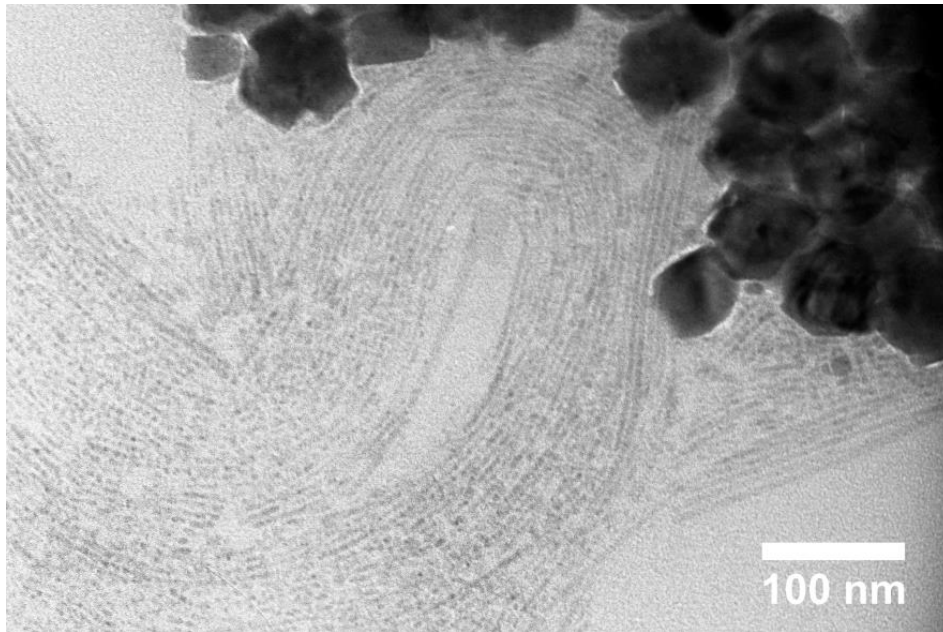


Fig. S1 Low- magnification TEM image of the mixed particle colloidal solution (discontinuous nanowires and nanoplatelets) immediately after the quenching with the cooled toluene.

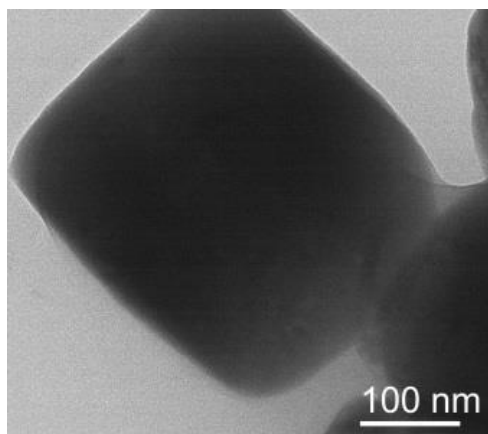


Fig. S2 Low- magnification TEM image of the particles when the whole synthesis is carried out room temperature. The image is taken after 7 days in the toluene-based solution.

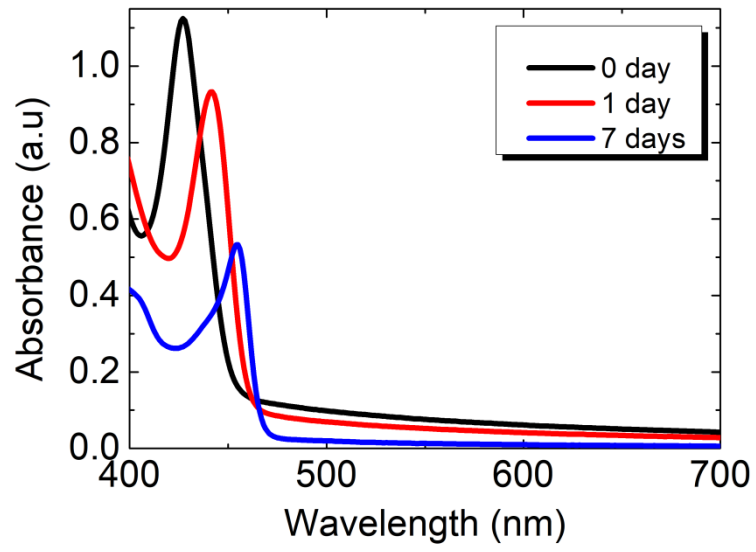


Fig. S3 UV-Vis absorption spectra of NWS' solution at different times after let the solution at room temperature without stirring.

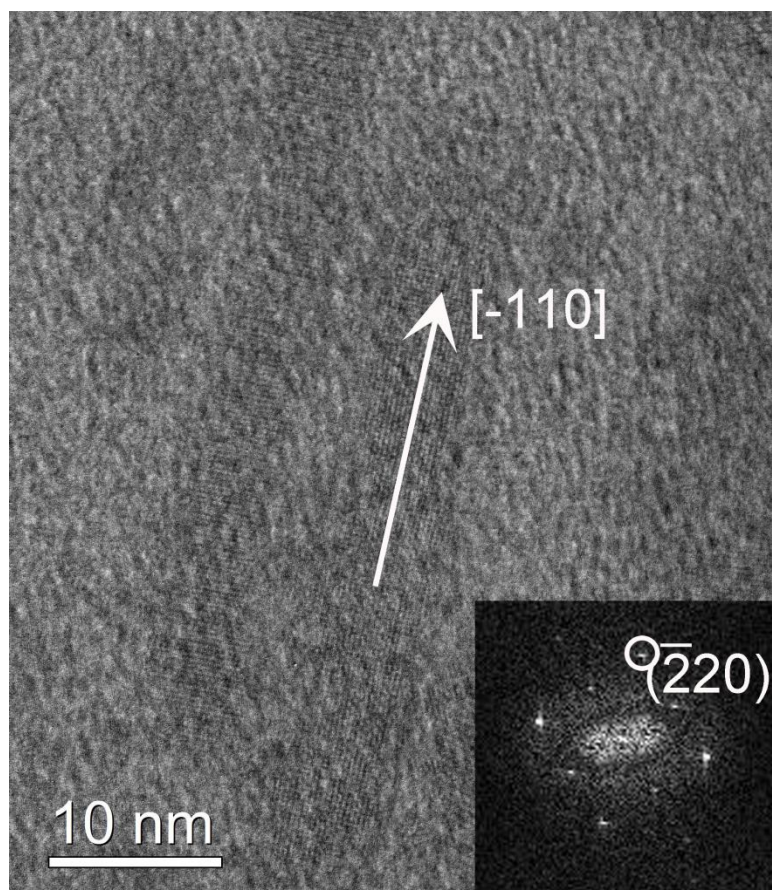


Fig. S4 HRTEM image (a) and corresponding FFT pattern (b) from small nanorods presented at the toluene-based colloidal solution at low temperature (directly after the addition of the stock precursor solution). The corresponding FFT pattern is calculated for an individual nanorod. The indexing has been performed according to the reference pattern of the orthorhombic structure of the CsPbBr_3 (ICSD, #97851).

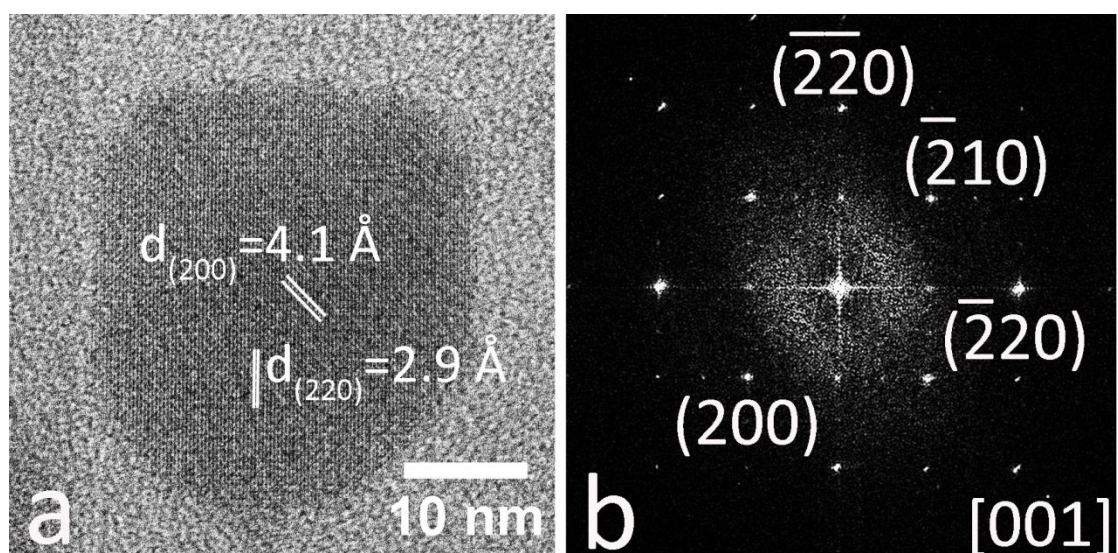


Fig. S5 HRTEM image (a) and corresponding FFT pattern (b) calculated from a thicker nanorod presented at the toluene-based colloidal solution at low temperature (directly after the addition of the stock precursor solution). The indexing has been performed according to the reference pattern of the orthorhombic structure of the CsPbBr_3 (ICSD, #97851).

Electron beam-induced phase transformation-degradation process

A thick NW, with a lot of small nanocrystals grown on it, is selected in order to have distinct reflections from the perovskite crystal structure and the possible reflections from a second material. Small Pb nanocrystals (darker contrast in the TEM images) are grown along the NWs due to the degradation of the NWs from the electron-beam irradiation through the TEM experiment.

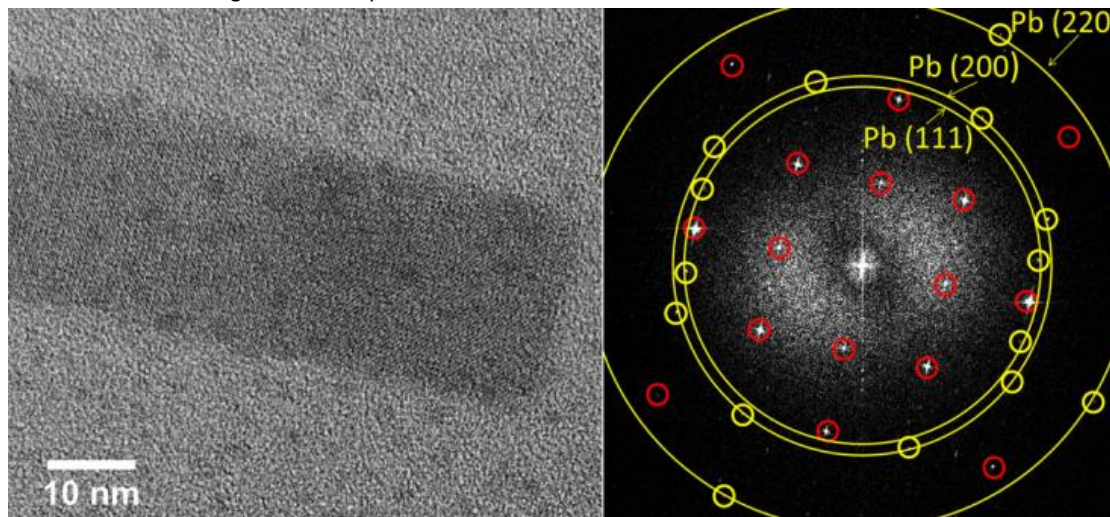


Fig. S6 HRTEM image and corresponding FFT pattern of the all-inorganic lead halide degraded NW from the electron-beam irradiation. The reflections indicated with the red circles are corresponded to the orthorhombic structure of the CsPbBr₃ (ICSD, #97851) while those with yellow circles to the fcc cubic structure of the metallic Pb (PDF, #04-0686).

Table S1. Optical parameters and NWs growth.

Time after reaction (days)	Absorbance peak position (nm)	PL peak position (nm)	PL FWHM (nm)
0	427	445	23.7
1	441	454	22.6
7	454	462	16.2

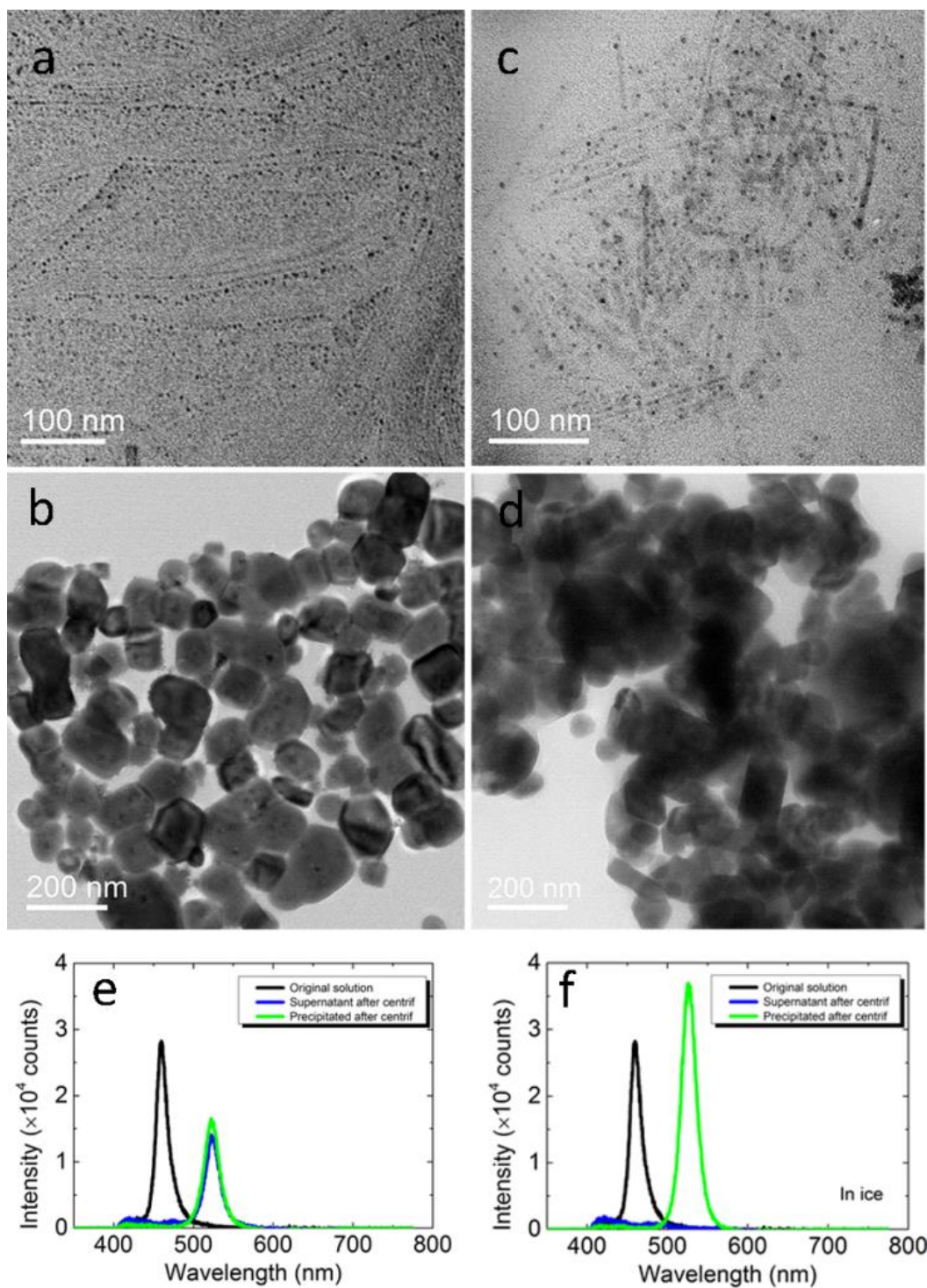


Fig. S7 Low-magnification TEM images and PL measurements of the supernatant and precipitated particles after centrifugation of the original solution (NWs and platelets) (a, b, e) and when the centrifugation done at low temperature (c, d, f).

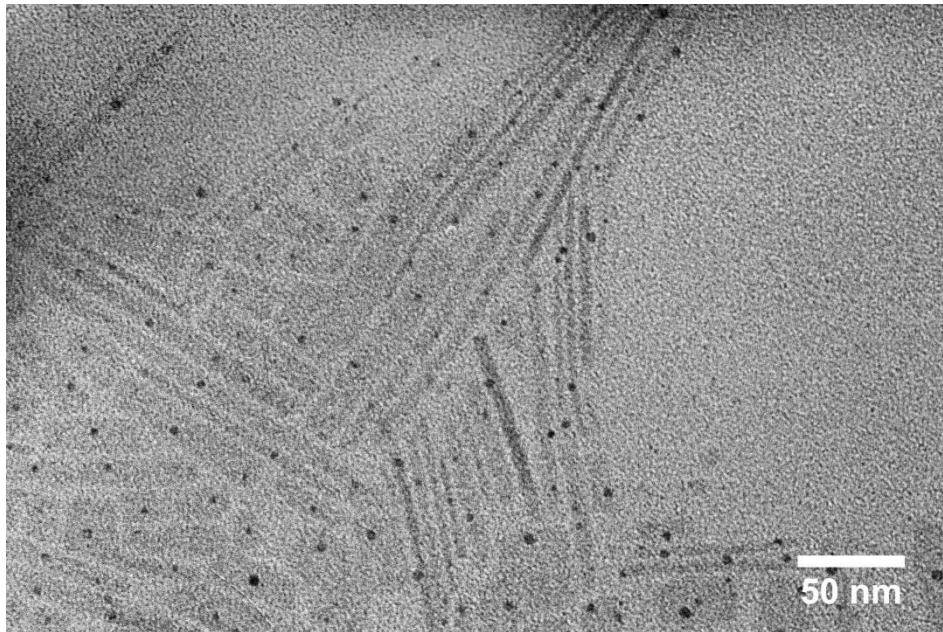


Fig. S8 Low-magnification TEM images of the NWs remained at supernatant after the centrifugation process.

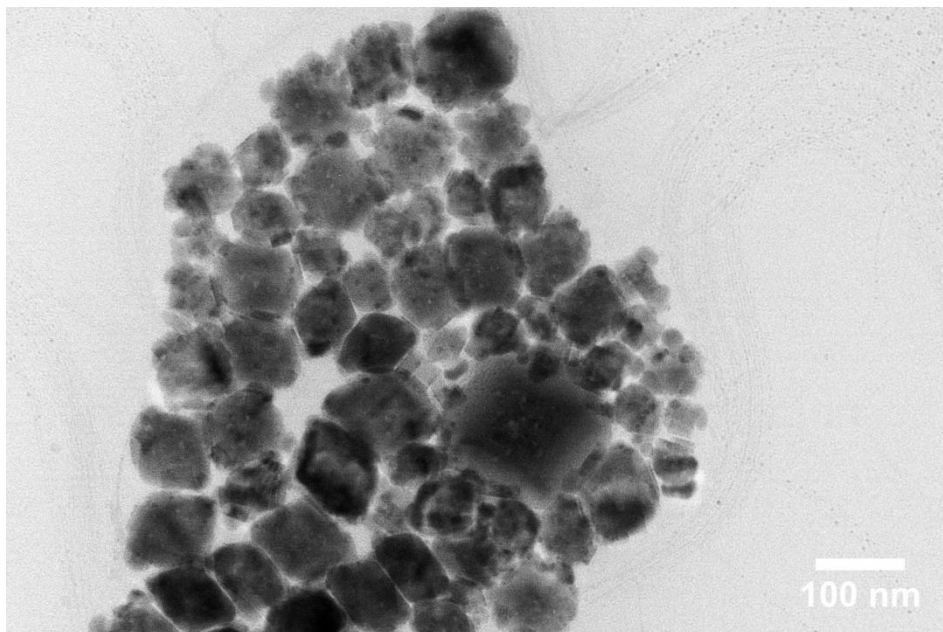


Fig. S9 Low magnification TEM images of larger particles remained in the supernatant after the centrifugation process.

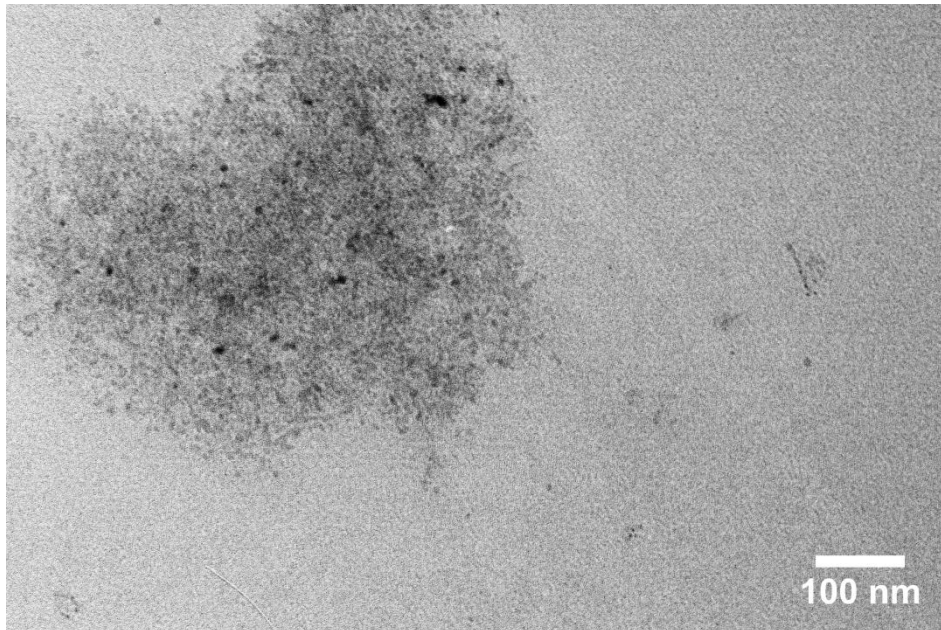


Fig. S10 Low magnification TEM images of small particles remained in the supernatant after the centrifugation process.

1. Diamond - Crystal and Molecular Structure Visualization, Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, <http://www.crystalimpact.com/diamond>.