

ELECTRONIC SUPPLEMENTARY INFORMATION

Luminescent Silver Nanoclusters Decorated on ZnO Tetrapods: Detailed Understanding of Their Role on Photoluminescence Features

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1. Materials

All chemicals were commercially available and used without further purification. Lipoic acid (LA), sodium borohydride (NaBH₄), silver nitrate (AgNO₃), Zn metal powder and polyvinyl butyral (PVB) were purchased from Sigma-Aldrich.

2. Materials synthesis

Synthesis of Ag₂₉(DH₁₂)₁₂ nanoclusters (AgNCs)

19 mg lipoic acid (LA, 92 μmol) and 7 mg NaBH₄ (0.19 mmol) were combined in 14 mL milliQ water and kept under constant stirring until the LA was fully dissolved ¹. Then, 700 μL 25 mM AgNO₃ (17.5 μmol) was added, followed by a colour change from clear to turbid, bright yellow. The freshly prepared solution of 10 mg NaBH₄ (0.26 mmol) in 2 mL water initiates the nanocluster formation, which occurs during stirring for further 3-5 h. Coverage of the vial with aluminium foil reduced the exposure to light to a minimum during the reaction at room temperature. Samples were stored in the dark at 4 °C.

Synthesis of ZnO Tetrapods

ZnO Tp were synthesized via flame transport synthesis (FTS). A detailed description of the flame transport synthesis process and its modified variant are available in previous works ²⁻⁵. In brief, Zn metal powder (diameter around 5 μm) was mixed with polyvinyl butyral powder (PVB) in the weight ratio of 1:2 as the primary precursor material. The mixture was filled in a ceramic crucible and then mounted in a muffle furnace heated to 900 °C for 30 minutes. The transformation of Zn metallic particles into ZnO tetrapods directly occurred in the flame inside the furnace. Due to high temperature, the Zn metallic particles were directly converted into atomic vapour. The growth of tetrapodal structures took place with the help of native oxygen, in a self-controlled process by the flame itself. The temperature, amount of precursor material, and oxygen content were the main controlling parameters for the aspect ratio of one-dimensional (1D) arms in the tetrapods. A modified variant of the flame approach was used to synthesize the ZnO tetrapods with excellent nanoscopic arms in the present case. After 30 minutes, the furnace was cooled normally. Then the cotton-like fluffy tetrapod powder was harvested, which was then used as backbone here for the decoration of ultra-small AgNC.

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Synthesis of AgNC@ZnO Tp hybrid

For the preparation of the AgNC@ZnO Tp hybrid material, 4 mL AgNC solution were placed in the top of a 3 kDa centrifugal filter and centrifuged in sets of 2:30 min at 9000 rpm at 20 °C until the volume is reduced to 500 μ L. In between the centrifugation steps, AgNC on the filter walls were resolubilized with a pipette (200 μ L). In a 2 mL Eppendorf tube, ZnO tetrapods were incubated in the 500 μ L concentrated AgNC solution for 5 h under constant shaking. Then, the supernatant was removed and the composite was dried to remove the remaining solvent.

3. Instrumental details

Confocal laser scanning microscopy was performed on a Zeiss LSM 510 Meta equipped with a Diode (405 nm), primary dichroic beam splitter (Hauptfarbteiler) 405/488, secondary dichroic beam splitter (Nebenfarbteiler) 545, and a Long pass filter (Langpassfilter) 615. Images under UV irradiation were collected in the BioDocAnalyze Biometra from Whatmann. For the centrifugation filtration, an Amicon Ultra-4 3 kDa cut-off centrifugal filter with a PLBC Ultracel-PL membrane was used in a Hettich Universal 320R centrifuge.

4. Transmission electron microscopy

All samples were dispersed on copper TEM grids (Plano GmbH) with lacy carbon film for TEM investigation at a Tecnai F30 STwin G² with 300 kV acceleration voltage. For atomic-number-dependent Z-contrast, the samples were investigated in high-angle annular dark-field (HAADF)-STEM mode. Energy dispersive X-ray (EDX) measurements are performed with a Si/Li detector (EDAX System).

5. Optical characterization of ZnO Tp, AgNC, and AgNC@ZnO Tp

Raman spectroscopy

Room temperature (RT) micro-Raman spectroscopy measurements were performed on a Horiba Jobin Yvon HR800 spectrometer equipped with a 600 gr mm⁻¹ grating, under the incidence of the 2.8 eV/442 nm line from a cw He-Cd laser (Kimmon IK Series) in backscattering configuration. The spectra were acquired using an objective of 50 \times magnification and neutral density filters (ND) were used to control the excitation density.

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RT excitation-density dependent PL

Steady-state PL measurements were performed using the 3.81 eV/325 nm line from a cw He-Cd laser (Kimmon IK Series) with a beam spot of ~ 1 mm and an excitation power density below 0.6 W cm^{-2} . For a comparison of the excitation density conditions, a 450 Xe lamp was also used. Additionally, the AgNC@ZnO Tp sample was also excited with the 2.8 eV/442 nm laser line of the same He-Cd laser. All the PL experiments were carried out under a 90° geometry. The luminescence was measured using a dispersive system SPEX 1704 monochromator (1 m , 1200 gr mm^{-1}) fitted with a water-cooled Hamamatsu R928 photomultiplier tube. All samples were investigated under the same excitation/detection conditions. During power-dependent steady-state PL, the excitation density was controlled by using neutral density filters.

RT PL excitation (PLE) experiments were conducted in a Fluorolog-3 Horiba Scientific set-up with a double additive grating Gemini 180 monochromator (1200 gr mm^{-1} and $2 \times 180 \text{ mm}$) in the excitation and a triple grating iHR550 spectrometer in the emission (1200 gr mm^{-1} and 550 mm). The same equipment was also used for additional RT PL measurements. A 450 W Xe lamp was used as the excitation source. The PLE was acquired by setting the monochromator to the maxima of the optically active defects that one wanted to study and, afterwards, the excitation was scanned to higher energies.

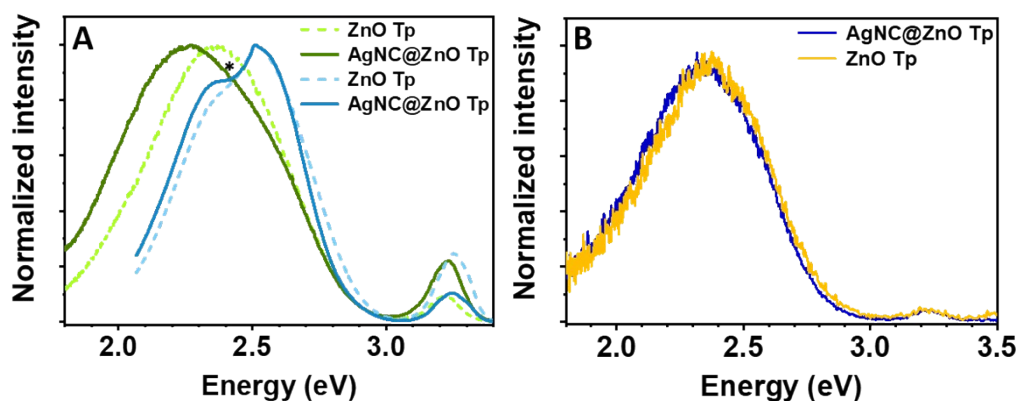


Figure S3. (A) Comparison of the normalized RT PL spectra obtained under 3.8 eV/325 nm excitation, exciting with either the Xe lamp (blue lines) or the He-Cd laser (green lines), for ZnO Tp (dashed) and AgNC@ZnO Tp (solid) samples. The asterisk denotes an artefact of the measurement system. The spectra were also obtained in two different measurement equipment, according to the type of excitation source. (B) Comparison between the normalized spectra obtained with the same excitation energy and acquired with 1% of the nominal laser power for the ZnO Tp and AgNC@ZnO Tp samples.

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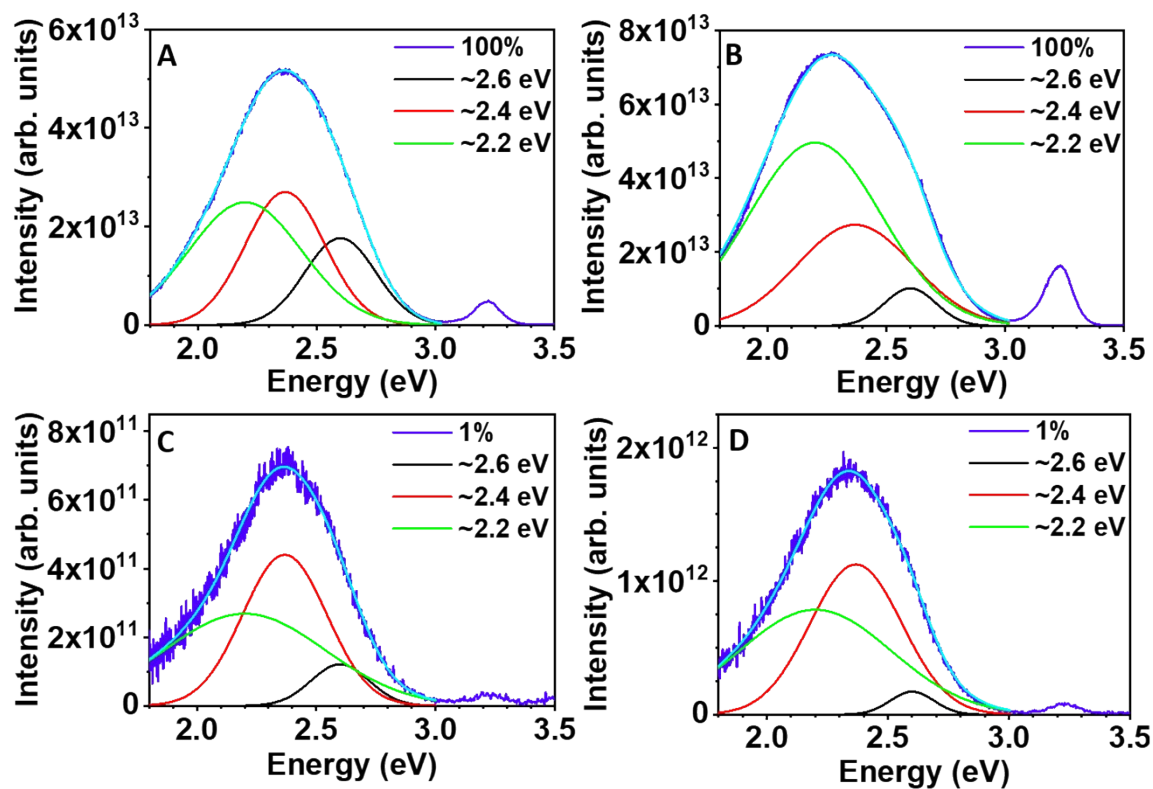


Figure S4. PL spectra acquired at RT for ZnO Tp (A) and AgNC@ZnO Tp (B) under 3.81 eV/325 nm laser excitation at 100 % density. (C) and (D): the same as in (A) and (B) for 1 % laser density. The fitting curve (light blue) resulted from the convolution of 3 Gaussian functions peaked at ~2.6 eV (black), ~2.4 eV (red), and ~2.2 eV (green), for both samples.

RT time-resolved PL

RT time-resolved PL (TRPL) spectra were acquired with the same Fluorolog-3 system using a pulsed Xe lamp (operating at up to 25 Hz) coupled to the same monochromator and with the excitation fixed at 3.81 eV/325 nm. The full width at half maximum (FWHM) of each lamp pulse was 3 μ s, so that lamp interference during the acquisition of decay curves is minimized. The measurement conditions were set to a sample window (duration of signal acquisition) of 10 ms, with 20 ms of time per flash (reciprocal of the repetition rate of the lamp pulses) and a flash count (number of lamp pulses contributing to each data point) of 200. Several time delays after flash were employed from 0.05 to 1 ms.

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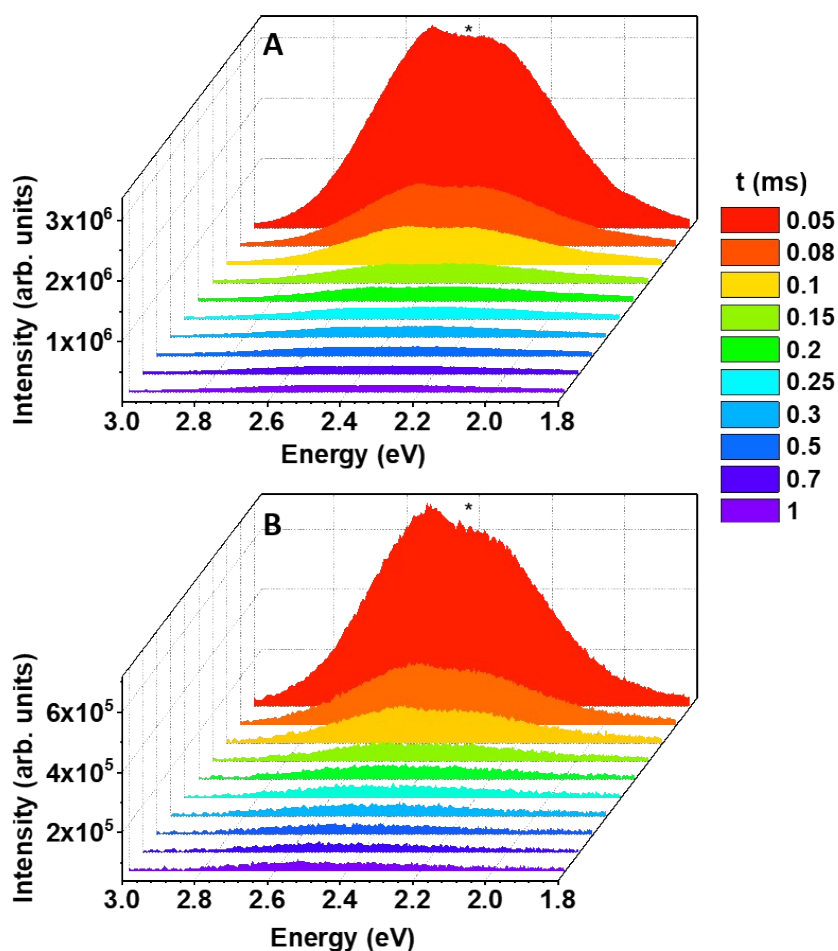


Figure S5. RT TRPL spectra with increasing delay times under 3.81 eV/325 nm excitation for ZnO Tp (A) and AgNC@ZnO Tp (B). The asterisk denotes an artefact of the measurement system.

Temperature-dependent PL

For the temperature-dependent measurements from 11 K to RT, the samples were placed in a cold finger He cryostat and the temperature was controlled from low to room temperature. The luminescence was measured using a dispersive system SPEX 1704 monochromator (1 m, 1200 gr mm⁻¹) fitted with a water-cooled Hamamatsu R928 photomultiplier tube and the samples were excited with the 3.81 eV/325 nm line of the He-Cd laser.

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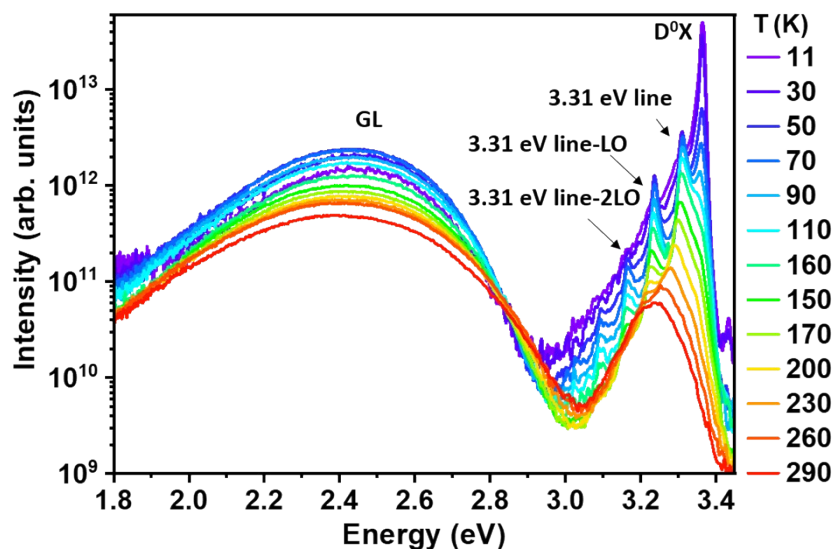


Figure S6. UV-Vis temperature-dependent PL study performed on the ZnO Tp sample excited with 3.81 eV/325 nm.

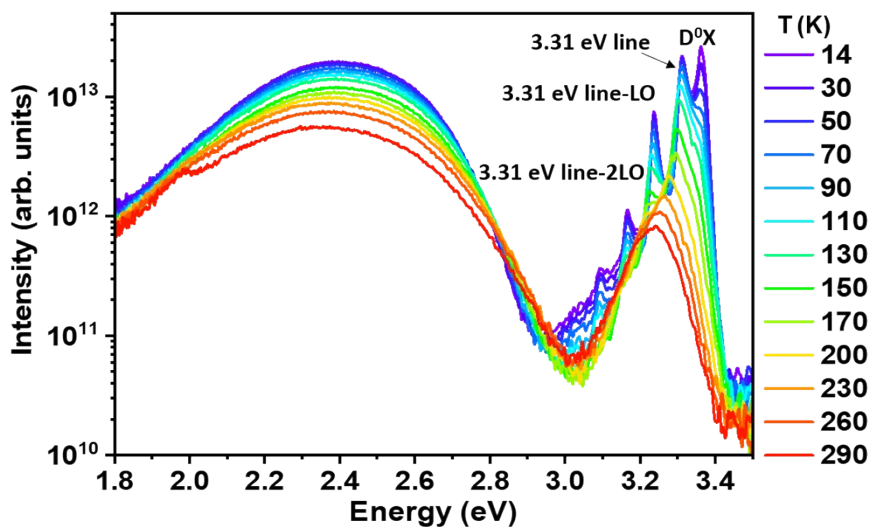


Figure S7. UV-Vis temperature-dependent PL study performed on the AgNC@ZnO Tp sample excited with 3.81 eV/325 nm.

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