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Shape Control of Colloidal Mn Doped ZnO Nanocrystals and Their Visible Light Photocatalytic Properties

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Figure S1. Overview TEM image of the as-synthesized Mn doped ZnO tetrapods obtained from the 10%Mn reaction, highlighting the high yield and quality of Mn doped ZnO tetrapods.



Figure S2. Additional HRTEM image of the branching arm from the 10%Mn doped ZnO tetrapods, showing the hexagonal WZ structure of the arm elongating along its [0001] direction.



Figure S3. (A) Image processing of atomic resolution TEM result for the central region of a 10%Mn doped ZnO bipod, more clearly showing the atomic structure of the ZB core and WZ branching arms. (B) and (C) Corresponding fast Fourier transform (FFT) patterns for the up-right branching arm and the core region in (A), respectively.



Figure S4. Typical UV-vis (A), EDX (B), TEM image (C) and HRTEM image (D) of initial growth seeds for 10%Mn doped ZnO tetrapods, respectively. The aliquots of Mn doped ZnO NCs were extracted at 2-3 min and carefully purified to remove the remaining precursors and solvent. The presence of Mn dopants in the initial growth seeds were supported by the UV-vis and EDX results. EDX analysis indicated that Mn dopants had been incorporated into the initial seeds with a concentration of *ca.* 6 at.%. Note that a sequence of stacking faults is observed at the arm/core interface regime even within the initially formed growth seeds, as indicated by the arrows.



Figure S5. (A) An enlarged HRTEM image and (B) corresponding atomic arrangements of the left branching arm in Figure 1A with a sequence of stacking faults observed at the arm/core phase interface. The yellow balls represent metal atoms in the lattices.



Figure S6. (A) TEM image of pure ZnO faceted NPs with size of *ca*. 15 nm obtained under similar reaction conditions for 8 min, inset showing the corresponding HRTEM image of ZnO faceted NPs with hexagonal WZ phase; (B) TEM image of ZnO faceted NPs with size of *ca*. 20 nm obtained under similar reaction conditions for 60 min.



Figure S7. (A) and (B) Image processing of atomic resolution TEM results for 10%Mn doped ZnO spherical NPs, viewed from different directions: (A) along the [2-1-10] zone axis, and (B) nearly parallel to the [0001] zone axis, respectively.



Figure S8. Representative SAED pattern for an ensemble of Mn doped ZnO NPs from the 10%Mn reaction, revealing the only hexagonal WZ phase of Mn doped ZnO NPs.



Figure S9. (A) and (B) Tauc plots from the UV-vis spectra to determine the optical band gaps of Mn doped ZnO tetrapods and NPs with different Mn doping concentrations, respectively. (C) Optical band gaps of Mn doped ZnO NCs with different Mn doping concentrations and reaction times. Pure ZnO NPs are included for comparison.



Figure S10. (A) XRD spectrum of MnO NPs synthesized at similar reaction conditions at *ca*. 290°C for 1 h. (B) TEM image of MnO NPs with size of *ca*. 10 nm (inset, enlarged image). (C) UV-vis spectra of purified ZnO NPs, MnO NPs, mixture of ZnO and MnO NPs, 10%Mn doped ZnO NPs and 2%Mn doped ZnO NPs, showing no obvious visible light absorption in the range of 380-500 nm, consistent with the wide band gaps of bulk ZnO and MnO (*ca*. 3.4 and 4.2 eV, respectively). When Mn dopants were introduced into ZnO NCs, even 2% in the precursors, a broad absorption band in the range of 380-500 nm appeared.



Figure S11. (A) UV-vis spectra and corresponding photographs (inset) of purified 10%Mn doped ZnO tetrapods before (a) and after (b) filtration with 0.22 μ m PTFE filter, (B) UV-vis spectra and corresponding photographs (inset) of purified 10%Mn doped ZnO NPs before (a) and after (b) filtration with 0.22 μ m PTFE filters.



Figure S12. Schematic drawing of substitutional Mn^{2+} ions in the tetrahedral coordination of ZnO

WZ structure.



Figure S13. (A) EPR spectra of Mn doped ZnO NCs at room temperature (300 K), (B) EPR spectra of Mn doped ZnO NCs at 100 K.



Figure S14. EDX analyses of Mn doped ZnO tetrapods (A) and NPs (B) from the 10%Mn reactions, both confirming the presence of elements Zn, Mn and O only. The Cu and Si signals come from the copper TEM grid and EDX detector, respectively.



Figure S15. (A-C) XPS spectra of Mn doped ZnO tetrapods from the 10%Mn reaction: (A) survey scan, (B) Mn 2p core level, and (C) Zn 2p core level; (D-F) XPS spectra of Mn doped ZnO NPs from the 10%Mn reaction: (D) survey scan, (E) Mn 2p core level, and (F) Zn 2p level. Detailed analyses of the Mn and Zn core levels suggest that the Mn and Zn are in the +2 oxidation states in both samples.



Figure S16. Photographs of the reaction solutions under *ca.* 290° C with different Mn precursor concentrations in the reagents, showing an obvious color transition of the reaction solution from orange to wine red when the Mn precursor concentration was increased from 5 mol.% to 20 mol.% .



Figure S17. Shape transition of doped ZnO NCs upon heating for *ca.* 1 h under 290°C: (A) ZnO NPs run for 8 min, and (B) ZnO NPs run for 1 h; (C) 5%Mn doped ZnO tetrapods run for 8 min, and (D) 5%Mn doped ZnO NPs run for 1 h; (E) 20%Mn doped ZnO tetrapods run for 8 min, and (F) 20%Mn doped ZnO NPs run for 1 h; (G) Mixture of tetrapods and bullet-shaped nanorods from the 50%Mn reaction run for 6 min, and (H) 50%Mn doped ZnO NPs run for 1 h. When the Mn precursor amount increased and approached 50 mol.%, the synthetic reaction for high-quality tetrapods was much less controllable and most of the products run for 6 min was already turned into bullet-shaped nanorods along with a minority of tetrapods. From the view point of controlled synthesis, we mainly focus on Mn doped ZnO NCs with Mn precursor concentrations in the range of 5-20 mol.% in this work. The TEM images for pure ZnO NPs are also included for comparison.

Table S1. ICP-AAS analysis of Mn doped ZnO NCs from the reactions with different Mn

precursor concentrations in the reagents.

[Mn] in precursors (mol.%)	[Mn] in TPs (at.%)	[Mn] in NPs (at.%)
5	2.88	2.86
10	5.38	4.70
20	11.80	10.00



Figure S18. Photographs of the resulting NCs from the reactions with different Mn precursor concentrations in the reagents, which display various colors depending on the Mn doping concentrations: (A) pure ZnO NPs, (B) 5%Mn doped ZnO tetrapods, (C) 10%Mn doped ZnO tetrapods, and (D) 20%Mn doped ZnO tetrapods. Note that Mn doped ZnO NPs from the same reactions with extended reaction time to *ca.* 1 h typically have similar colors with those of tetrapods.



Figure S19. XRD wide (A) and narrow (B) spectra of pure ZnO and Mn doped ZnO NPs with different Mn precursor concentrations in the reagents, demonstrating that pure ZnO and Mn doped ZnO NPs typically adopt the same hexagonal WZ structure (space group P6₃mc, JCPDS 36-1451). The red lines (bottom) represent the diffraction peaks of bulk ZnO. The (002) diffraction peaks were observed to shift continuously to the low angle side in the spectra with increasing Mn doping level, indicating an increased lattice constants induced by the Mn doping in the ZnO host lattice.



Figure S20. Temporal evolution of the FTIR spectra recorded from the 10%Mn reaction: (A) full spectra; (B) narrow spectra with the region 400-500 cm⁻¹ highlighted to show the evolution of Zn-O bonds at *ca*. 413 cm⁻¹. The C=C stretch at 1641 cm⁻¹ from ODE is selected as the standard, and all the IR spectra are normalized.



Figure S21. (A) and (B) TEM and HRTEM images of the 10%Mn doped ZnO bipods, which are observed from time to time beside the bullet-shaped nanorods. It is evident that the branching arms are readily detached from the main body of tetrapods at the arm/core interfaces.



Figure S22. (A) TEM image of 5%Cd doped ZnO NCs run at 270°C for 6 min, showing that under this reaction condition most of the branching arms have already detached from the main body of tetrapods at the arm/core interfaces. This result was associated with much larger lattice strain induced by Cd doping. (B) HRTEM image of the central region of Cd doped ZnO tetrapods, revealing the presence of stacking faults at the arm/core interfaces. In comparison with Mn doped ZnO tetrapods, the branching arms of Cd doped ZnO tetrapods were almost completely detached in a short time (6 min), under a low reaction temperature (270°C) and a low doping level (5%), reflecting the much larger lattice strain induced by Cd doping, since Cd²⁺ had a much larger ionic radius (0.95 Å) than that of Mn²⁺ (0.80 Å).



Figure S23. (A) TEM image of bullet-shaped nanorods (NRs), along with minor fractions of bipods and tripods, from the 10%Mn reaction run for 15 min. (B) and (C) Histograms showing the distributions of diameters and lengths of the bullet-shaped nanorods, respectively. The arm widths and lengths were determined from TEM images by counting over 300 nanorods. (D) TEM image of spherical NPs, from the 10%Mn reaction run for *ca.* 1 h. (E) Corresponding histogram showing the distribution of diameters of the 300 randomly selected NPs. (F) schematic diagram showing that the NC volume remained nearly constant during the shape transition from bullet-shaped nanorods to spherical NPs.



Figure S24. Variation of Mn doping concentrations in the resulting NCs from the 10%Mn reaction as a function of reaction time. The final Mn doping concentrations in NCs were determined by ICP-AAS with purified NCs taken from the reaction solution.



Figure S25. Temporal evolution of the UV-vis spectra of Mn doped ZnO NCs from the 10%Mn reaction during the synthesis, showing that there was no obvious change in the dopant-related optical features.



Figure S26. TEM images of 10%Mn doped ZnO NCs with additional 0.1 mmol of HSt in the precursors. (A) Mn doped ZnO tetrapods run for 6 min, (B) Mn doped ZnO NPs run for 60 min.



Figure S27. TEM image of the aggregated products from the 10%Mn reaction with additional 0.1 mmol of $MnCl_2$ in the precursors run for 8 min.