Surfactant-free Synthesis of GeO_2 Nanocrystals with Controlled Morphologies (supporting information)

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Experimental

a. Reagents and materials,

Tetraethoxygermane (TEOG, 99.99%) was purchased from Gelest, stored in an argon-filled glovebox and used as received. Ammonium hydroxide (29.3 wt% NH_3 in water) was purchased from Sigma-Aldrich. High-purity DI water (18.2 MΩ/cm) was obtained from a Barnstead Nanopure Diamond purification system.

b. Synthesis,

For a typical synthesis, 100 μL TEOG (0.113 g, 0.45 mmol) was added dropwise with rapid stirring to 1.0 ml of a water/ethanol solution (2-100 vol. % water) of appropriate ammonium hydroxide concentration. A white precipitate forms at rates dependent upon the reaction mixture water content. Stirring was continued for 24 hours to ensure complete hydrolysis and condensation. Finally, the white precipitate was isolated via centrifugation (3000 rpm), washed with anhydrous ethanol (three times), and dried in a vacuum oven at 110 °C for 12 hours.

c. Material Characterization

Electron Microscopy. Bright field Transmission Electron Microscopy **(**TEM) and Energy Dispersive X-ray Spectroscopy (EDX) analyses were performed using a JEOL 2010 (LaB_6 filament) electron microscope with an accelerating voltage of 200 keV. Samples were by drop coating ethanol suspensions of GeO_2 nanoparticles onto carbon-coated 200-mesh Cu grids.

High resolution (HR) TEM images were obtained from Hitachi-9500 electron microscope with an accelerating voltage of 300 kV and were processed using Gatan ImageJ software (version 1.46r). Samples were prepared by drop coating solutions of GeO_2 nanoparticles dispersed in ethanol onto a holey carbon coated copper grid (400 mesh). High-resolution TEM (HRTEM) and Selected Area Electron Diffraction (SAED) were obtained from Hitachi-9500 electron microscope with an accelerating voltage of 300 kV.

Scanning electron microscopy (SEM) images were obtained by using a JEOL 6301F field-emission scanning electron microscope with an acceleration voltage of 5 kV. Samples were prepared by dropcasting GeO_2 nanoparticles from ethanol suspensions onto a clean Si (100) wafer.

X-ray Diffraction (XRD) and FT-IR. XRD was performed using an INEL XRG 3000 X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.54 Å). Crystallinity of all samples was evaluated using mounted on a low-intensity background Si (100) holder. Fourier-Transform

Infrared Spectroscopy (FT-IR) of powders of isolated particles was performed on a Nicolet Magna 750 IR spectrophotometer.

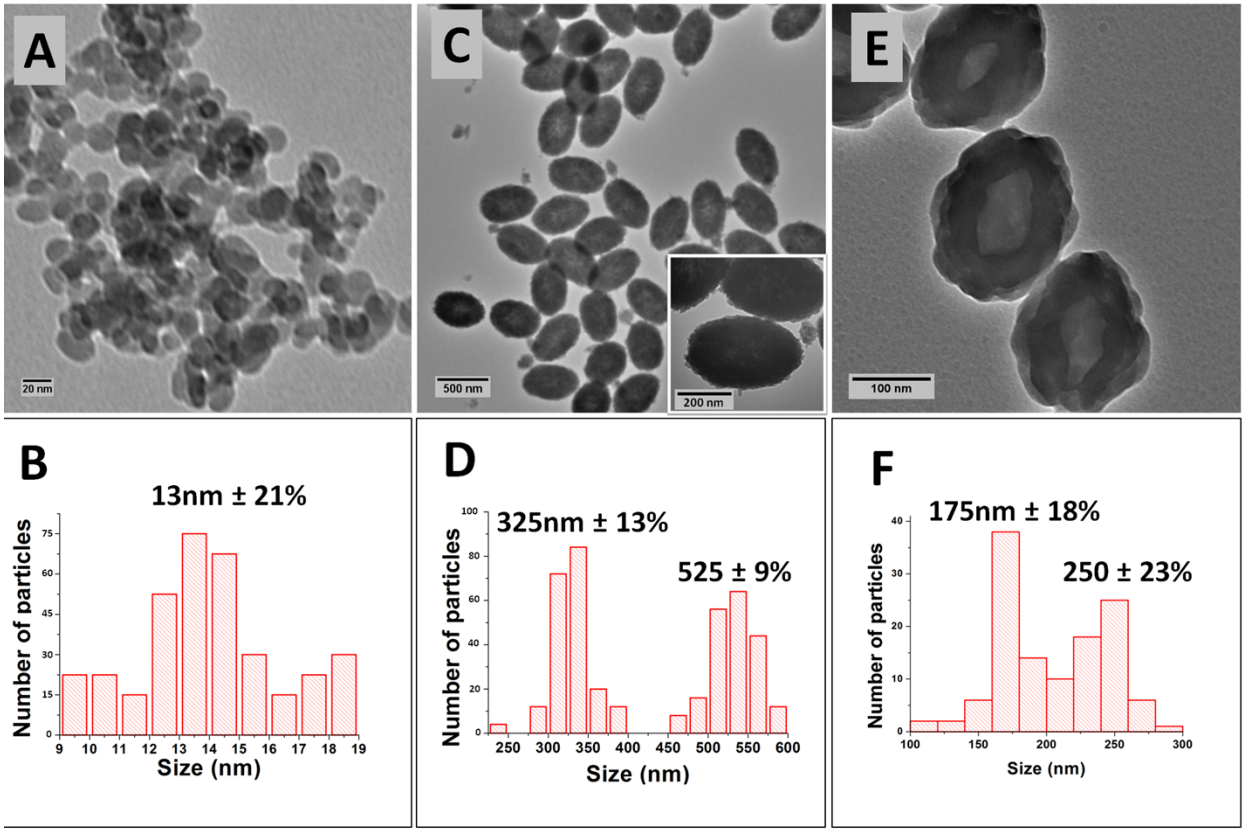

Figure S1. TEM analysis of GeO_2 NPs prepared in different water/ethanol ratios: **A,B)** Pseudospherical NPs (10 vol. % H_2O); **C,D)** Eggs (30 vol. % H_2O), Rough surfaces of GeO_2 eggs (inset) are because of agglomeration of small particles; **E,F)** Spindles (50 vol. % H_2O). Particles size distributions shown in D and F highlight distributions of the widths and lengths of the presented asymmetric GeO_2 eggs and spindles.

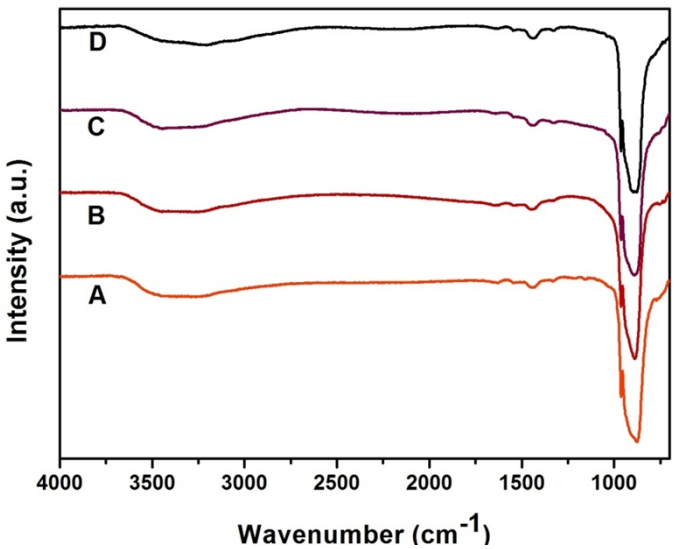

Figure S2. Typical IR spectra of GeO_2 nanoparticles: **A)** nanocubes; **B)** spindles; **C)** eggs; **D)** pseudospherical NPs.

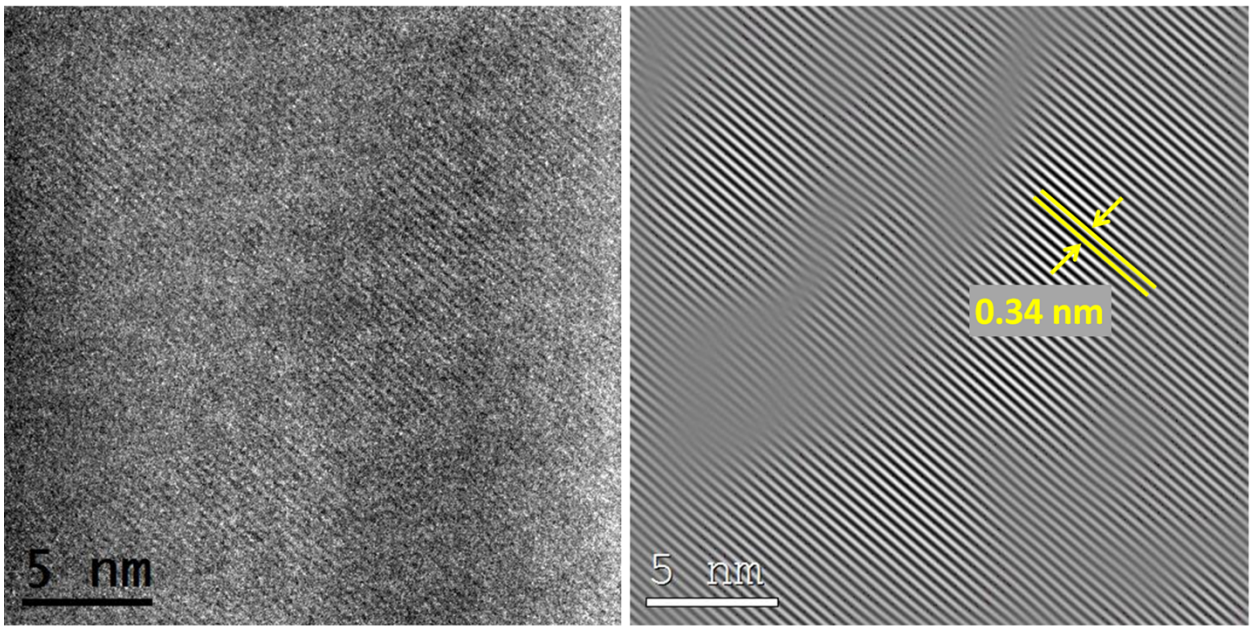

Figure S3. A) High resolution transmission electron microscopy (HRTEM) image of GeO_2 nanocubes; **B)** Fourier transformed image of (A) showing lattice spacing = 0.34 nm consistent with the α-GeO_2 (10-1) and (011)] planes.

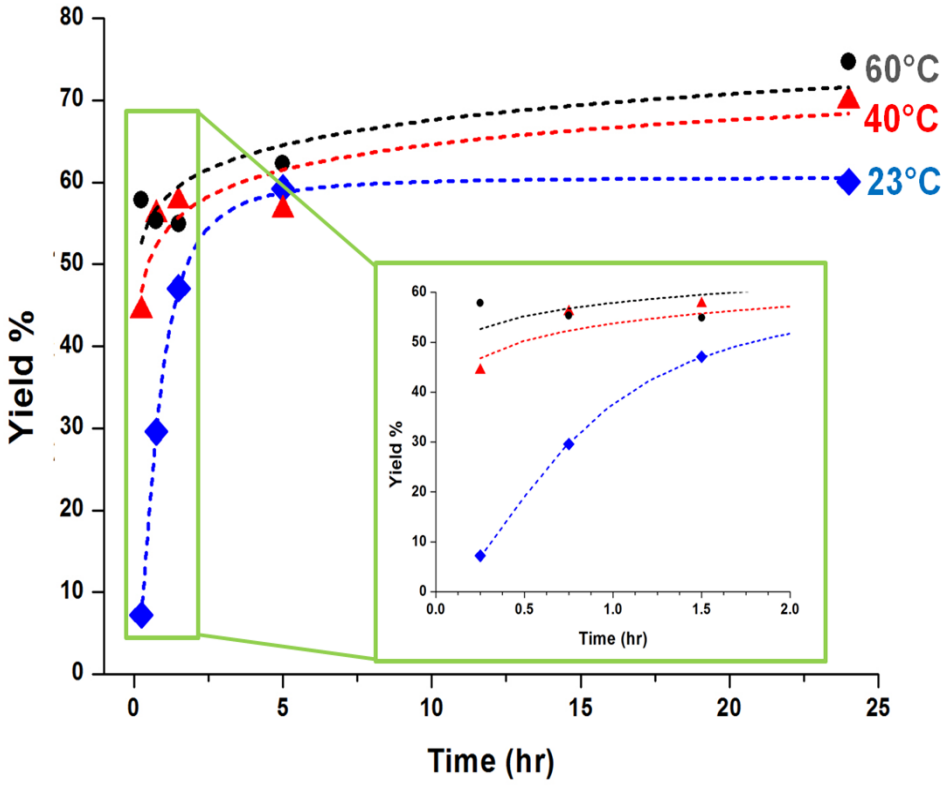

Figure S4. Influence of reaction time and temperature on the yield of GeO_2 NPs.

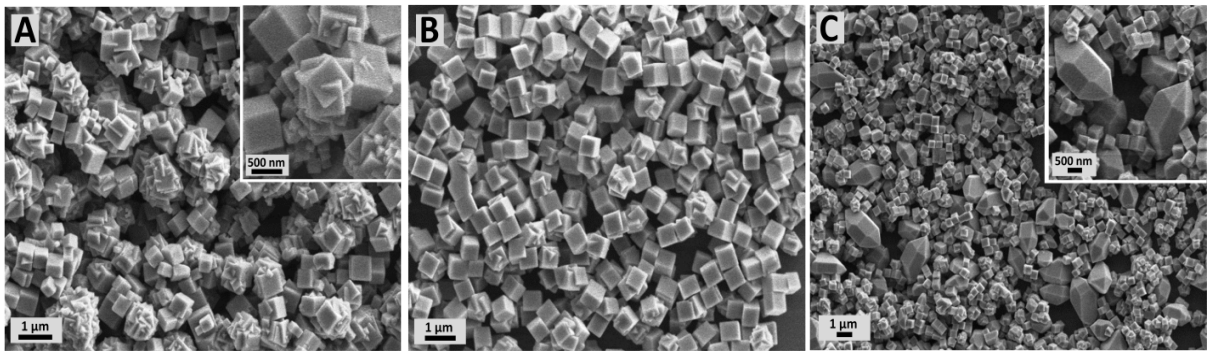

Figure S5. Dominant morphology of GeO_2 NPs synthesized at different times and temperatures: **A)** short time (0-2 h for 23 °C, 0-15 minutes at 60 °C); **B)** Moderate time (2- 20 h for 23 °C and 15min-2 h at 60 °C); **C)** Long aging time (>24 h for 23 °C >6 h at 60 °C).