Supporting Information

Shaping Up: Spontaneous Formation of Ordered Mesoscopic Salt Bowls

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Experimental Section

Synthetic procedure for MnSO₄ bowls:

In a typical synthesis, 0.50 g of MnSO₄·H₂O salt (Merck) dissolved in 10 ml ethanol was mixed with 1.00 g polyvinylpyrrolidone (Aldrich, Mₔ=13,00,000) polymer to make a homogeneous, viscous slurry. The slurry was then poured into a glass petri dish (50 mm diameter) and aged for 10 h in an oven at 80 °C. The transparent film of manganous sulfate–PVP composite thus obtained was calcined at different temperatures (200, 370, 420, 470, and 550 °C) for a duration of 5 h with a heating rate of 1 °C min⁻¹. In all the cases the sample was cooled to room temperature at a rate of 3 °C min⁻¹.

Synthetic procedure for gold bowls using MnSO₄ bowls as template:

To prepare gold replicas of the MnSO₄ bowls, gold was sputtered onto a sample of MnSO₄ bowls (10 mg) by using a plasma-induced sputtering technique for 2 minutes in an argon atmosphere, which resulted in a coating (ca. 60 nm) of gold over the bowls. The MnSO₄ salt was removed by soaking the gold sputtered sample in water for 1 h followed by washing with excess water and drying at room temperature.
Sample characterization

The morphologies of the samples obtained in all the experiments were examined with Field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, The Netherlands), Scanning electron microscope (SEM, LeicaS-440-I Instrument, U.K), and TEM (JEOL JEM-3010 with an accelerating voltage at 300 kV). Powder X-ray diffraction (XRD) patterns were measured by using RICH-SIEFERT 3000-TT diffractometer employing Cu Kα radiation. Thermo gravimetric analysis (TGA) was performed using Mettler Toledo TGA 850 instrument. SEM analysis of the samples is done after a mild gold coating to avoid charging as per the standard procedure.
Supporting Information S1. (a) Low magnification SEM image of a curled film containing ordered array of MnSO₄ bowls. (b) higher magnification SEM image of the encircled portion.

Supporting Information S2. TEM image showing that the bowl is made up of smaller particles.
Supporting Information S3. Electron diffraction pattern of the MnSO$_4$ bowls showing their polycrystalline nature.
Supporting Information S4. Thermo gravimetric analysis (TGA) curves of MnSO₄ salt (blue), MnSO₄ salt-PVP composite (red) and PVP polymer (black).
Supporting Information S5. FESEM image of the top-view of the hemi-spherical bowls emerging out of the polymer film after calcining at 420 °C for 5 h.
Supporting Information S6. SEM image of the bowls showing the uneven surface of the polymer film after calcination at 550 °C for 5 h leading to the less organized bowls.
Supporting Information S7. FESEM image of some intermediate, oblate-shaped structures obtained upon heating at 470 °C for 5h.
Supporting Information S8. SEM image of the ordered arrays of ball-in-bowl shaped microstructures formed from shrinking of the oblate spheroids.
Supporting Information S9. SEM image of the ring shaped microstructures obtained by using only water as the solvent.
Supporting Information S10. FESEM images of the ring shaped tubular microstructures obtained by using polyvinylalcohol (PVA) polymer instead of PVP.
Supporting Information S11. EDAX profile of the gold bowls obtained after dissolving the MnSO$_4$ core (the minor peaks for 'Mn' are from the negligible amount (~ 4 %) of salt left over after its dissolution).