Electronic Supplementary Material (ESI) for RSC Advances


# Supporting Information

## Shaping Up: Spontaneous Formation of Ordered Mesoscopic Salt Bowls

**Katla Sai Krishna,[a,#] Bosukonda V. V. S. Pavan Kumar [a] and Muthusamy Eswaramoorthy [a,*]**

[a]Nanomaterials and Catalysis Laboratory, Chemistry and Physics of Materials Unit and DST Unit on Nanoscience, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore, India 560064.

Fax: (+91)80-220-2766,Tel: (+91)80-2208-2870

[#]Present Address: Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, USA 70806

# Experimental Section

## Synthetic procedure for $MnSO_4$ bowls:

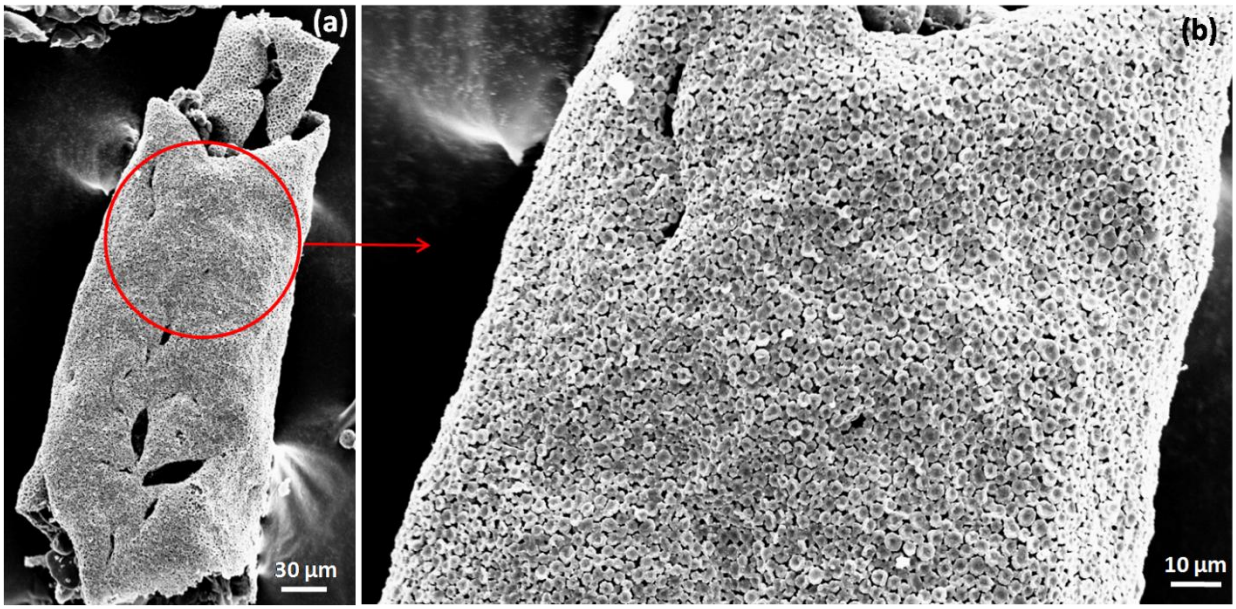
In a typical synthesis, 0.50 g of $MnSO_4.H_2O$ salt (Merck) dissolved in 10 ml ethanol was mixed with 1.00 g polyvinylpyrrolidone (Aldrich, $M_w$=13,00,000) polymer to make a homogeneous, viscous slurry. The slurry was then poured into a glass petri dish (50 mm diameter) and aged for 10 h in an oven 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 $MnSO_4$ bowls as template:

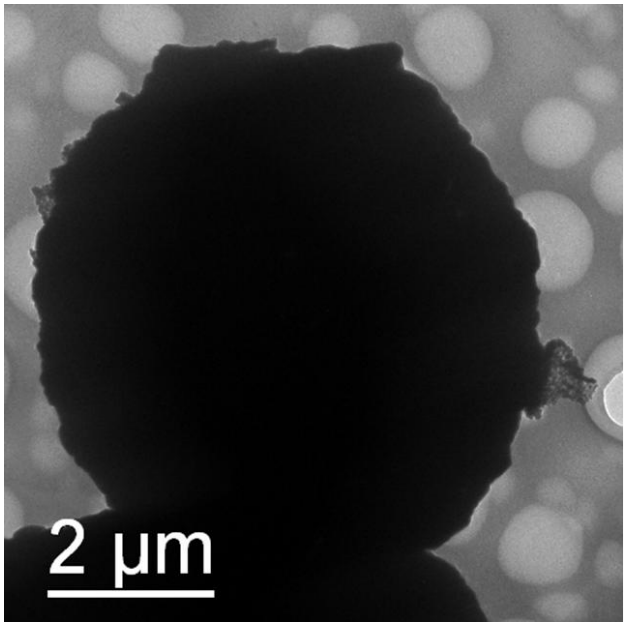
To prepare gold replicas of the $MnSO_4$ bowls, gold was sputtered onto a sample of $MnSO_4$ bowls (10 mg) by using a plasma-induced sputtering technique for 2 minutes in an argon atmosphere, which resulted in a coating (ca. 60 nm) of gold over the bowls. The $MnSO_4$ salt was removed by soaking the gold sputtered sample in water for 1 h followed by washing with excess water and drying at room temperature.

## Sample characterization

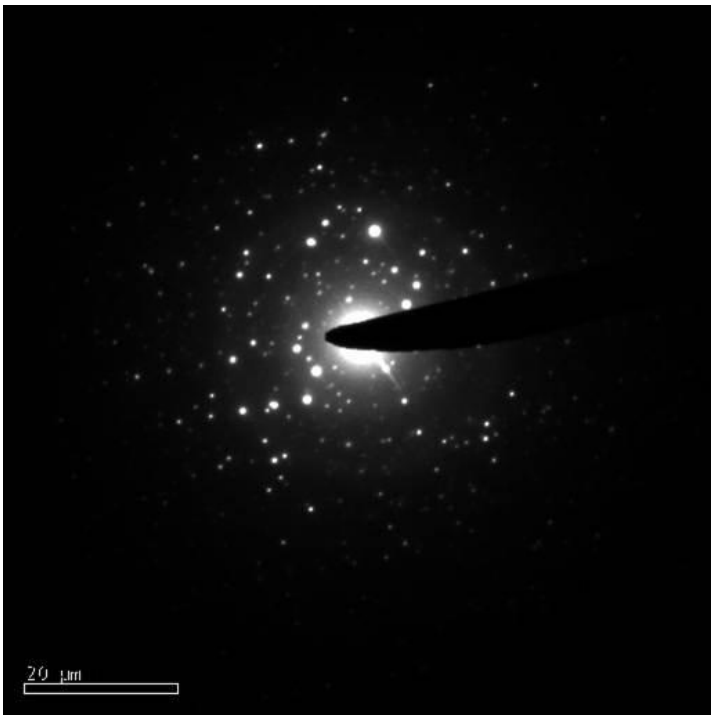
The morphologies of the samples obtained in all the experiments were examined with Field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, The Netherlands), Scanning electron microscope (SEM, LeicaS-440-I Instrument, U.K), and TEM (JEOL JEM-3010 with an accelerating voltage at 300 kV). Powder X-ray diffraction (XRD) patterns were measured by using RICH-SIEFERT 3000-TT diffractometer employing Cu $K_{\alpha}$ 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.



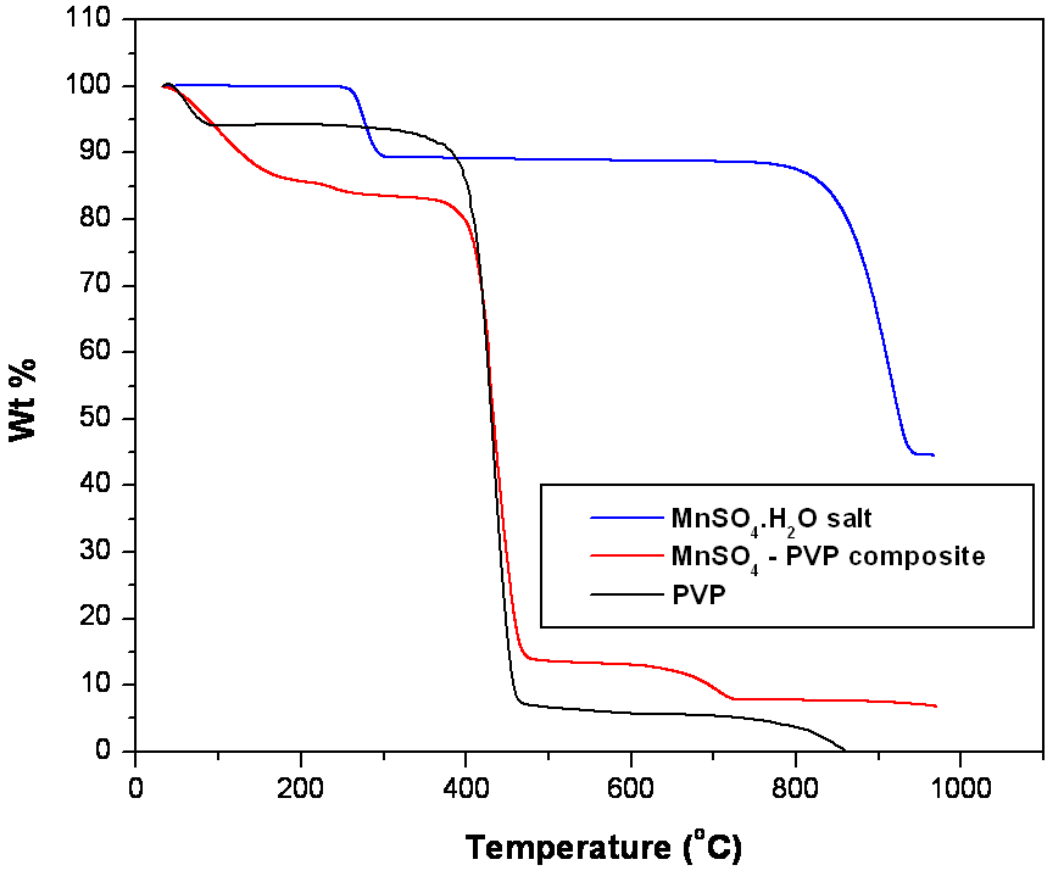

**Supporting Information S1.** (a) Low magnification SEM image of a curled film containing ordered array of $MnSO_4$ bowls. (b) higher magnification SEM image of the encircled portion.



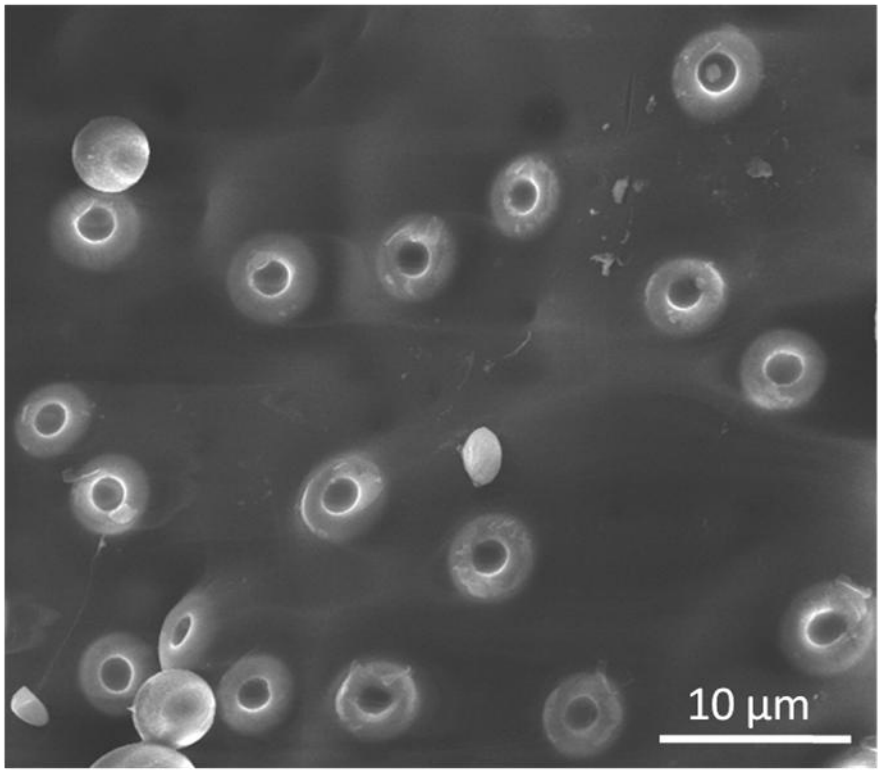

**Supporting Information S2.** TEM image showing that the bowl is made up of smaller particles



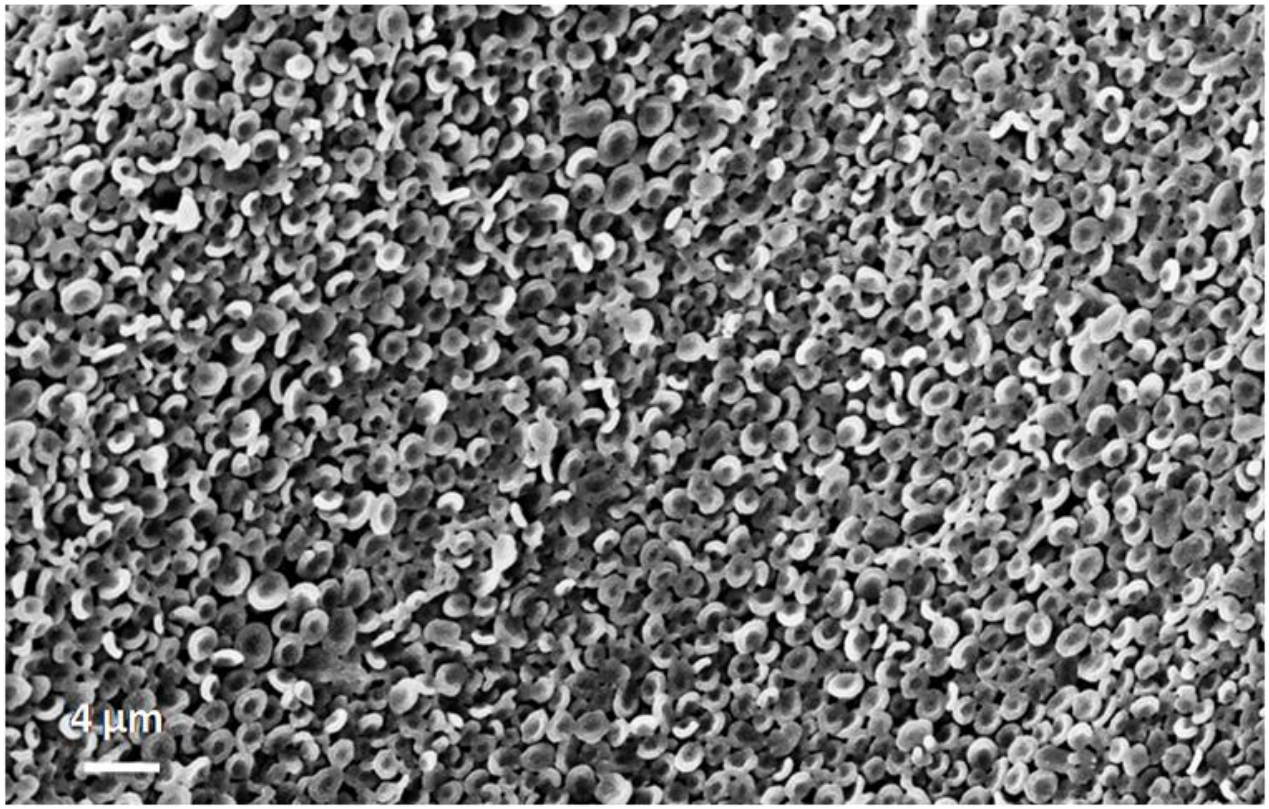

**Supporting Information S3.** Electron diffraction pattern of the $MnSO_4$ bowls showing their polycrystalline nature.



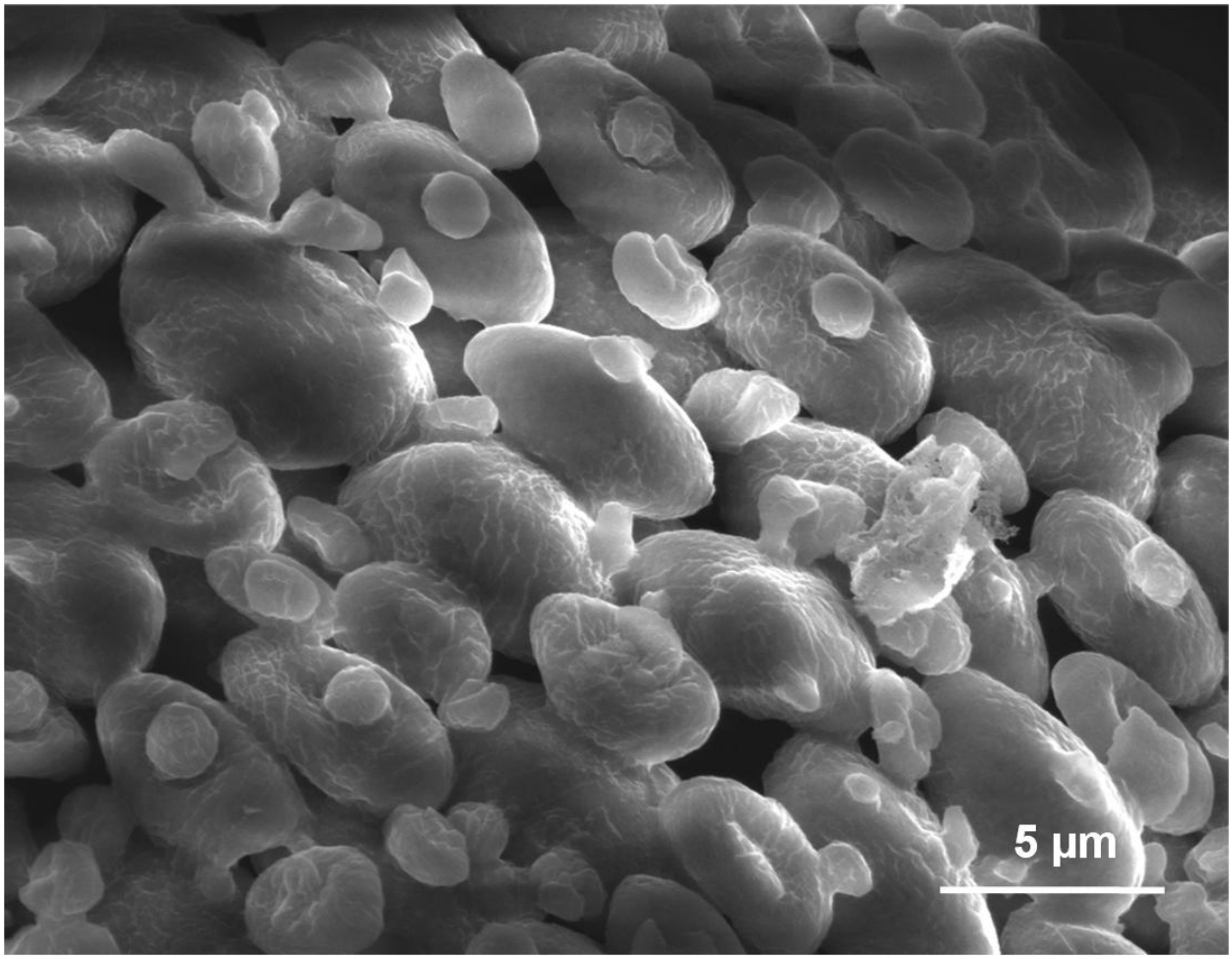

**Supporting Information S4.** Thermo gravimetric analysis (TGA) curves of $MnSO_4$ salt (blue), $MnSO_4$ salt-PVP composite (red) and PVP polymer (black).



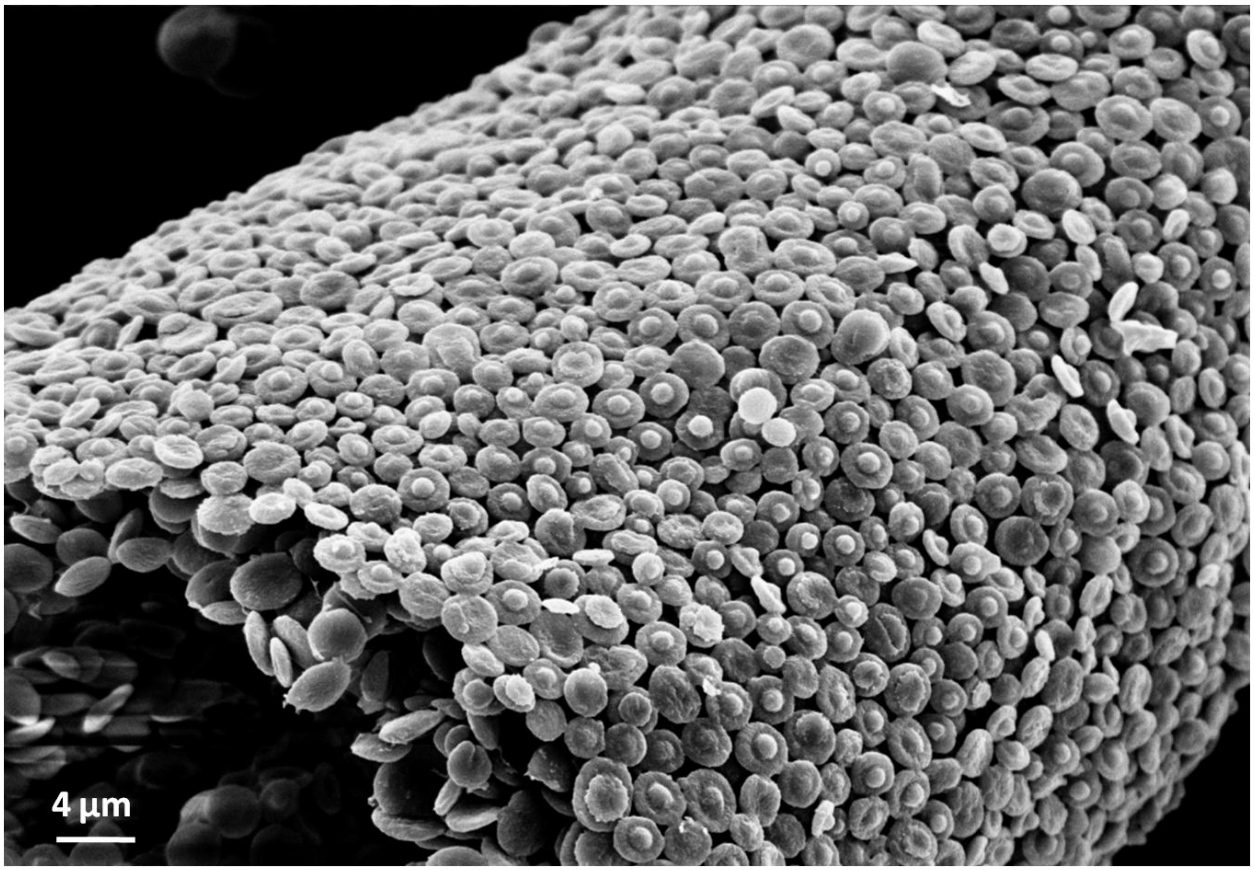

**Supporting Information S5.** FESEM image of the top-view of the hemi-spherical bowls emerging out of the polymer film after calcining at 420 °C for 5 h.



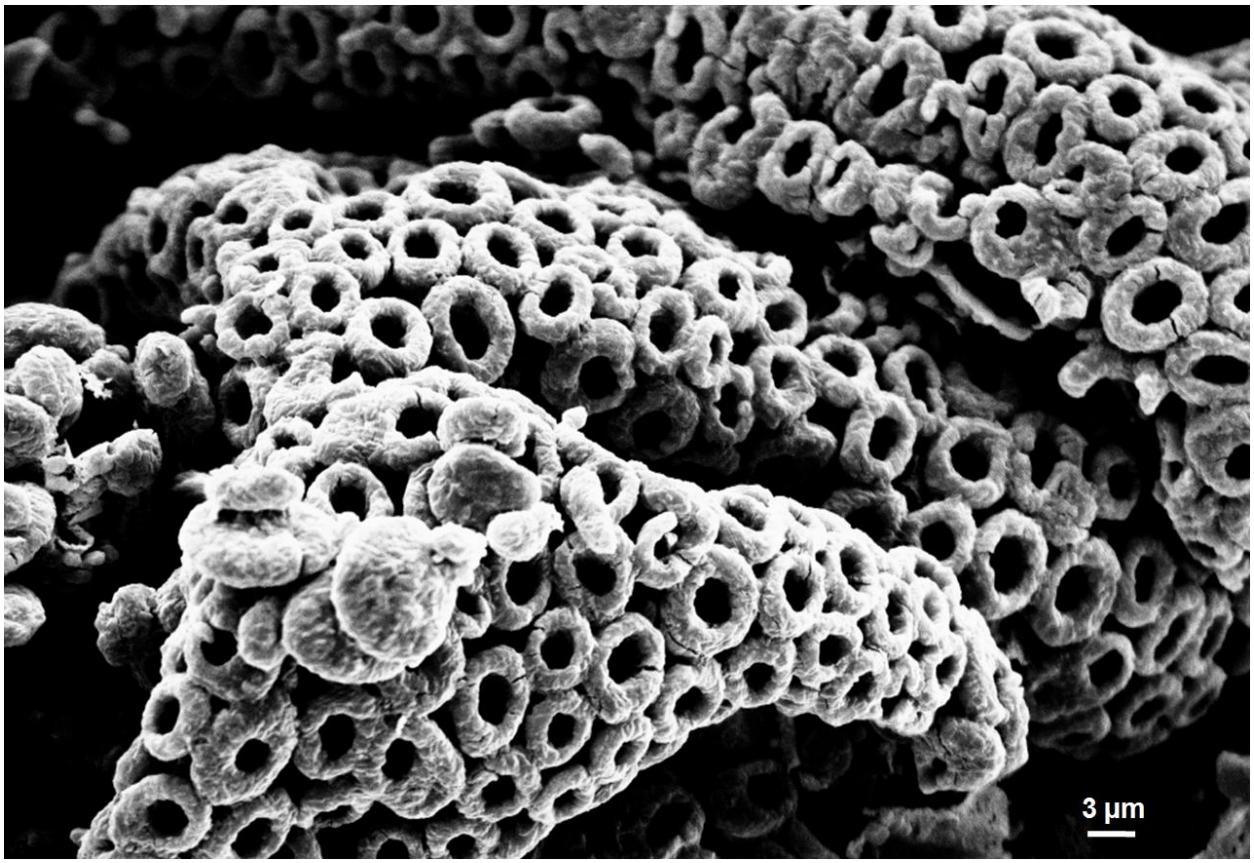

**Supporting Information S6.** SEM image of the bowls showing the uneven surface of the polymer film after calcination at 550 °C for 5 h leading to the less organized bowls.



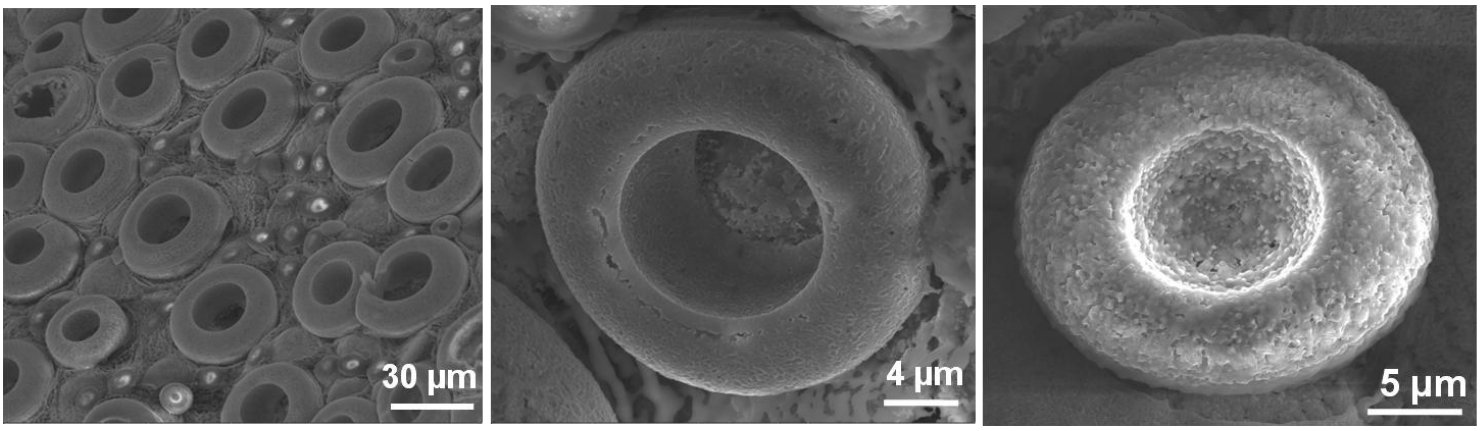

**Supporting Information S7.** FESEM image of some intermediate, oblate-shaped structures obtained upon heating at 470 °C for 5h.



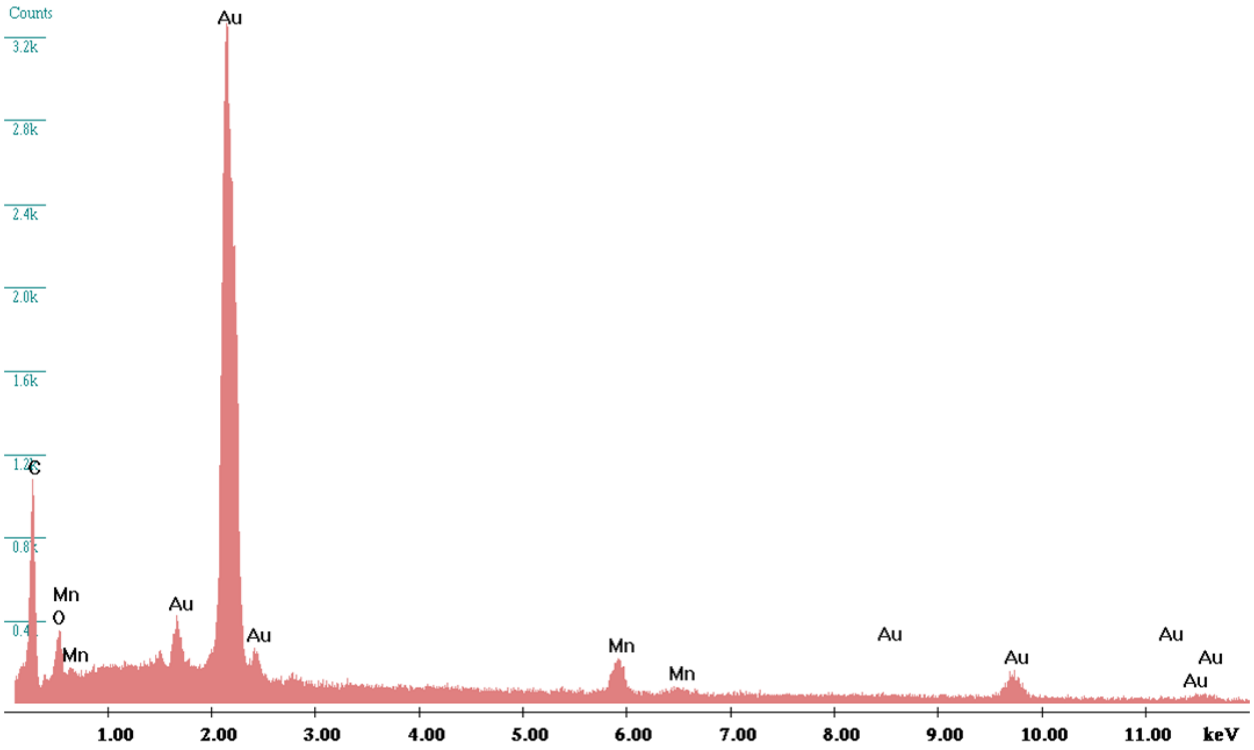

**Supporting Information S8.** SEM image of the ordered arrays of ball-in-bowl shaped microstructures formed from shrinking of the oblate spheroids.




**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).