Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

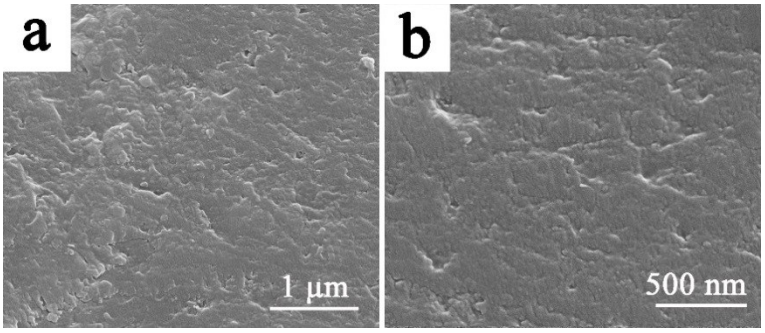

Figure S1. SEM images of the polished transverse cross sections of sea urchin spines before dissolution process.

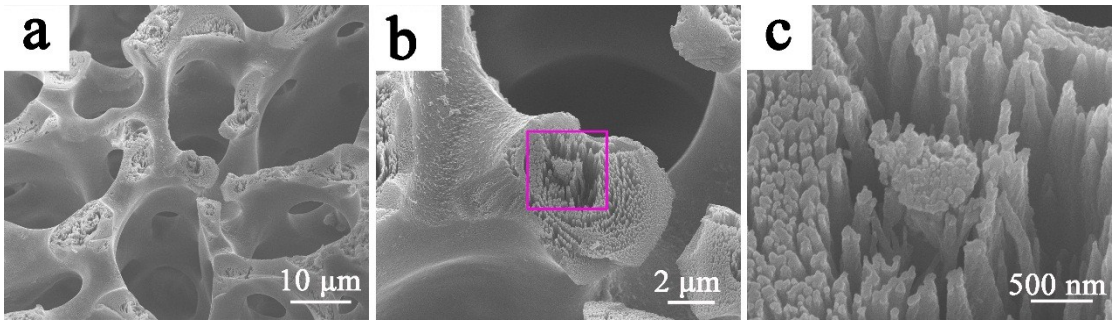

Figure S2. Side view SEM images of the calcite microneedle arrays formed on the center area (or stereom parts) of the transverse cross sections of sea urchin spines after 15 h of dissolution in aqueous solution in the presence of $Cu(NO_3)_2$ (20 mM) at 50 °C (tilting angle: 23°).

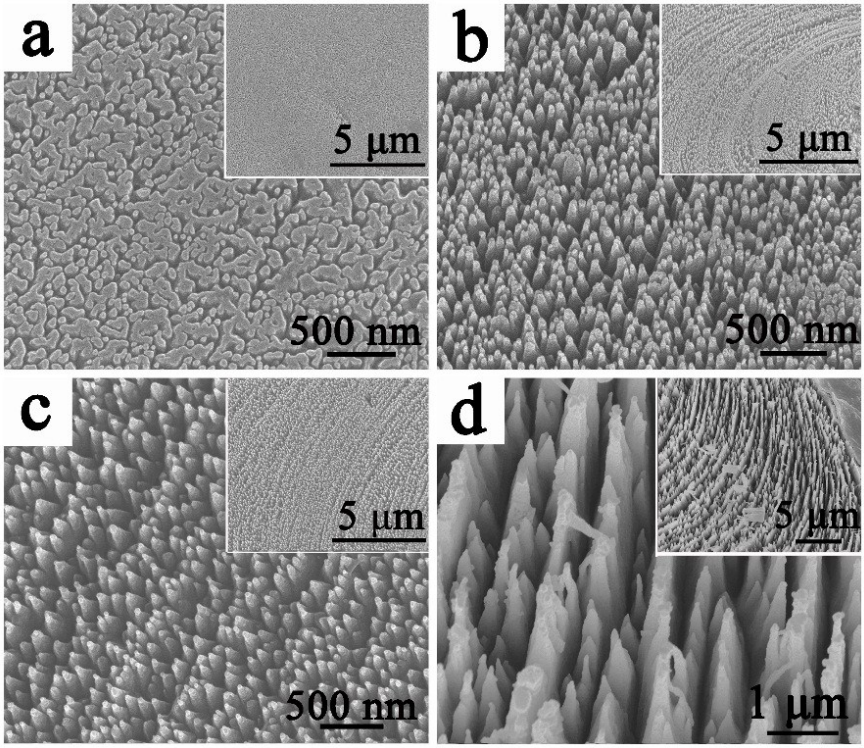

Figure S3. Side view SEM images of the sea urchin spine transverse cross sections after different dissolution times in the presence of 20 mM of $Cu(NO_3)_2$ at 50 °C. (a) 5min; (b) 15 min; (c) 30 min； (d) 5h (tilting angle: 15°)

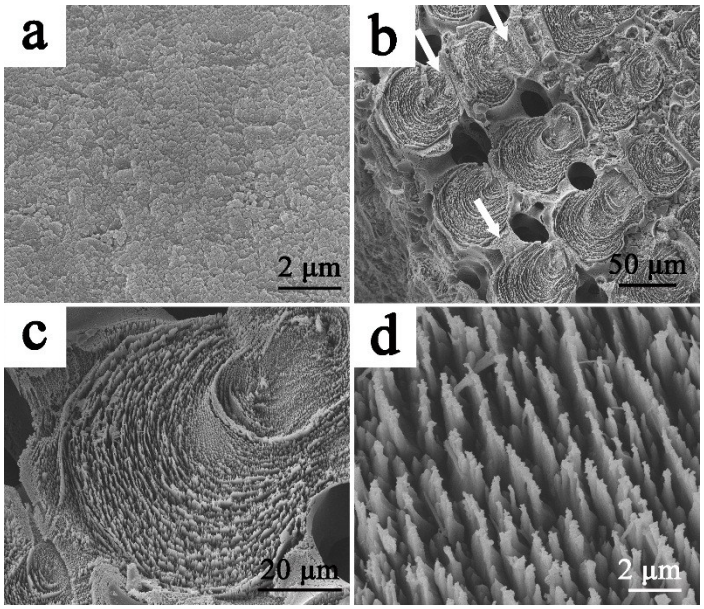

Figure S4. Side view SEM images of SU spines soaked with NaClO solution for 12 hours (a) and then dissolved in aqueous solution for 15 hours in the presence of $Cu(NO_3)_2$ (20 mM) at 50 °C (b-d) (tilting angle: 15 °).

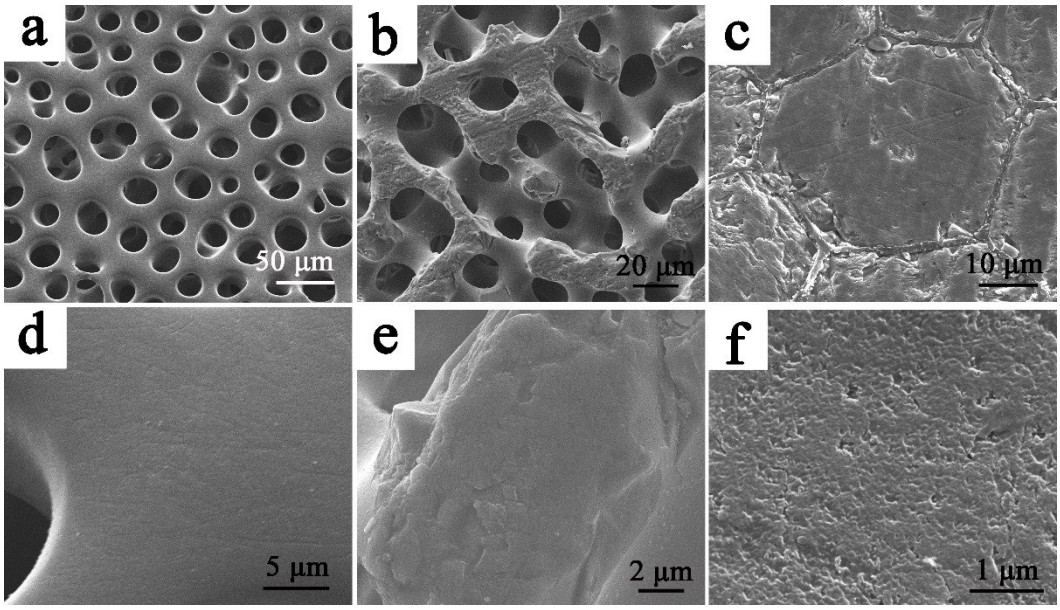

Figure S5. Side view SEM images of polished transverse cross sections of (a, d) sea urchin tests, (b, e) sea star ossicles, (c, f) calcitic prism layers of mollusk shells before dissolution process. (tilting angle: 15 °).

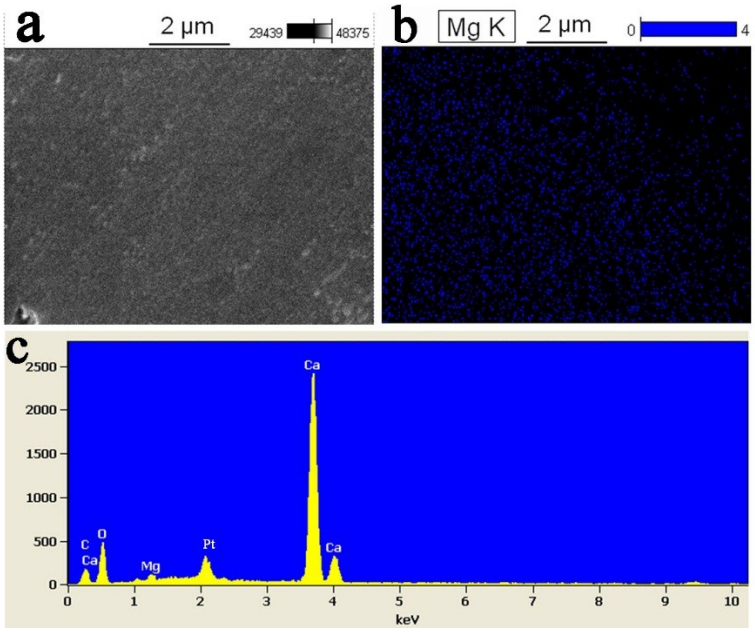

Figure S6. EDX analyses of polished transverse cross sections of SU spines before dissolution process. (a) SEM image, (b) Mg mapping image of (a), (c) EDS spectrum of (a).

Table S1 Characterizations on the concentrations of the Ca^{2+} via ICP and the pH values of the solutions before and after the dissolution process of sea urchin spines in aqueous solution for 15 hour with the presence of $Cu(NO_3)_2$ of different concentrations.

$[Cu(NO_3)_2]$ / (mM)	$[Ca^{2+}]$ / (μ g/ml)	pH before dissolution	pH after dissolution
20	10.27±0.18	4.28	4.72
10	6.16±0.31	4.43	4.83
5	4.03±0.35	4.60	4.96
0.1	0.91±0.57	5.28	5.46