Electronic Supplementary Information

Li^+ ion induced three-dimensional aggregation growth of single-crystal perovskite octahedrons

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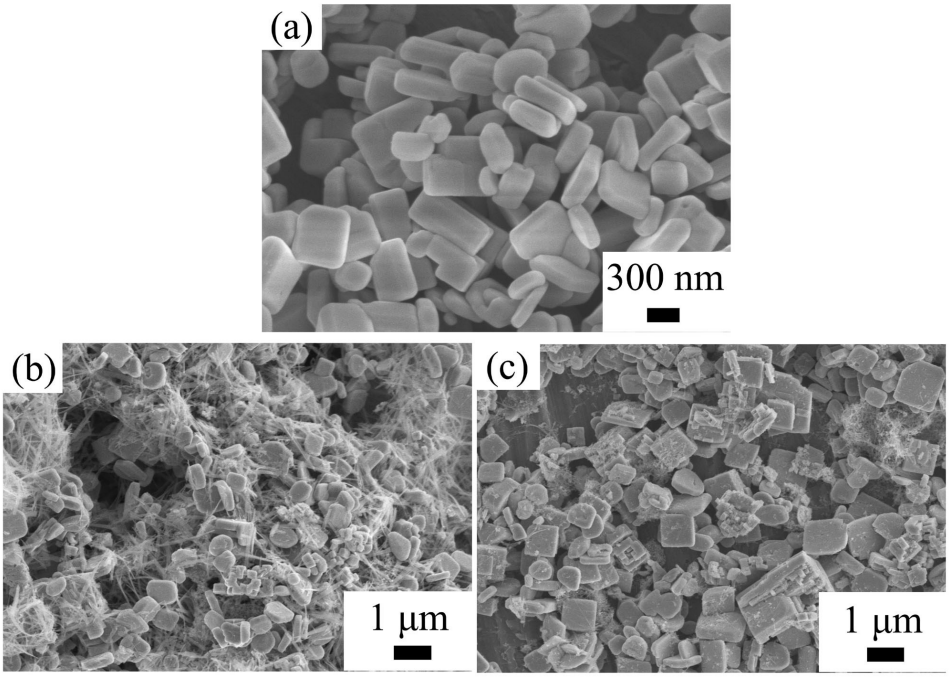

Fig. S1 Typical SEM images of hydrothermally synthesized products assisted by (a) no surfactant, (b) $NaNO_3$ and (c) KNO_3.

Fig. S1 shows the morphology of the hydrothermally synthesized products by using different ionic surfactants. Without surfactant, the products were nanoplates with lateral size of about 600 nm and 100 nm in thickness. By employing $NaNO_3$ and KNO_3 as surfactant respectively, the morphology of the products changed from mixture of nanoplates and nanowires to mixtures of nanoplates and nanoparticles.

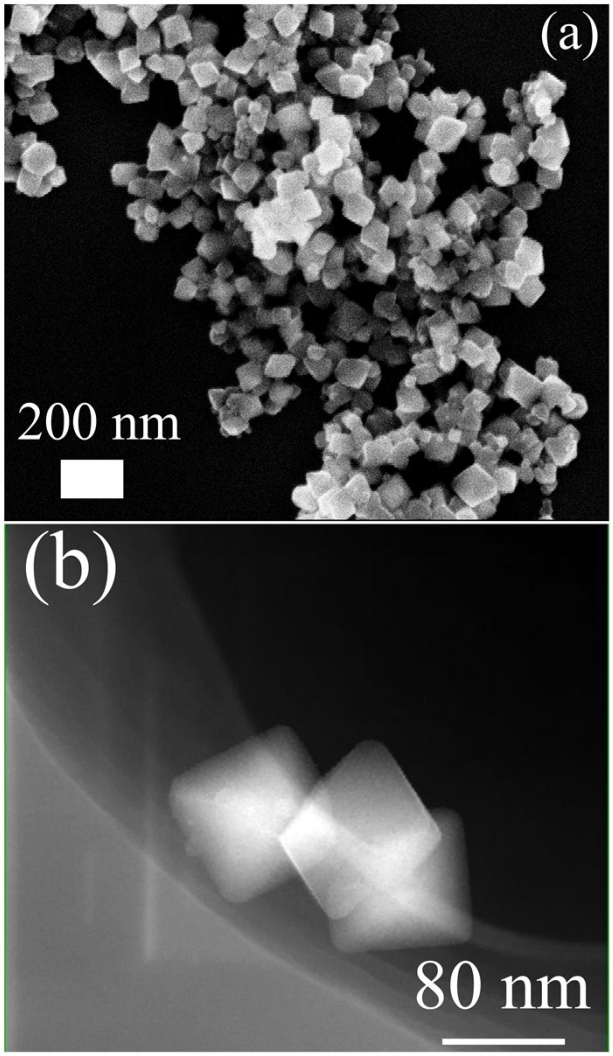

Fig. S2 Typical SEM and TEM image of the as-synthesized perovskite PT octahedrons by lithium nitrate assisted hydrothermal method.

Fig. S2 presents typical perovskite PT octahedrons synthesized by lithium nitrate assisted hydrothermal method at 200 ^{o}C for 12 h. The as-synthesized particles exhibited a regularly faceted shape of octahedron with a uniform size of about 50-80 nm. The perovskite PT octahedrons have eight equivalent {111} facets exposed with smooth outline and clean surface [1].

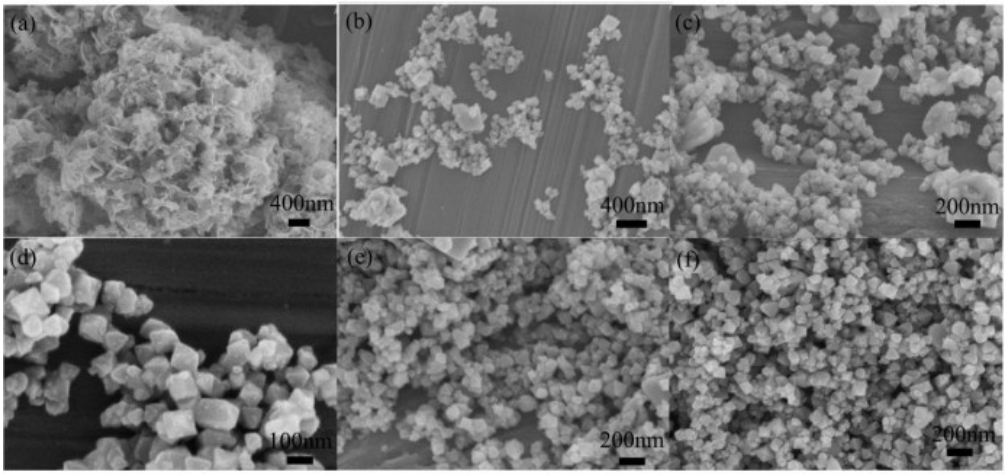

Fig. S3 SEM images of the products prepared by 81.3 wt% Li^+ assisted hydrothermal method at 200 ^oC for different times: (a) 0.5 h, (b) 1.0 h, (c) 2.0 h, (d) 4.0 h, (e) 8.0 h and (f) 16 h.

When the sample was prepared at 0.5 h, the amorphous and seriously agglomerated petal-like morphology was observed with size of 10-100 nm (Fig. 2a). With the hydrothermal reaction time prolonged to 1-2 h, the well-dispersed square-like and sheet-like products were formed, both of which were perovskite PT structure (Fig. 2b-c). The free-standing octahedral shaped nanoparticles were obtained with a rough surface when the reaction time is in the range of 4~8 h (Fig. 2d-e). It is can be observed that such octahedrons with an uniform size were synthesized after 4 h, where no obvious amorphous particles or sheets existed. When the reaction time was further prolonged to 16 h, octahedrons with smooth surface were synthesized, with size of about 50-100nm and of perovskite phase in pure.

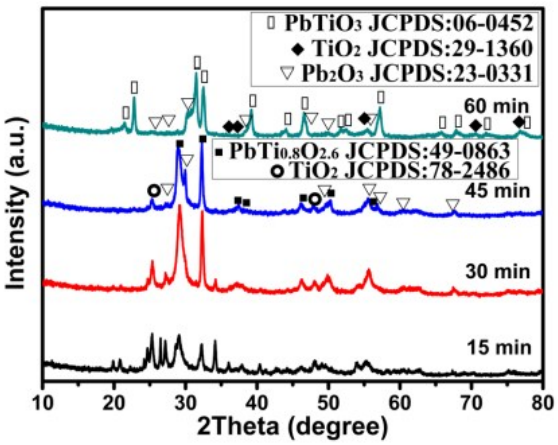

Fig. S4 XRD patterns of the hydrothermally prepared samples at 200 ^oC for various reaction time: 15 min, 30 min, 45 min and 60 min.

Fig. S4 shows the XRD patterns of the as-synthesized products by Li^+ assisted hydrothermal method for different reaction time within 1 h. It is obvious that perovskite PT firstly come to form when reaction time was prolonged to 60 min. And the products before 60 min included complex phases, mainly lead oxides and titanate oxides, as shown in Fig. S4.

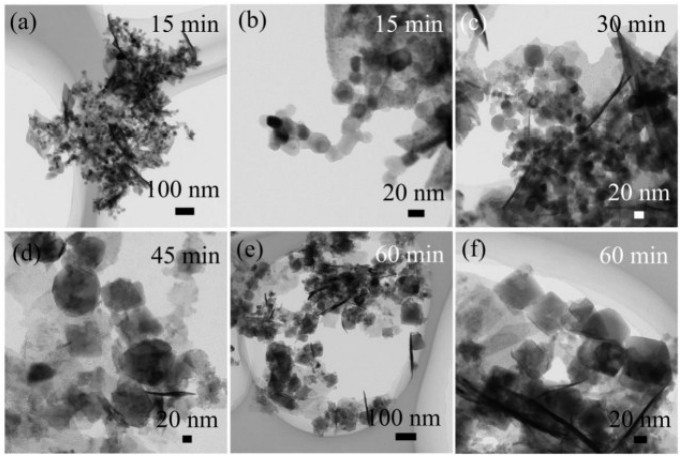

Fig. S5 TEM images of the hydrothermally prepared samples at 200 °C for various reaction time: 15 min, 30 min, 45 min and 60 min.

Fig. S5 shows the TEM images of the as-synthesized products by Li^+ assisted hydrothermal method for different reaction time within 1 h. it can be seen that octahedron started to form when the hydrothermal reaction time was 60 min. And before that, the product consisted of irregular shaped nanoparticles, and the morphology evolution experienced a round shape to faceted shape as the reaction time extended.

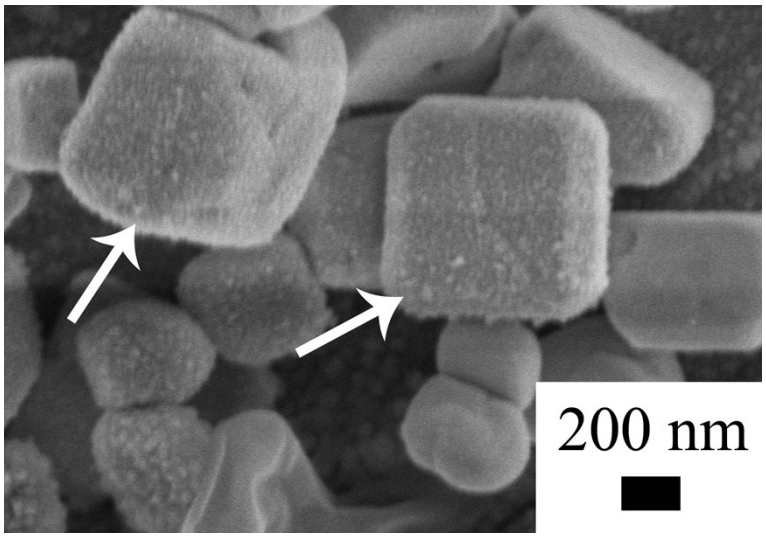

Fig. S6 High magnitude SEM image of typical product hydrothermally synthesized when the concentration of lithium nitrate was 12.7 wt%.

Fig. S6 shows the typical magnified SEM image of the as-synthesized perovskite PT nanostructure via hydrothermal process assisted by 12.7 wt% lithium nitrate. The hexahedral shaped nanoparticles in lateral size of 600 nm exhibited a relatively coarse surface, where nanoparticles with size of tens of nanometers were obvious. The nanoparticles on the surface of hexahedrons can be remarkable and solid evidence to prove that the Li^+ ions assisted hydrothermal products have experienced an oriented aggregation growth process.

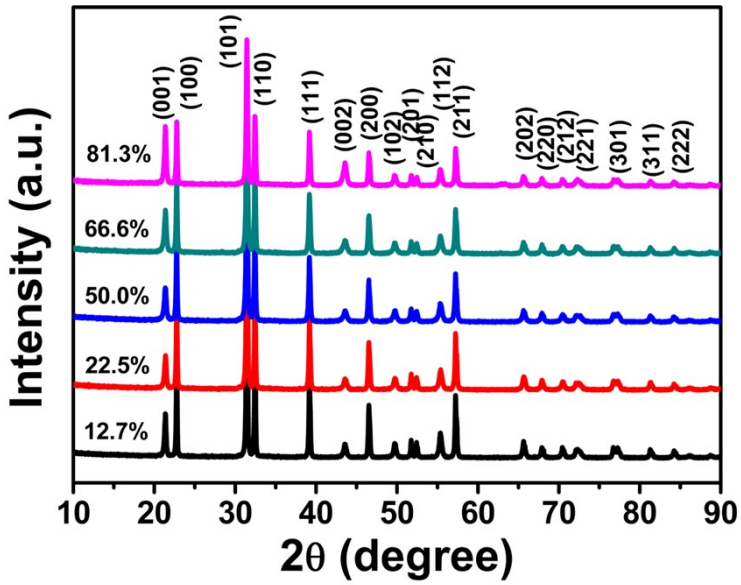

Fig. S7 XRD patterns of the products hydrothermally synthesized and assisted with lithium nitrate as the ionic capping reagent at 200 °C for12 h. Lithium nitrate concentration: (a) 12.7%, (b) 22.5%, (c) and (d) 50.0%, (e) 66.6% and (f) 81.3%.

Fig. S7 shows the corresponding XRD patterns of the PT samples hydrothermally synthesized at 6M KOH assisted with lithium nitrate as the ionic capping reagent. It is clearly observed that all the diffraction peaks can be indexed to tetragonal perovskite PT structure with the lattice parameters, a=b=3.899 Å and c=4.153 Å , corresponding well with the reported data ($PbTiO_3$, JCPDS file no. 06-0452). The strong and sharp diffraction peaks suggest that the as-prepared samples are all well crystallized. And no impurity peaks have been detected. Moreover, the (001)/(100) diffraction intensity ratio remarkably increased as the lithium nitrate concentration increased from 12.7% to 81.3%, which could be ascribed to the increasingly prevailed (001) planes.

Reference:

[1] Simin Yin, He Tian, Zhaohui Ren, Xiao Wei, Chunying Chao, Jingyuan Pei, Xiang Li, Gang Xu, Ge Shen and Gaorong Han, *Chem. Commun.*, **2014**, *50*, 6027-6030.