Hydrothermal Synthesis, Hierarchical Structures and Properties of Blue Pigments $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$

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General procedure for nanoplates self-assembled microspheres of $SrCuSi_4O_{10}$. 10 mL 0.5mol/L $SrCl_2$•$6H_2O$, 40 mL 0.5mol/L Na_2SiO_3•$9H_2O$ and 0.4 g CuO powders as starting materials were mixed together. The pH value of the solution was adjusted to 8 using 1 mol/L HCl aqueous solution. The concentrated ammonia solution was added and the final pH value of the solution is 12.5. The solution was sealed in autoclave with a Teflon liner (80 mL), then heated up to 250 ℃ and kept it for 48 h, followed by cooling to room temperature by switching off the furnace. Dark blue powders were washing with distilled water and were added into 100 ml 0.4 mol/L HCl aqueous. The dark blue powders were mixtures of CuO and $SrCuSi_4O_{10}$. After 12 hours, the CuO was dissolved and blue powders of pure phase $SrCuSi_4O_{10}$ were obtained. The yield of the compound is 65%.

General procedure for microplates assembled microspheres of $SrCuSi_4O_{10}$. 10 mL 0.5mol/L $SrCl_2$•$6H_2O$, 40 mL 0.5mol/L Na2SiO_3•$9H_2O$ and 0.4 g CuO powders as starting materials were mixed together. The pH value of the solution was adjusted to 10 using 1 M/L HCl aqueous solution. The concentrated ammonia solution was added and the final pH value of the solution is 13. The solution was sealed in autoclave with a Teflon liner (80 mL), then heated up to 250 ℃ and kept it for 48 h, followed by cooling to room temperature by switching off the furnace. Dark blue powders were washing with distilled water and were added into 100 ml 0.4 mol/L HCl aqueous solution. The dark blue powders were mixtures of CuO and $SrCuSi_4O_{10}$. After 12 hours, the CuO was dissolved and blue powders of pure phase $SrCuSi_4O_{10}$ were obtained. The yield of the compound is 50%.

Captions of Fig.s

Fig. S1 Perspective view of $MCuSi_4O_{10}$ (M = Sr, Ba) with the Cu^{2+} ions (green) in a square planar complex.

Fig. S2. SEM images and EDS analysis of (a) $SrCuSi_4O_{10}$ and (b) $BaCuSi_4O_{10}$. For $SrCuSi_4O_{10}$ the EDS result is O 58.34%, Si 27.33%, Sr 6.42%, Cu 7.90%; For $BaCuSi_4O_{10}$ the EDS result is O 66.42%, Si 24.71%, Ba 4.74%, Cu 4.13%.

Fig. S3a. SEM images of the multi-layered $SrCuSi_4O_{10}$ microparticles self-assembled by nanoplates

Fig. S3b. SEM images of the $SrCuSi_4O_{10}$ microspheres self-assembled by nanoplates

Fig. S3c. SEM images of the $SrCuSi_4O_{10}$ microspheres assembled by microplates on the surface

Fig. S3d. SEM images of the $BaCuSi_4O_{10}$ porous microspheres self-assembled by nanoplates, nanoplates break off from the surfaces of the microspheres, a cutted microsphere, and the pores.

Fig. S4. (a) XPS spectra of $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$. The XPS analysis shown further confirms that the powders contain Ba, Cu, Si, and O. (b) Si(2p) XPS spectra for $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$. (c) Cu(2p) XPS spectra for $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$. (d) Sr(3d) and Ba(3d) XPS spectra for $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$, respectively.

Fig. S5. FTIR spectra for $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$.

Fig. S6. XRD patterns for $SrCuSi_4O_{10}$ with different hierarchical structures. Multi-layered microsparticles self-assembled by nanoplates (top), microspheres self-assembled by nanoplates (middle) and microspheres assembled by microplates on the surface (bottom). [The powder XRD patterns of products were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ=0.15418 nm) of 40 KV and 30 mA at room temperature by step scanning in an angle rang of $5° \leq 2\theta \leq 90°$ and increments of 0.02 °were employed.]

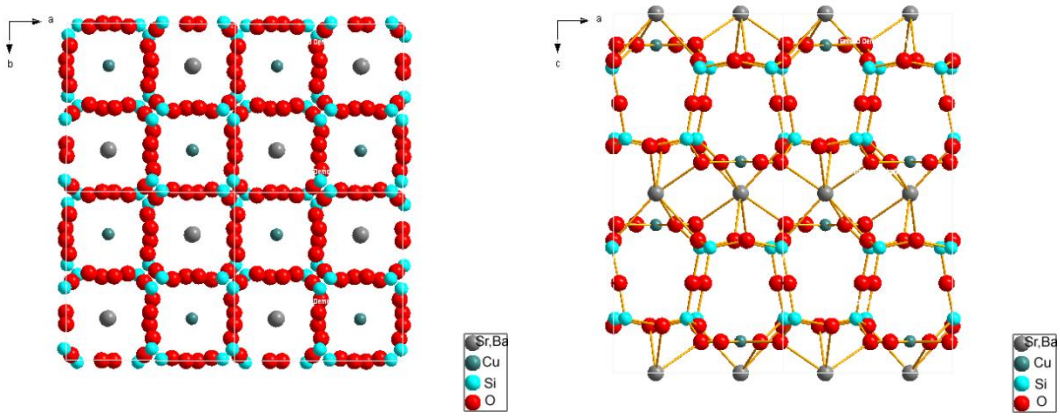
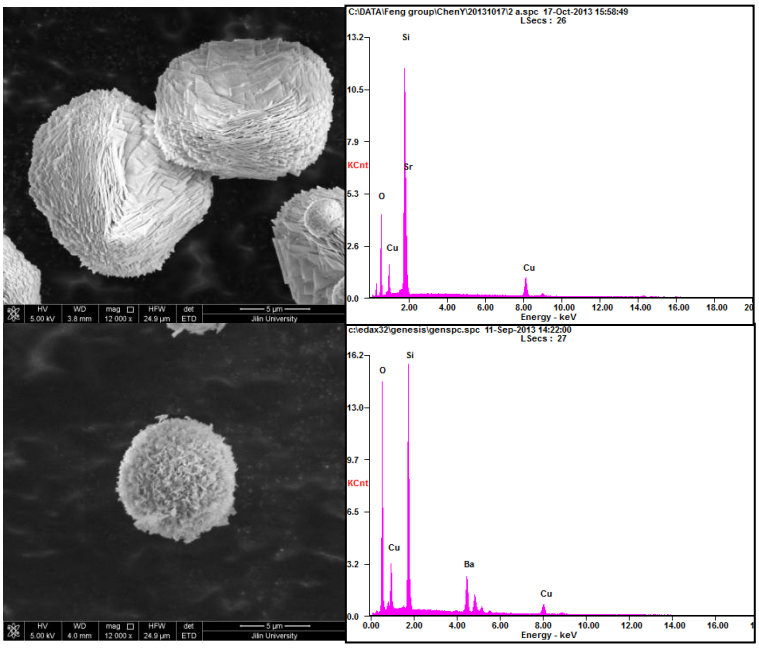


Fig. S1 Schematic depiction of an isolated layer of $MCuSi_4O_{10}$ (M = Sr, Ba) with the Cu^{2+} ions (green) in a square planar complex.



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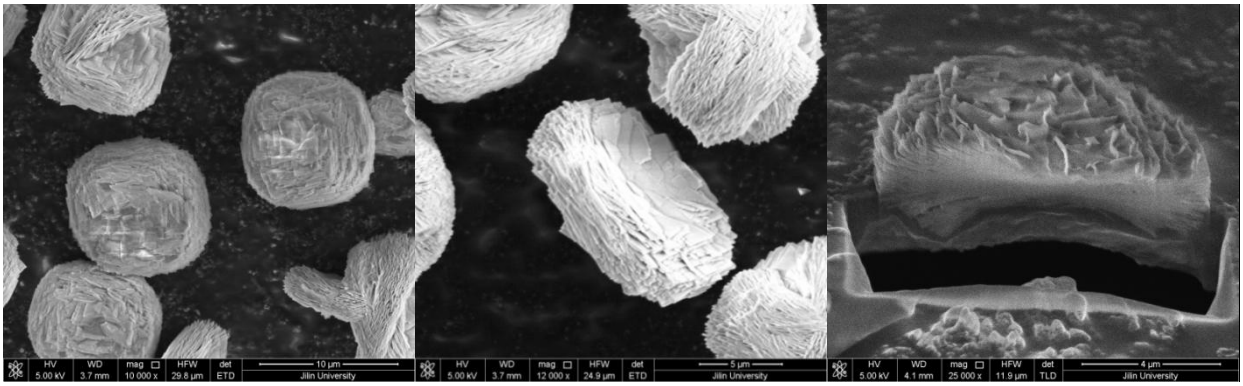


Fig. S3a. SEM images of the multi-layered $SrCuSi_4O_{10}$ microparticles self-assembled by nanoplates

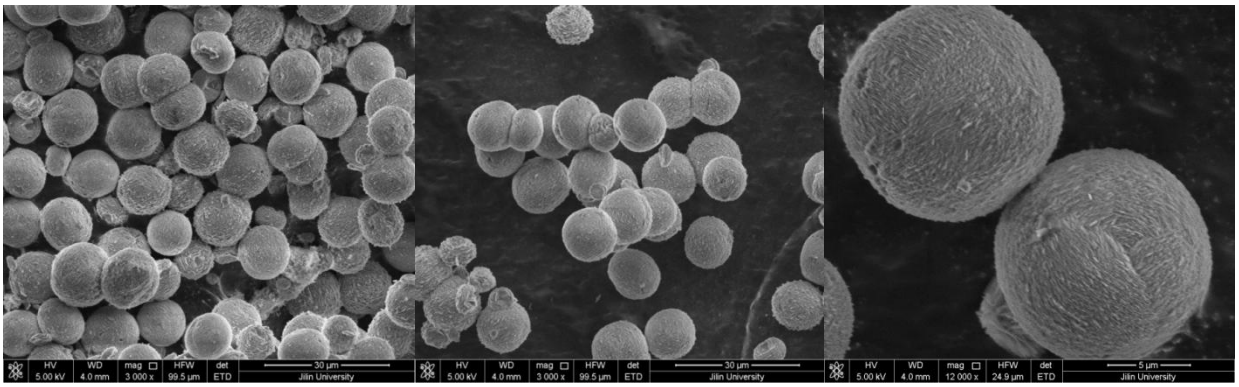


Fig. S3b. SEM images of the $SrCuSi_4O_{10}$ microspheres self-assembled by nanoplates.

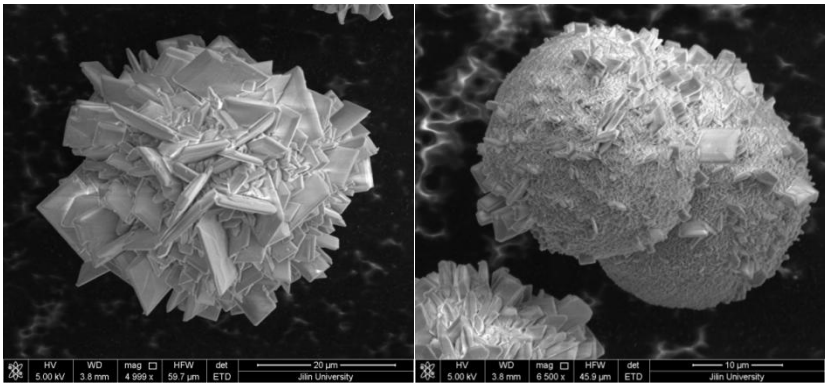
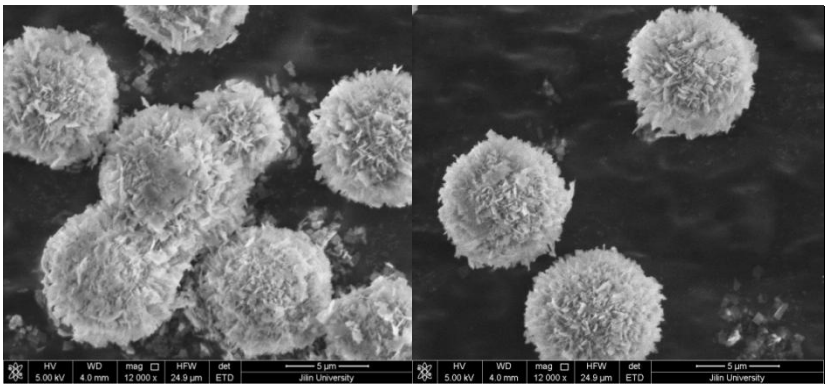
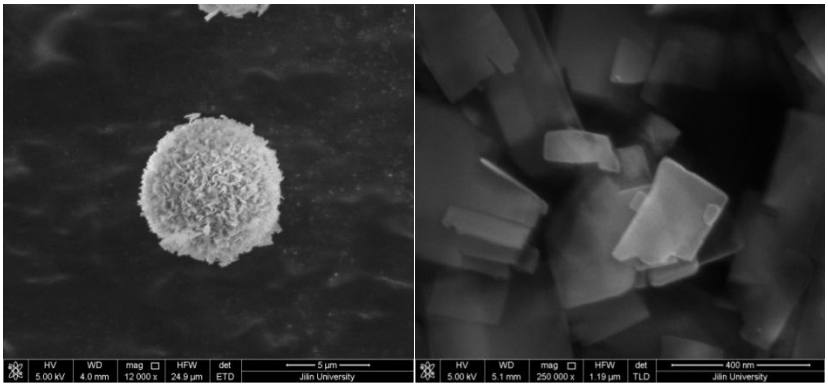


Fig. S3c. SEM images of the $SrCuSi_4O_{10}$ microspheres assembled by microplates on the surface





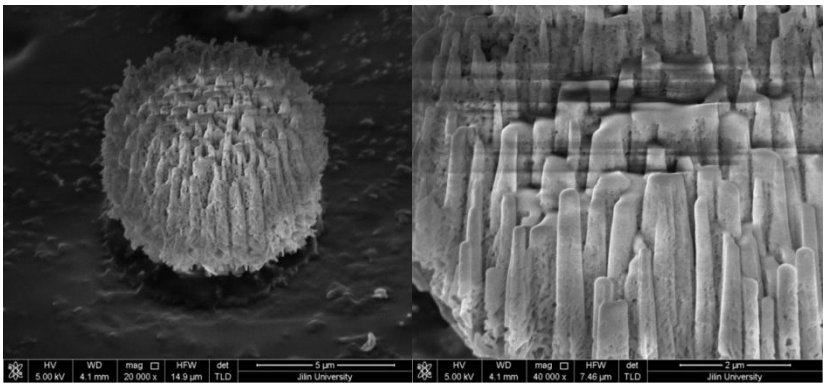
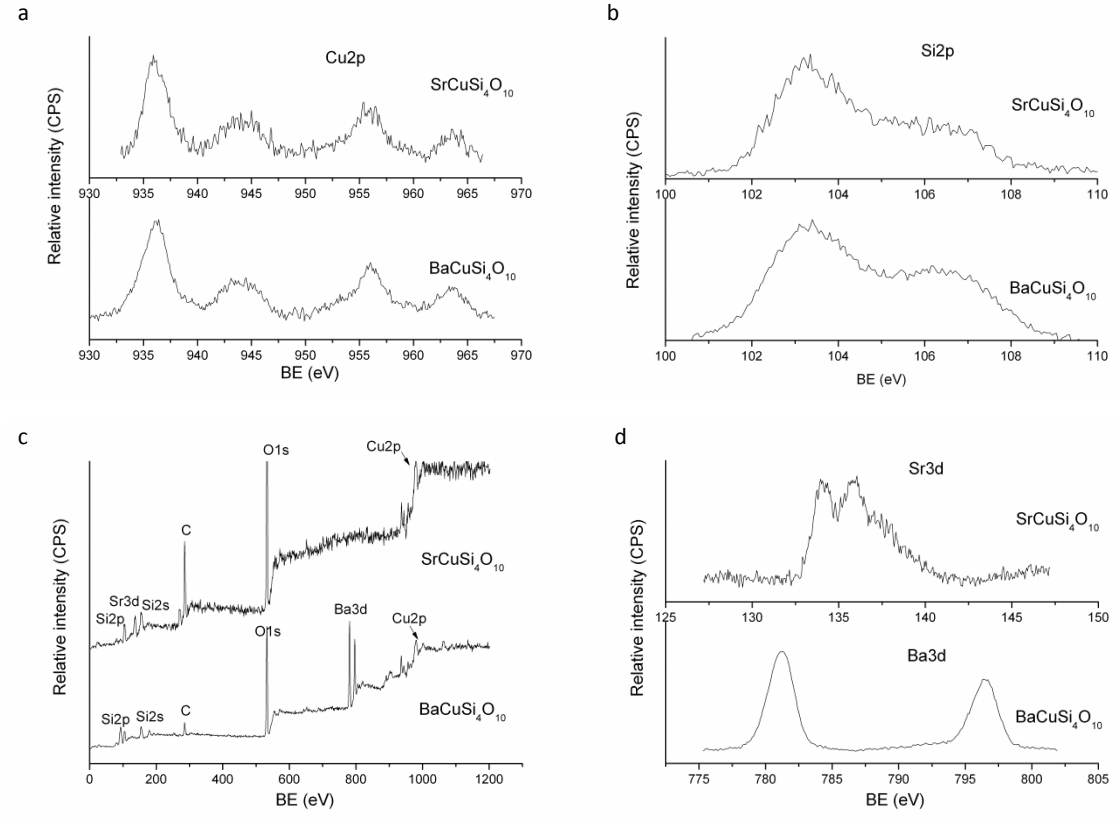


Fig. S3d. SEM images of the $BaCuSi_4O_{10}$ porous microspheres self-assembled by nanoplates, nanoplates break off from the surfaces of the microspheres, a cutted microsphere, and the pores.



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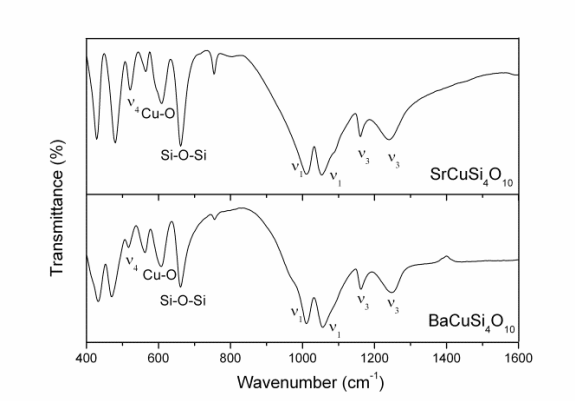
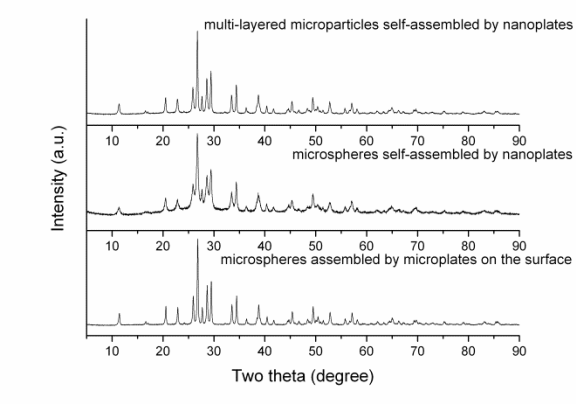


Fig. S5. FTIR spectra for $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$.



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