Electronic supplementary material (ESI) for Journal of Materials Chemistry

Controlled Synthesis of Europium Doped Lutetium Compounds Nanoflakes, Nanoquadrels, and Nanorods

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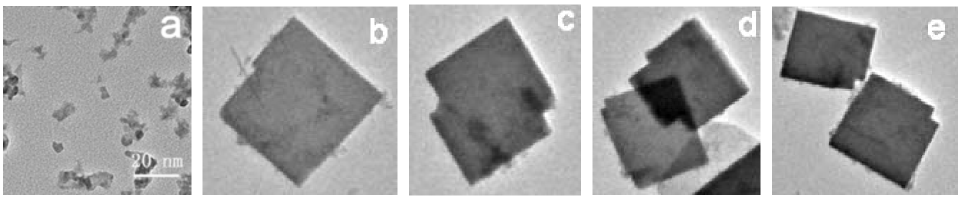

Fig. S1 (a) Representative TEM images of $Lu(OH)_3$ colloid and (b~e) several especial nanoflakes selected from Figure 1A.

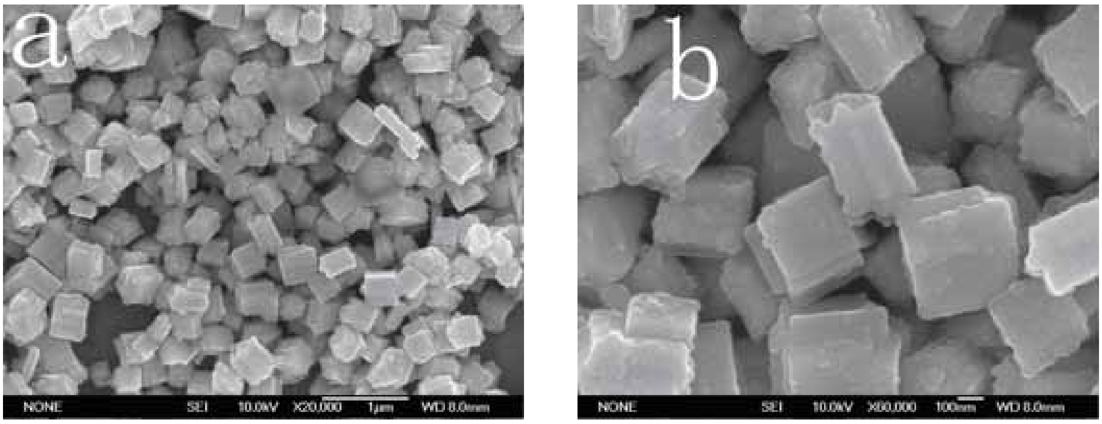

Fig. S2 Lower (a) and higher (b) magnification FESEM images of L2

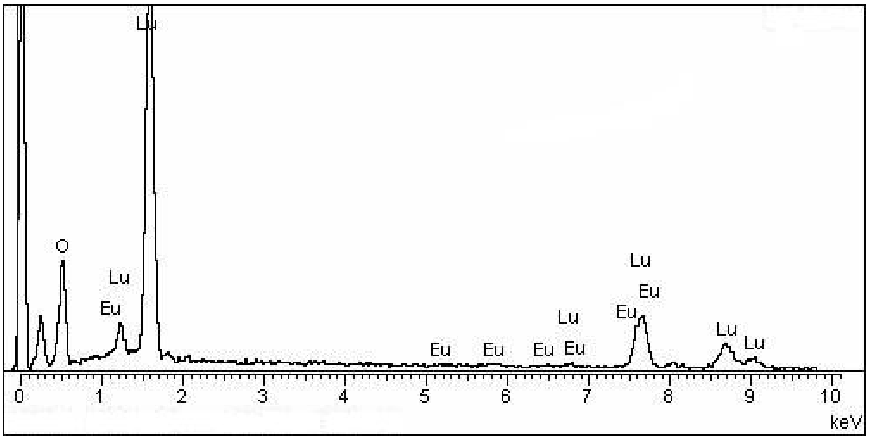

Fig. S3 EDS spectrum of L1

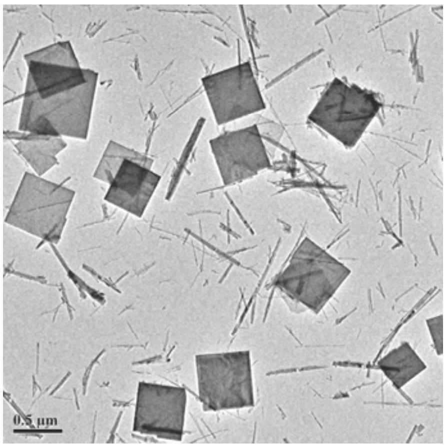

Fig. S4 TEM image of the as-synthesized sample by the hydrothermal treating of the Lu(OH)$_3$:Eu with the concentration of 0.028 M at PH=6 and 170 ℃ for 24 hours.

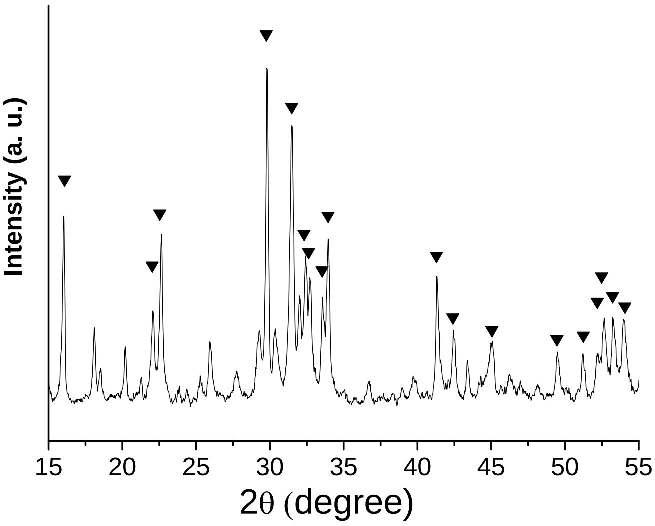

Fig. S5 Powder XRD pattern of L2’. ▼ indicates the diffraction peaks of monoclinic LuOOH.

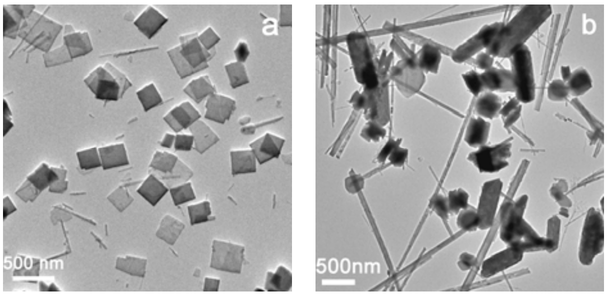

Fig.S6 TEM images of L1’ (a) and L2’ (b).

Text 1. Formation of nanoflakes, nanoquadrels and nanorods prepared by the hydrothermal treatment

Hydrothermal methods have been shown to be effective in the synthesis of nanowires, nanorods and nanocubes.[1-2] In our cases, although the exact formation mechanisms of these nanostructures are still unclear, it is believed that their growths are not assisted by a catalyst and also not directed by a template. It is likely that the growths of nanoflakes, nanoquadrels and nanorods are governed by a solution-solid process (SS). In our experiments, the colloidal precursors were made by adding the $Lu(NO_3)_3$ and $Eu(NO_3)_3$ mixed solution into NaOH solution. This process is a rapid adjustment of the pH value of the $Lu(NO_3)_3$ and $Eu(NO_3)_3$ solution, leading to the formation of a white precipitate (Figure S1 a) which immediately appears in a strong basic solution. This can be regarded as a similar process to the “injection” technique adopted by Peng, et al.[3] This method can ensure a higher monomer concentration so that the obtained precipitates will have many anisotropic seeds for the following hydrothermal treatment.

Figure S1-a shows the representative TEM micrograph of $Lu(OH)_3$:Eu colloidal precursors. The precursor $Lu(OH)_3$:Eu is composed of many nanoparticles with irregular morphologies whose sizes are about 10 nm or below. When the concentration of the $Lu(OH)_3$ colloid is 0.03 M, the “perfect” square nanoflakes are obtained via the hydrothermal treatment. Scheme 1a shows the formation process of square nanoflakes. The $Lu(OH)_3$ colloidal nanoparticles dissolve in water to form superstaturated solution and then the large numbers of the square seeds are formed which cling to the $Lu(OH)_3$ colloidal nanoparticles during the hydrothermal treatment. Subsequently, the small seeds grow into flake-like nanostructure through a dissolution-recrystallization process.[4] It is clear that the colloidal nanoparticles are precursors for the further crystal growth rather than ionic species, the SS mechanism has an analogy to the vapor-solid (VS) process for nanobelt growth.[5-6] The high pH values ensure the formation of completely square nanoflakes. When the pH value of the colloidal precursor is ~6, only a half of the obtained products via the hydrothermal treatment are nanoflakes and the others are nanorods (Figure S4).

Figure S1 b-e which are selected from Figure 1A show several special nanoflakes. It is clearly seen that there are two types of “abnormal” growing square nanoflakes in the as-synthesized product. One is nanoflake with only one side losing partly (Figure S1 b and c) and another is nanoflake with two sides losing partly (Figure S1 d and e). They seem to be growing into square nanoflakes. Thus, we think that they are intermediate objects during the nanoflakes growing. According to the observation and analysis, the different growth process of the nanoflake is proposed and illustrated in Scheme 1b. The schematic illustration of the growth mechanism called as “side wrapping” are based on the morphologies of several intermediate nanoflakes with one or two side losing partly. This growth mechanism of “side wrapping” is different from the “surface wrapping” which is used to explain the growth of Co_3O_4 nanocubes.[7] The model of “side wrapping” shows a logical repetition of two types of peculiar nanoflakes while the whole square structure is well maintained during the nanoflakes growing. According to the model, a smaller nanoflake grows into a bigger one via wrapping anisotropic seeds, arround coming from the supersaturated solution. Further investigations are being carried out to reveal the growth dynamics of square nanoflakes of lutetium compound.

When the concentration of the $Lu(OH)_3$ colloid is increased from 0.03 M to 0.09 M, the majority in the obtained products of L2 are nanoquadrels except very minor nanoflakes. The high-magnification FESEM image of L2 shows a single nanoquadrel with a sandwich-like structure (Figure 6). Although the actual formation process is not clear at present, it is obvious that the nanoquadrel in the center of the image is composed of four pieces of square nanoflakes via surface joints. Observing of the whole FESEM images (Supplementary material: Figure S2), it can be seen that the nanoquadrels are formed by 2-5 pieces of thin nanoflakes. Thus, it is considered that the square nanoflakes are the intermediate products during the formation process of nanoquadrels. The fact that some thin nanoflakes exist in the as-synthesized product of L2 (Figure 1C) can prove this conclusion. During hydrothermal treatment, a lot of nanoflakes develops, much more than those in sample L1, because of the higher concentration of the Lu(OH)$_3$ precursor. Overfull nanoflakes connected each other with surface joints of 2-5 pieces of nanoflakes via self-reorganization.

To test the concentration's effects, we greatly increased the concentration of the colloidal precursor to 0.32 M, the obtained product L3 (main LuOOH) is composed of many thin nanorods via the hydrothermal treatment. In this case, it is reasonable to imagine that the driving force for the anisotropic growth of LuOOH nanorods derives from the inherent crystal structure of LuOOH and their chemical potential in solution. The growth behavior of nanorods must be closely related to the intrinsic properties of LuOOH. At the same time, it was reported that it would be advantageous to have a higher chemical potential in the case of one-dimensional nanostructure growth.[8-9] A higher concentration of the colloidal precursor implies a higher concentration of Lu(OH)$_3$ nanoparticles, higher Na^+ and OH^- ion concentration and a higher chemical potential. A higher chemical potential is preferable for the growth of one-dimensional nanosized materials. Thus, many thin nanorods were obtained via the hydrothermal treating of the colloidal precursor with higher concentration. Simultaneously, a higher chemical potential makes Lu(OH)$_3$ dehydrate to produce LuOOH. Thus, the obtained products via the hydrothermal treating of the colloidal precursor with lower concentration were partly or fully not in the form of LuOOH. The dehydration process is supposed to be: $Lu(OH)_3 \longrightarrow LuOOH + H_2O$. Furthermore, when the hydrothermal treatment was carried out at lower temperature, the obtained powder was crystallized Lu(OH)$_3$ powder, not LuOOH which is only obtained at higher temperature under hydrothermal conditions.

Text 2. Processing's effects on morphology

During our experiments, it is interesting to find that the morphologies of the as-synthesized products are different from those of the above products when the NaOH solutions were slowly added into the mixed Lu(NO$_3$)$_3$ and Eu(NO$_3$)$_3$ solutions and the other experiment conditions are completely consistent. For the converse processing, the as-synthesized product of L1' consists of not only "perfect" square nanoflakes but also some nanorods (Figure S6 a). Comparable to that of the as-synthesized L2, the morphology of L2' are very diverse (Figure S6 b). In addition to several nanoquadrels, there are nanorods, nanosheets and thick rods in the sample of L2'. Powder XRD pattern of L2' can show its phase of monoclinic LuOOH (Figure S5). This is also not consistent with the phase of L2 which only consists of a small quantity of LuOOH. Therefore, it can be concluded that we can't obtain nanosized powders of lutetium compounds with uniform morphology via the hydrothermal treatment of the colloidal $Lu(OH)_3$ precursor by slowly adding NaOH solution being slowly added into $Lu(NO_3)_3$ solution. When $Lu(NO_3)_3$ solution was slowly added into NaOH solution, the colloid was rapidly formed at a very high pH. This process similar to the 'injection' technique can ensure the obtained precipitates having many anisotropic seeds. However, the white precipitates which happened at pH = ~6 were gradually formed only when NaOH solution was slowly added into the $Lu(NO_3)_3$ solution. Apparently, this process can provide fewer anisotropic seeds than its converse process.[3]

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