Author(s): Prakasam, Balasubramaniam Arul; Lahtinen, Manu; Peuronen, Anssi; Muruganandham, Manickavachagam; Sillanpää, Mika

Title: Facile fabrication of flower like self-assembled mesoporous hierarchical microarchitectures of In(OH)3 and In2O3: In(OH)3 micro flowers with electron beam sensitive thin petals

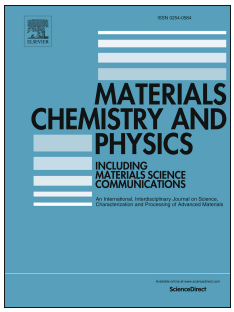
Year: 2016

Version:

Please cite the original version:

Prakasam, B. A., Lahtinen, M., Peuronen, A., Muruganandham, M., & Sillanpää, M. (2016). Facile fabrication of flower like self-assembled mesoporous hierarchical microarchitectures of In(OH)3 and In2O3: In(OH)3 micro flowers with electron beam sensitive thin petals. Materials Chemistry and Physics, 184, 183-188. https://doi.org/10.1016/j.matchemphys.2016.09.040

Accepted Manuscript



Facile fabrication of flower like self-assembled mesoporous hierarchical microarchitectures of $In(OH)_3$ and In_2O_3: $In(OH)_3$ micro flowers with electron beam sensitive thin petals

Balasubramaniam Arul Prakasam, Manu Lahtinen, Ansssi Peuronen, Manickavachagam Muruganandham, Mika Sillanpää

PII: S0254-0584(16)30703-9

DOI: 10.1016/j.matchemphys.2016.09.040

Reference: MAC 19186

To appear in: *Materials Chemistry and Physics*

Received Date: 29 January 2016

Revised Date: 10 July 2016

Accepted Date: 12 September 2016

Please cite this article as: B. Arul Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham, M. Sillanpää, Facile fabrication of flower like self-assembled mesoporous hierarchical microarchitectures of $In(OH)_3$ and In_2O_3: $In(OH)_3$ micro flowers with electron beam sensitive thin petals, *Materials Chemistry and Physics* (2016), doi: 10.1016/j.matchemphys.2016.09.040.

Facile fabrication of flower like self-assembled mesoporous hierarchical microarchitectures of $In(OH)_3$ and In_2O_3: $In(OH)_3$ micro flowers with electron beam sensitive thin petals

Balasubramaniam Arul Prakasam [a*], Manu Lahtinen [b], Ansssi Peuronen [b], Manickavachagam Muruganandham [c], Mika Sillanpää [a]

[a] *Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland*

[b] *Department of Chemistry, Laboratories of Inorganic and Analytical Chemistry, P.O.Box 35, FI-40014 , University of Jyväskylä, Finland*

[c] *Department of Civil and Environmental Engineering, Temple University, Philadelphia, PA 19122, USA*

ABSTRACT

A template and capping-reagent free facile fabrication method for mesoporous hierarchical microarchitectures of flower-like $In(OH)_3$ particles under benign hydrothermal conditions is reported. Calcination of $In(OH)_3$ to In_2O_3 with the retention of morphology is also described. Both $In(OH)_3$ and In_2O_3 microstructures were analyzed with SEM, EDX, TEM and powder X-ray diffraction. The crystal sizes for $In(OH)_3$ and In_2O_3 were calculated using the Scherrer

* Corresponding author.

E-mail address: arul7777@yahoo.com (B. Arul Prakasam).

equation. In $In(OH)_3$ the thin flakes at the periphery of micro flowers were electron beam sensitive. The mechanism of self-assembly process was analyzed as well.

Keywords: Microstructure; Oxides; Semiconductors; Microporous materials

1. Introduction

Micro structured materials show a clear correlation between their morphology and function, which in turn decides their applications. Micro/superstructures with good interconnectivity and conductivity are useful in several fields [1]. As size and shape of materials are controlling factors, thereby influencing to the physical and chemical properties, it is natural that the synthesis of materials with fascinating morphologies is of researchers' interest. In particular, porous hierarchical architectures with interesting applications are materials of wide importance. Synthesis methods based on a hydrothermal process are especially beneficial due to its simplicity and modifiability, and also it is environmentally benign. In surfactant-free, simple hydrothermal process crystals as large as a few micrometers can be obtained simply by extending the reaction period under controlled conditions.

In_2O_3 is an *n*-type semiconductor with the band gap of 3.6 eV, and has applications in optoelectronics [2], touch screens [3] and in photocatalysis [4]. It is also used as a sensor for H_2 [5, 6], Cl_2 [7], O_3 [8], CO_2 [5] and NO_2 [6] gases. Since the conversion of $In(OH)_3$/InOOH to In_2O_3 was found to proceed with a retention of morphology, the morphological regulation of In_2O_3 depends on its precursors [9-19]. Furthermore, research on metal hydroxides is still relatively limited compared to metal oxides and sulfides. In an attempt to prepare morphologically interesting $In(OH)_3$ and In_2O_3 structures, herein we report template and capping-reagent free hydrothermal synthesis of flower like $In(OH)_3$ microstructures and its

conversion to In_2O_3. To the best of our knowledge this is the first report on the synthesis of mesoporous hierarchical microarchitectures with a flower-like morphology for both $In(OH)_3$ and In_2O_3.

2. Experimental

2.1. Hydrothermal synthesis and calcination

Milli Q-Plus water (resistance = 18.2 M•Ω) was used for all experimental work. $In(OH)_3$ microstructures with a flower-like morphology were prepared using indium nitrate (3 g, 10 mmol) and biuret (6.2 g, 60 mmol). Both were separately dissolved in about 100 mL of water and heated to the boiling point. The hot solutions were mixed under stirring (200 rpm), and after 30 min the mixture was transferred into a 250 mL Teflon cup. The sealed Teflon vessel was put into a stainless steel flask and kept in an autoclave at 200 °C for 15 h. After hydrothermal reaction, the flask was allowed to cool to room temperature and the precipitate was filtered, washed with water and alcohol to eliminate the possible impurities. It was then dried in an air oven at 120 °C for 2 h. In the next step In_2O_3 micro flowers were prepared by calcining the precursor at 450 °C for 3h in a hot air oven. The oven was allowed to cool down to room temperature and the sample was collected. In an alternative process, first the reaction temperature was decreased respectively to 150 °C within 10 h time. The total quantity of water was about 150 ml for preparing In(OH)3 microcubes. The subsequent calcination was made at 450 °C for 3h to yield porous In_2O_3 microcubes. This paper focuses only on the characterization of mesoporous hierarchical microarchitectures of $In(OH)_3$ and In_2O_3, as micro cube morphology has been well reported [9, 16, 18, 19]. The experimental part reports only the optimized

experimental conditions in which uniform morphologies are observed, and the conditions which yielded inhomogeneous morphologies were deliberately avoided.

2.2. Characterization

The morphology was examined using a Hitachi S-4100 scanning electron microscope (SEM). Prior to SEM measurements, the samples were mounted on a carbon platform that was then coated with platinum using a magnetron sputter for 10 minutes. The In/O ratio within the sample was analyzed using an energy-dispersive X-ray spectrophotometer installed in the SEM. For the transmission electron microscope (TEM) study, the sample was dispersed onto a Cu grid with holey carbon supporting film and studied at room temperature in a FEI Tecnai 12 microscope operated at 120 kV. The powder X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance diffractometer (Cu $K_{\alpha 1}$ source, λ= 1.5406 Å) with step size of 0.01° 2θ and step time of 0.5 sec. The specimen was prepared on a silicon zero-background holder using petrolatum jelly as an adhesive.

The Scherrer equation was used for assaying the crystal size of the substances. Obtained values were corrected by the instrumental broadening which was determined by highly crystalline corundum sample measured with the same instrument settings.

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

wherein D stands for average size of the crystals, K as shape-dependent Scherrer's constant (0.9), λ as radiation wavelength (1.5406 Å), and β as FWHM of the peak profile subtracted by instrumental broadening; given in radians. Qualitative and semi-quantitative phase

analysis (reference intensity ratio method; RIR) and Scherrer equation based crystal size estimations were all made by the HighScore Plus program v 4.5 [20].

Nitrogen sorption isotherms were measured at 77 K using a Quantachrome Nova-1000 instrument. The Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model were used for specific surface area calculation and porosity evaluation, respectively. The sample was degassed at 175 °C before analysis.

3. Results and Discussion

3.1. SEM and TEM studies

The hydrothermal reaction products present flower-like morphology in the diameter range of 2 to 3.5 µm, as evidenced by SEM images (Fig. 1). These microstructures are 3D hierarchical structures assembled from nano-sized flakes with the thickness of about 30 to 50 nm (Fig. 1d). The results from the EDX spectrum (Fig. SM1) suggest formation of $In(OH)_3$ as the determined In/O ratio is close to 1:3; which is further confirmed unambiguously by the powder X-ray diffraction (see following sections). TEM images (Fig. 2) of the hydrothermal products indicate that the micro flowers are composed of thin flakes which are devoid of specific size. These flakes at the periphery of the micro flowers are electron beam sensitive. When the sample was irradiated with high energy electron beam (TEM), pore structures are formed due to decomposition, as shown in Fig. 2e-f. It should also be noted that the similar flake-like structures in In_2O_3 micro flowers are stable under TEM experimental conditions (discussed subsequently), and hence the formation of pores under electron beam for $In(OH)_3$ microstructures may be due to a dehydration process induced by the beam. It is interesting to note that the similar decomposition (and thereby the formation of porous structures, which are called mesocrystals

[21]) has been reported recently [16]. These mesocrystals or otherwise known as colloidal crystals and are found to have interesting applications due to their larger surface area [16].

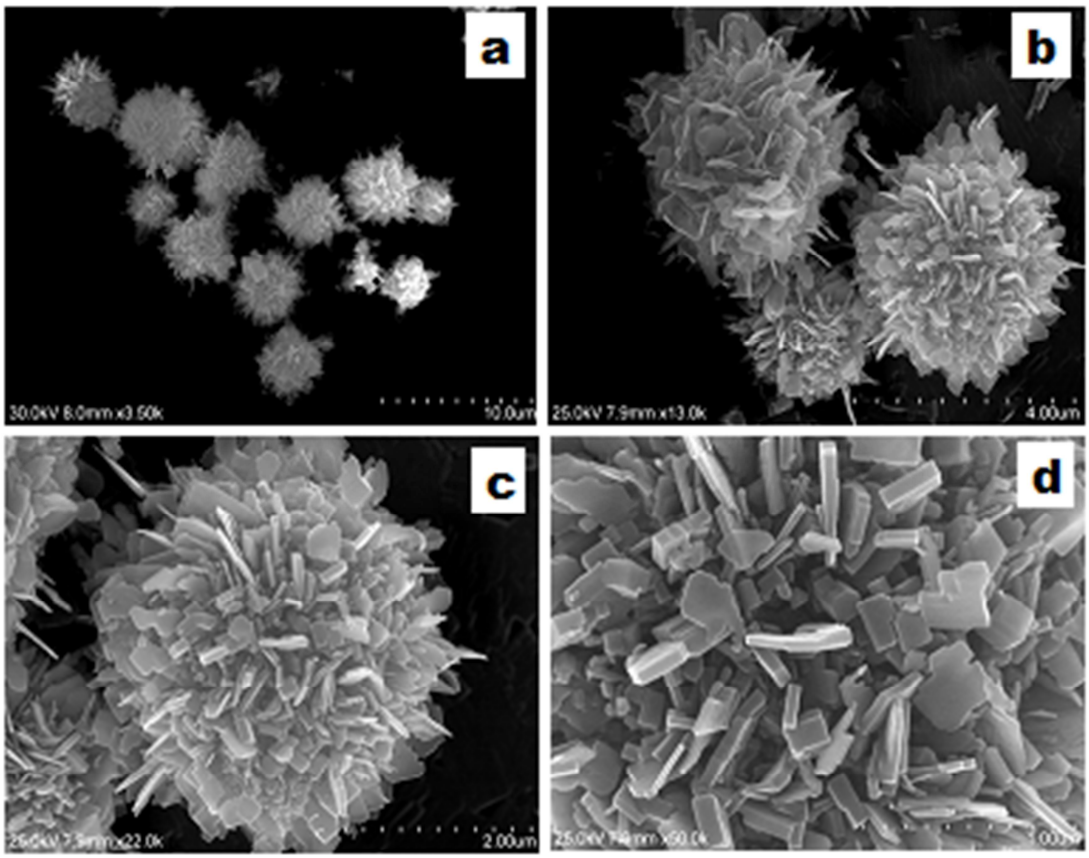


Fig. 1. SEM images of (a-c) $In(OH)_3$ micro flowers; (d) Micro flower composed of thin flakes.

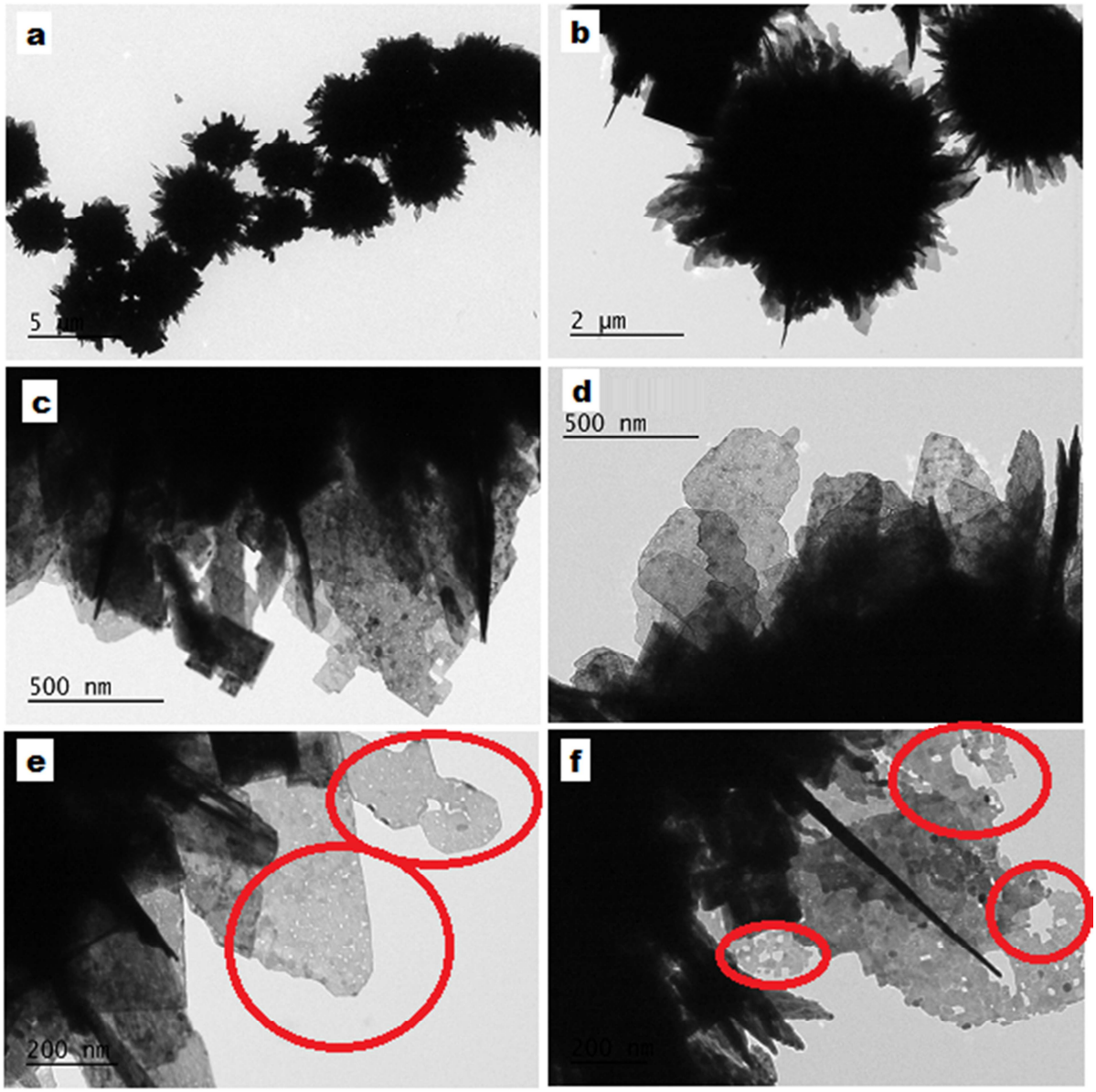


Fig. 2. TEM images of (a-b) $In(OH)_3$ micro flowers; (c-d) Flakes at the periphery of the micro flowers; (e-f) Electron beam induced formation of pore structures.

The EDX spectrum of calcination product (Fig. SM2) indicates that In_2O_3 has been formed as the In:O ratio is close to 2:3. From SEM images (Fig. 3) it can be observed that porous microstructures were formed as, by calcination with the retention of flower like morphology. It was also observed that the micro flowers are composed of nano flakes which are thin and curly

(Fig. 3f) instead of irregularly shaped as in the case of the precursor ($In(OH)_3$). High-magnification TEM images (Fig. 4) (Fig. 4d) evidence the porous nature of calcinated product. These pores are due to dehydration from $In(OH)_3$. The low-magnification TEM images (Fig. 4a-c) exemplify the flower like morphology and the thick nucleus of the microstructures. The SEM images of $In(OH)_3$ and In_2O_3 micro cubes are shown in Fig. 5a and b respectively. As discussed in the experimental part the discussions were limited to micro flower architectures.

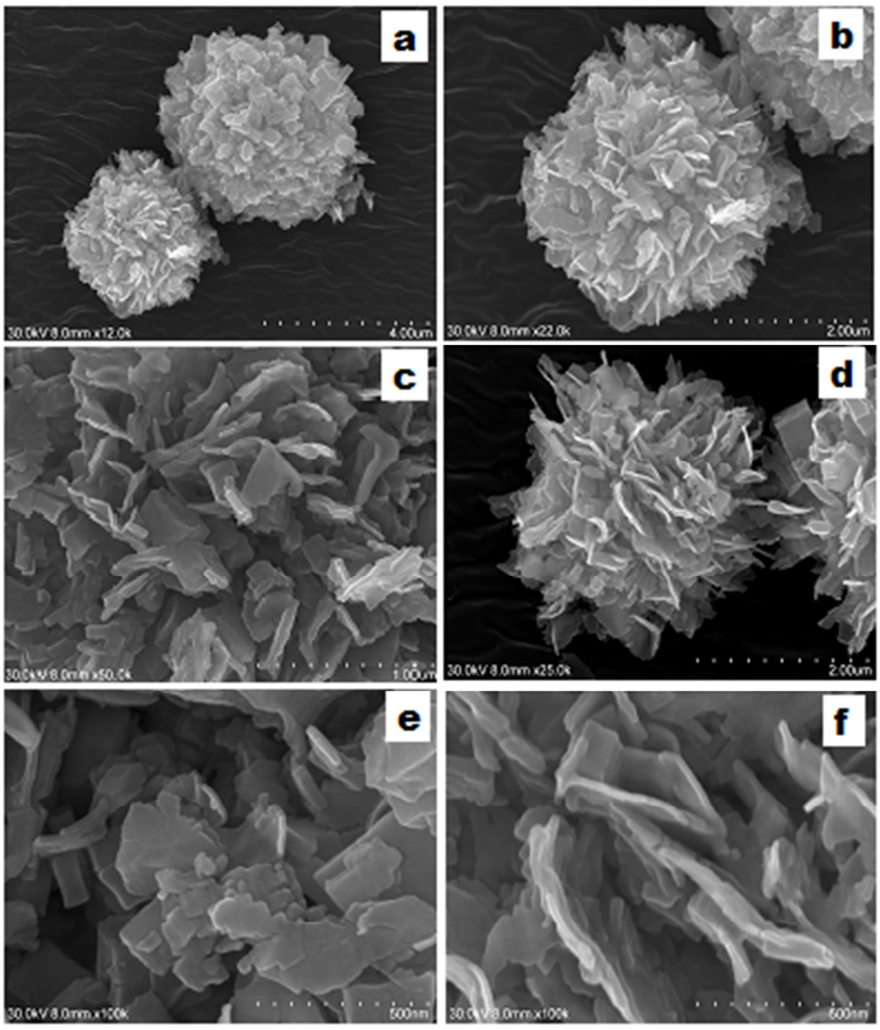


Fig. 3. SEM images of (a-b) In_2O_3 micro flowers; (c-f) Thin and curly nano flakes present in micro flower morphology.

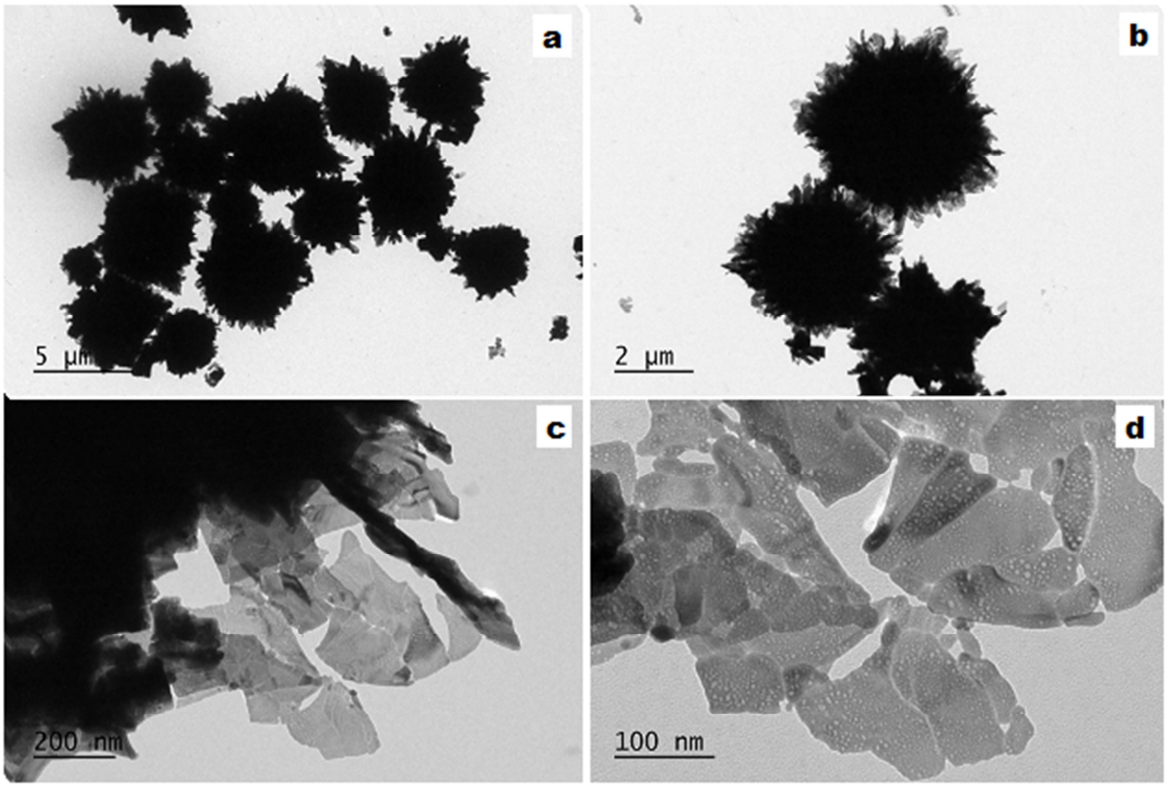


Fig. 4. TEM images of (a-b) In_2O_3 micro flowers; (c) Flakes at the periphery of micro flowers; (d) Porous petals of In_2O_3 micro flowers (pores formed by calcination).

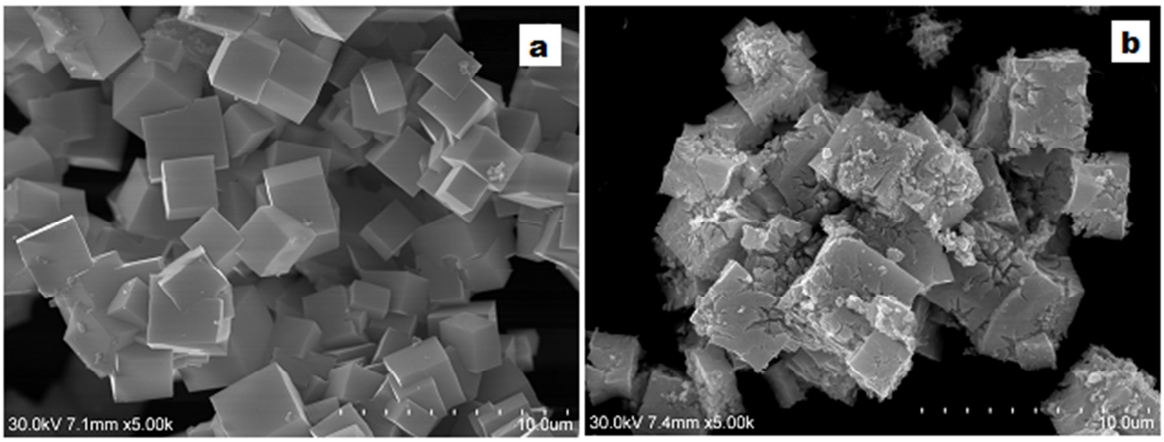


Fig. 5. SEM images of (a) $In(OH)_3$ micro cubes with smooth surface; (b) In_2O_3 micro cubes with porous surface.

3.2. Powder XRD analysis

The powder X-ray diffraction pattern of the hydrothermal product indicates that its main component is cubic $In(OH)_3$, as all the significant diffraction peaks correspond to the ICDD [22] reference pattern 01-085-1338 (Fig. 6a) [23]. In addition, few weak peaks e.g. at 25.93° and 33.97° 2θ indicate that a small amount of orthorhombic InO(OH) [ICDD: 04-010-2484] exist in the sample [24]. Simple semi-quantitative analysis with the reference intensity ratio method (RIR) indicates about 3 % weight fraction for the minor component. Typically InO(OH) is regarded as a metastable form. However, it has been reported that excess of OH^- ions is key factor for favoring formation of $In(OH)_3$ over InO(OH) [16], which in our case may have been the compensating factor for the pressurized conditions prevailing in the hydrothermal process. XRD analysis of calcination product confirms that impurity free cubic In_2O_3 [ICDD: 04-014-4391] [25] is formed (Fig. 6b). Crystal size determinations were made both for $In(OH)_3$ and In_2O_3 samples with the Scherrer method. Three representative isolated peaks at 31.91°, 39.29° and 51.38 2θ with Miller indices of (220), (222) and (420) for $In(OH)_3$, and at 30.79°, 35.67° and 51.23° with indices of (222), (400) and (440) for In_2O_3 were used in the analyses. In the case of $In(OH)_3$ sample, the assigned peaks gave average crystal sizes of 145, 104 and 101 nm, respectively. For In_2O_3 sample crystal sizes were found to be 41, 38 and 32 nm, indicating significant decrease in crystal size between the hydrothermal and the calcination product. The observed difference in XRD results for $In(OH)_3$ and In_2O_3 micro flowers are in line with the electron microscopic study conclusions presented in the previous section, where the thin and curly nano-flakes formation was evidenced after calcination.

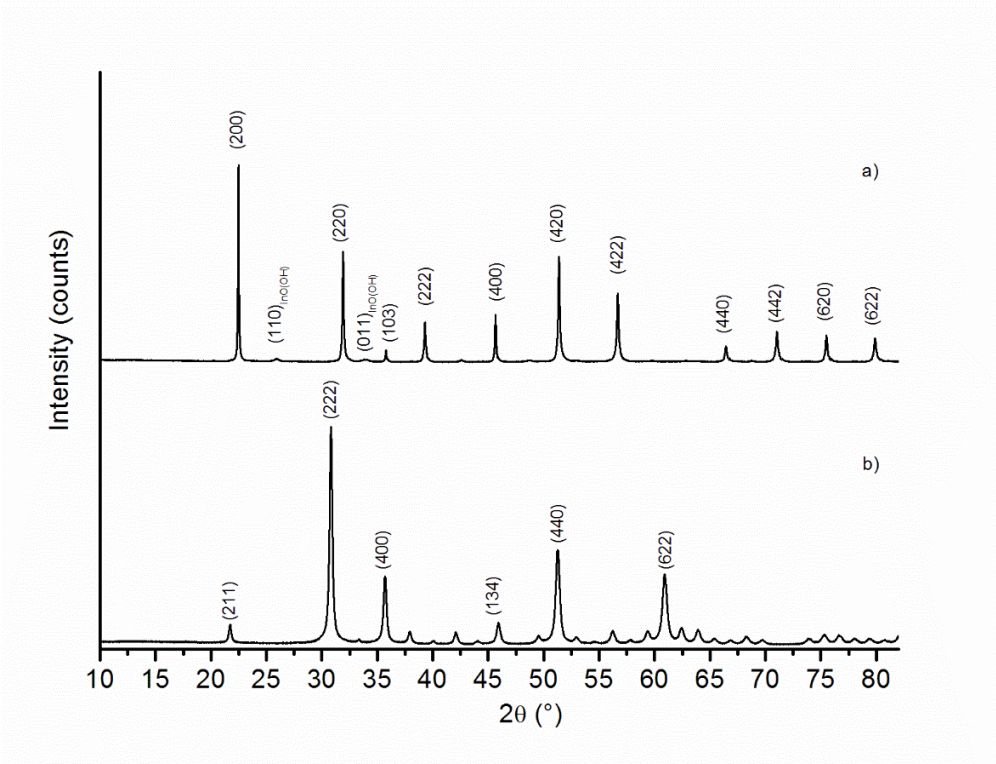


Fig. 6. Experimental powder X-ray diffraction patterns of a) $In(OH)_3$ and b) In_2O_3 micro flowers.

3.3. Surface area analysis

Fig. 7 shows the typical sorption isotherms of In_2O_3 microflowers. The prepared In_2O_3 microflowers exhibited a hysteresis loop in a high relative pressure range of 0.57-0.97, which is characteristic of type IV isotherm, evidenced the presence of mesopores. The BET surface area is found to be 46.84 $m^2 g^{-1}$. The total pore volume is 0.07921 $cm^3 g^{-1}$ and the average pore diameter is 67.6 Å. The observed results exemplified the mesoporous nature of In_2O_3 micro flowers.

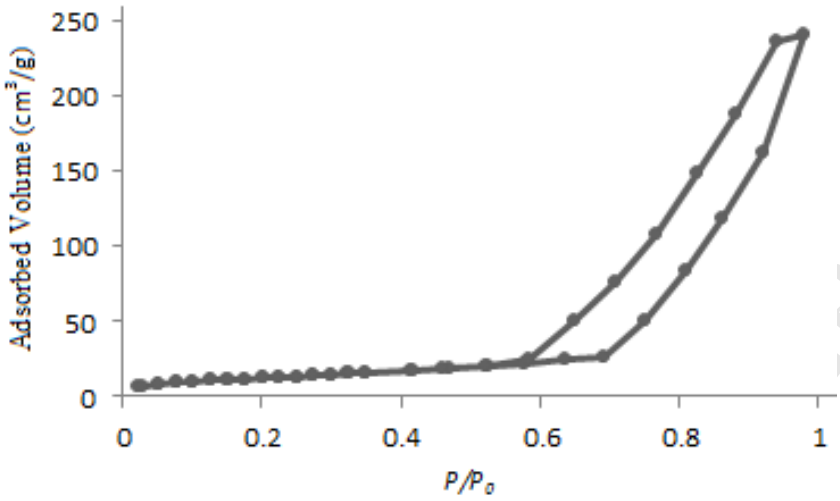


Fig. 7. Nitrogen adsorption-desorption isotherm of In_2O_3 micro flowers.

3.4. Role of biuret and product formation

The triple role of urea (surface anchored organic molecule; chelating agent) as an alkaline medium has been recently been reported [9], and in this study biuret is used instead as it is expected to have a similar role. The formation of $In(OH)_3$ is expected to proceed according to equations 1-3, and calcination of $In(OH)_3$ to In_2O_3 by eq. 4.

$$NH_2CONHCONH_2 + 2\ H_2O \rightarrow 3NH_3 + 2CO_2 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$In^{3+} + 3OH^- \rightarrow In(OH)_3 \quad (3)$$

$$2\ In(OH)_3 \rightarrow In_2O_3 + 3H_2O \quad (4)$$

In both the cases, after reactions under hydrothermal conditions, the resulting $In(OH)_3$ is supersaturated in the solution. Followed by nucleation (Fig. 7), the self-assembly of particles proceeds in such way that surface energy will be minimum and hence the thermodynamically

driven Ostwald ripening could be the process which results in stable larger crystals. The energetically unfavorable small particles are dilute in solution thereby easing the formation of larger (micro) structures with least surface energy. It was already reported that the similar process was the key factor behind the formation of cubic $In(OH)_3$ microstructures [9] and it is the key process which determines the morphology of the final products in template free hydrothermal reactions [26].

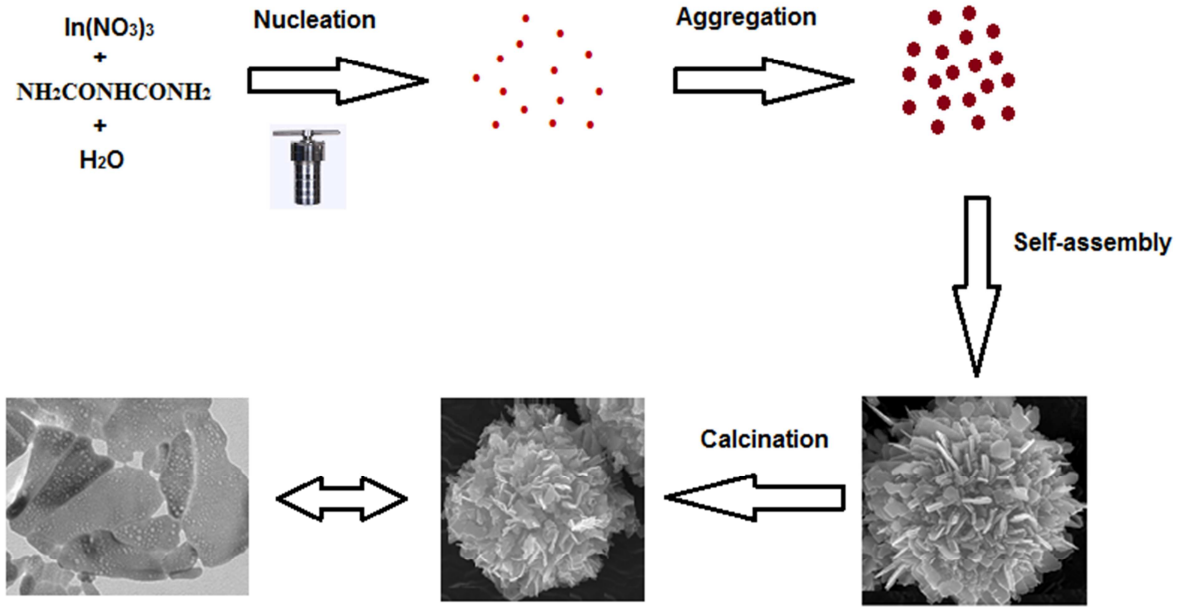


Fig. 8. Schematic formation of $In(OH)_3$ and In_2O_3 micro flowers.

4. Conclusions

Hydrothermal fabrication of mesoporous hierarchical microarchitectures of $In(OH)_3$ with a flower like morphology using indium nitrate and biuret is reported. Biuret is expected to have a triple role as alkaline media, chelating agent and surface anchored organic molecule. The plausible mechanism for the formation of hierarchical architectures of $In(OH)_3$ might be Ostwald

ripening. Calcination of $In(OH)_3$ results in mesoporus In_2O_3 hierarchical architectures. For In_2O_3 the average crystal size is ~ 37 nm. The hierarchical microarchitectures of $In(OH)_3$ and In_2O_3 are interesting candidates for photocatalytic and sensing applications due to their porosity as well as larger surface area.

References

[1] W. L. Noorduin, A. Grinthal, L. Mahadevan, J. Aizenberg, Science, 340 (2013) 832-837.

[2] H. Cao, X. Qiu, Y. Liang, Q. Zhu, M. Zhao, Appl. Phys. Lett. 83 (2003) 761-763.

[3] S. Parthiban, K. Ramamurthi, E. Elangovan, R. Martins, E. Fortunato, Appl. Phys. Lett. 94 (2009) 212101.

[4] B. Li, Y. Xie, M. Jing, G. Rong, Y. Tang, G. Zhang, Langmuir, 22 (2006) 9380-9385.

[5] W. Y. Chung, G. Sakai, K. Shimanoe, N. Miura, D. D. Lee, N. Yamazoe, Sens. Actuator B, 46 (1998) 139-145.

[6] M. Liess, Thin Solid Films, 410 (2002) 183-187.

[7] J. Tamaki, C. Naruo, Y. Yamamoto, M. Matsuoka, Sens. Actuator B, 83 (2002) 190-194.

[8] E. Gagaoudakis, M. Bender, E. Douloufakis, N. Kataarakis, N. Natsakou, V. Cimalla, G. Kiriakids, Sens. Actuator B, 80 (2001) 155-161.

[9] Z. He, Z. Chen, Y. Li, Q. Zhang, H. Wang, CrystEngComm. 13 (2011) 2557-2565.

[10] H. Y. Lai, T. H. Chen, C. H. Chen, CrystEngComm. 14 (2012) 5589-5595.

[11] Z. Li, Y. Li, Y. Luan, J. Li, A. Song, CrystEngComm. 15 (2013) 1706-1714.

[12] J. Zai, J. Zhu, R. Qi, X. Qian, J. Mater. Chem. A, 1 (2013) 735-745.

[13] S. Guo, X. Zhang, Z. Hao, Z. Gao, G. Li, L. Liu, RSC Adv. 4 (2014) 31353-31361.

[14] D. Han, P. Song, H. Zhang, H. Yan, Q. Xu, Z. Yang, Q. Wang, RSC Adv. 4 (2014) 50241-50248.

[15] J. Yang, C. Lin, Z. Wang, J. Lin, Inorg. Chem. 45 (2006) 8973-8979.

[16] Z. Zhuang, Q. Peng, J. Liu, X. Wang, Y. Li, Inorg. Chem. 46 (2007) 5179-5187.

[17] D. V. Shinde, D. Y. Ahn, V. V. Jadhav, D. Y. Lee, N. K. Shrestha, J. K. Lee, H. Y. Lee, R. S. Mane, S. H. Han, J. Mater. Chem. A, 2 (2014) 5490-5948.

[18] X. Liu, L. Zhou, R. Yi, N. Zhang, R. Shi, G. Gao, G. Qiu, J. Phys. Chem. C, 112 (2008) 18426-18430.

[19] Q. Wu, J. Chen, F. Zhang, P. Xiao, Y. Lu, X. Wang, Z. Hu, CrystEngComm. 14 (2012) 3397-3403.

[20] HighScore Plus 4.1, 2014, PANalytical B V Almelo, The Netherlands.

[21] H. Colfen, M. Antonietti, Angew. Chem. Int. Ed. 44 (2005) 5576-5591.

[22] International Centre for Diffraction Data, ICDD-PDF4+, Release 2014, 12 Campus Boulevard, Newton Square, Pennsylvania USA, 2014.

[23] A. N. Christensen, N. C. Broch, O. von Heidenstam, A. Nilsson, Acta Chem. Scand. 21 (1967) 1046-1056.

[24] A. N. Christensen, R. Gronbaek, S. E. Rasmussen, Acta Chem. Scand. 18 (1964) 1261-1266.

[25] J. Popovic, E. Tkalcec, B. Grzeta, C. Goebbert, V. Ksenofontov, M. Takeda, Z. Kristallogr. S26 (2007) 489-494.

[26] W. Shi, S. Song, H. Zhang, Chem. Soc. Rev. 42 (2013) 5714-5743.

- Hydrothermal fabrication $In(OH)_3$ self-assembled porous hierarchical architectures.
- Induced dehydration in beam sensitive $In(OH)_3$ micro flowers.
- Calcination of $In(OH)_3$ to In_2O_3 with the retention of flower like morphology.
- Phase pure synthesis of In_2O_3 with the average crystal size of ~ 37 nm.