

## The preparation of core-shell structural ZnO@4A nano-materials

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**Abstract:**Core-shell structural material has received much attention, this materials are different from the symbiotic synthesized two phase molecular sieve, but has ordered core-shell structure which retains the composition characteristics of the molecular sieve and has a variety of active center and dual channel structure. This work systematically expounded the synthesizing and characterizing results of core-shell material ZnO@4A. In this article, we used guiding agent method to synthesize 4A molecular sieve particle which morphology size between 200-300nm. Experimental aging time, template agent dosage and crystallization time effecting on 4A molecular sieve synthesis were investigated. Then two-step method was used to synthesize nano-ZnO which features diameter between 400-600nm. Layer by layer poly-electrolyte method(LBL) was adopted to get ZnO@4A, XRD, SEM and Energy Disperse Spectroscopy(EDS) were carried out to give its character.

### Introduction

Nano-porous material composed of zeolite molecular features mutual cross-linking pore canal has a selectivity for different molecular of different size. Multifarious pore size, morphology, extending structure and framework give zeolite molecular unique properties based on which are used in realm like catalyzing, ion exchanging, gas and liquid separating as well as adsorbent[1, 9].

LBL can achieve either coating polymer on inorganic nano-particle to realizing its capisulazed or coating in converse order to forming size controllable organic/inorganic materials. LBL is a way of using, firstly, static electricity self-assemble a layer of poly electrolyte on inorganic particles or poly micro-balls and then put it into the opposite charge solution of a chosen materials. Through static electricity interaction over the boundary, inorganic particles or poly micro-balls can then attached to the other micro-balls. The warped particles can finally achieve products size controllable after several times of washing, centrifuging and warping. This experimenting way features this whole package:diameter controllable, wide range of shell materials are optional etc. Polystyrene(PS) and mesoporous SiO<sub>2</sub> have widely been used as the template of core-shell materials[10]. Wang adopt PS as a template using alternative absorption method of cationic poly-electrolyte proptyene chloride amine(PAH) and anionic polyelectrolyte poly sodium styrene sulfonate(PSS) to absorb SiO<sub>2</sub> nano-sphere, they obtained mult-coated hybrid porous micro-balls materials after its further hydrolysis of tetrabutyl titanate and its removal of PS template. Caruso used LBL method had achieved a various coating of materials like SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub> on the surface of inorganic particles.

In this work, preparation of core-shell structural ZnCl<sub>2</sub>@4A has been investigated, guiding agent method was firstly adopted to synthesize 4A molecular sieve and using XRD to ensure it was our target products, factors like experimental aging time, template agent dosage and crystallization time among which may have influence on the size distribution、crystallization and dispersion of the sample were studied, SEM were adopted to analyzing the samples in the purpose of finding out size controllable factors and checking our desired products were successfully synthesized. Then, using two-step method to synthesizing nano-ZnO and by ways of XRD and SEM to make sure it is the core material we needed. Lastly, LBL was adopted to synthesizing ZnO@4A materials. EDS, XRD and SEM were employed to make a confirmation whether we had gone through our work.

## Experiment section

### Materials

Diethylene glycol(DEG),  $\text{Na}_2\text{SiO}_3$ ,  $\text{Zn}(\text{Ac})_2$  and sodium hydroxide were provided by Tianjing Zhiyuan Chemical Company of China. Sodium metal-aluminate was obtained from Chemical Reagent Company. Tetramethyl ammonium hydroxide( $\text{TMAOH} \cdot 5\text{H}_2\text{O}$ ) was purchased from Aladdin Chemical Company.

### Experimental procedure

#### Guiding agent method to synthesis 4A molecular sieve

The preparation of 4A molecular sieve was carried out at a certain molar ratio of  $3.165\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.926\text{SiO}_2:128\text{H}_2\text{O}:\text{Al}_2\text{O}_3:\text{TMAOH} \cdot 5\text{H}_2\text{O}=1:1;n(\text{NaAlO}_2)=0.0758\text{mol}$ . Firstly,  $0.732\text{g}$   $\text{NaOH}$  was dissolved into  $70\text{mL}$  deionized water and divided into two parts noted as solution A and B. Then,  $\text{NaAlO}_2$  and  $\text{TMAOH} \cdot 5\text{H}_2\text{O}$  were slowly and orderly added into A together with magnetic stirring for several minutes to get transparent solution and  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  was slowly added into B at  $35^\circ\text{C}$  with stirring to get another transparent solution. Treating each new solutions with ultrasonic processing  $3\text{ min}$  and quickly pour B into A with stirring for  $45\text{min}$  together with ultrasonic processing for  $15\text{mins}$  to get initial gel. Finally, putting the gel into  $50\text{mL}$  hydro-thermal reaction kettle to proceeding crystallization, calcine was eventually used to get 4A molecular sieve.

#### Two-step method synthesise nano-ZnO

1. Having  $0.03\text{mol}$   $\text{Zn}(\text{Ac})_2$  put into  $300\text{mL}$  DEG with stirring, then leaching for night to get layer distinguished solution and kept the upper solution.
2. Adding  $0.03\text{mol}$   $\text{Zn}(\text{Ac})_2$  into  $300\text{mL}$  DEG with stirring and rising temperature associated with refluxing. At  $150^\circ\text{C}$ , adding A's upper solution  $1\text{-}2\text{mL}$  drop-wisely and maintain  $160^\circ\text{C}$  for  $1\text{h}$ , then removing the heater and cooling down to room temperature.

#### Primary coating

Soaking nano-ZnO into  $0.1\text{mol/L}$   $\text{NaCl}$  solution(consists of  $0.3\%$   $\text{PPS}^-$ ) for  $20\text{min}$  and then centrifugation was used to separating the precipitate, rinsed with deionized water 3 times after which using  $0.1\text{mol/L}$   $\text{NaCl}$  solution(consists of  $0.3\%$   $\text{PDDA}^+$ ) to repeated the above procedure. Applying  $5\text{g}$  4A molecular sieve into  $20\text{g}$  deionized water with ultrasonic processing for  $1\text{h}$  and continuing add some deionized water to make it a  $5\%$  suspension, putting ZnO above into  $10\text{mL}$  suspension solution for  $20\text{min}$  and then took out precipitate washing 3 times with the deionized water.

#### Secondary growth

The primary coated products was dispersed in solution B, repeating the procedure of synthesizing molecular sieve to make sure the secondary sample grows well.

## Results and discussion

Table 1 The Synthetic Conditions of Samples

Sample Number	Aging time[h]	Crystallize time[h]	Dosage of template[g]
SSS-0	40°C Ultrasonic 4	4	6.8992
SSS-1	40°C stirring 12	4	6.8992
SSS-2	40°C stirring 24	4	6.8992
SSS-3	No aging	12	6.8992
SSS-4	No aging	4	6.8992
SSS-5	40°C Ultrasonic 4	4	10.3488

### Characterization of 4A molecular sieve

The 4A molecular sieve we gained were synthesized based on the condition of Table 1. XRD was firstly carried out on the phase analysis of 4A molecular sieve.

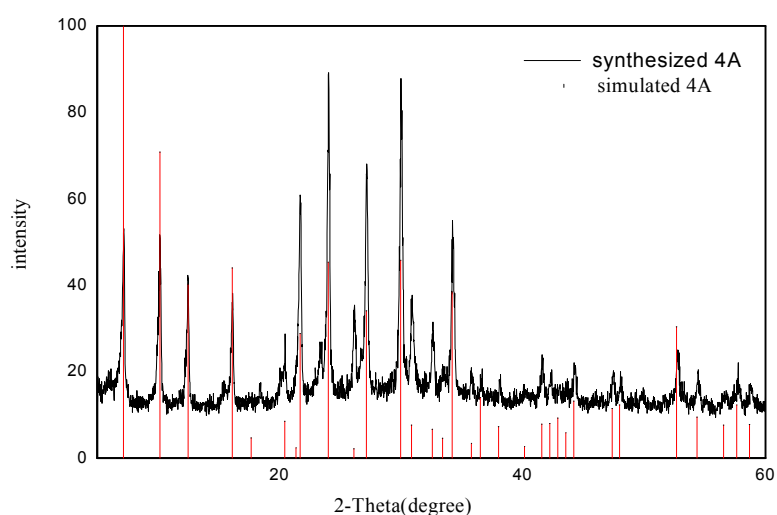
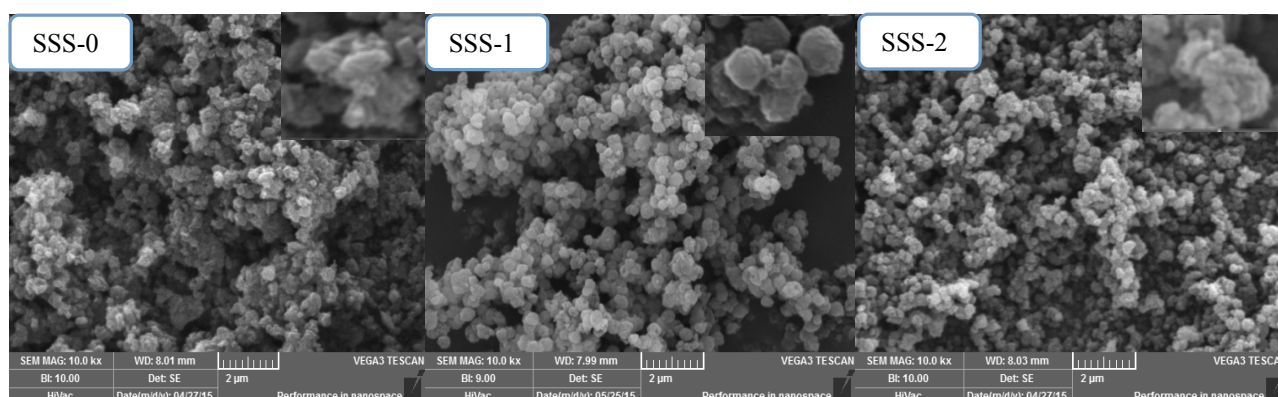


Fig. 1 XRD analysis of 4A molecular sieve (All sample went accord with this)

Figure. 1 shows the XRD patterns of 4A molecular sieve, it went well with the standard spectrogram which indicated we have successfully synthesized 4A molecular sieve.



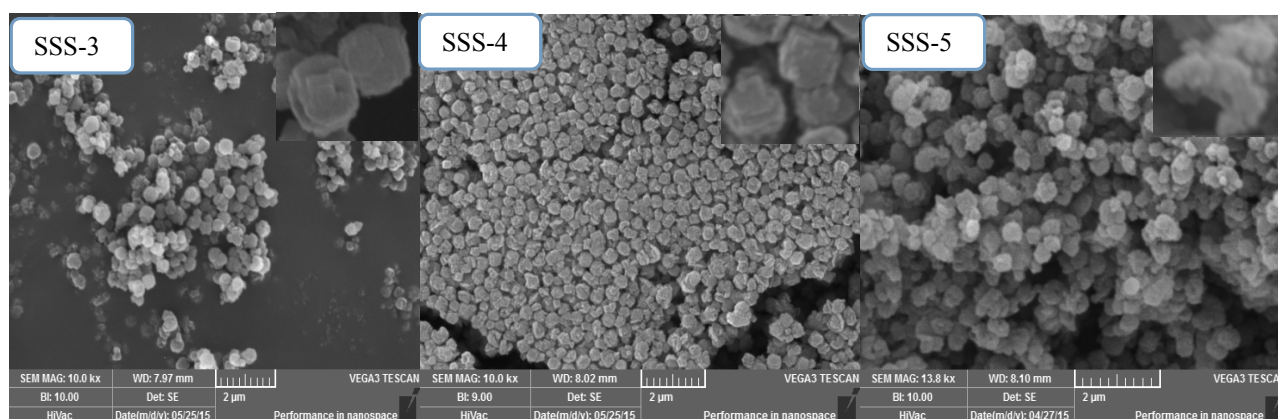


Fig. 2 SEM analysis of 4A molecular sieve

SEM was applied to characterizing samples from 0-5, Fig. 2 shows the morphology of the 4A sieve, it can be easily concluded from SSS-1 to SSS-2 that the appropriate aging time is 12h which gives sample good dispersibility and sphere-like morphology. Comparing sample SSS-3 with SSS-4, crystallizing time has a little influence on the crystallization. Comparing sample SSS-0 with SSS-5, as the dosage of template increasing there was no agglomeration improving but lead to size of 4A sieve increased, so we choose template quality as 6. 8992g.

### Characterization of ZnO

XRD was carried out on the phase analysis of nano-ZnO. Results were shown in Fig. 3.

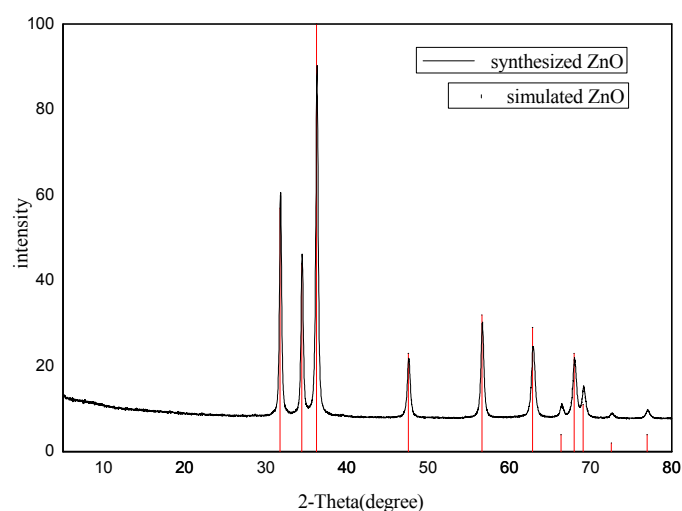


Fig. 3 XRD analysis result of nano-ZnO

It was found that ZnO diffraction peak matches the standard spectrogram very well which shows we have successfully synthesized ZnO, in order to find out its morphology, SEM was then adopted to characterize ZnO and the result shows in Fig. 4.

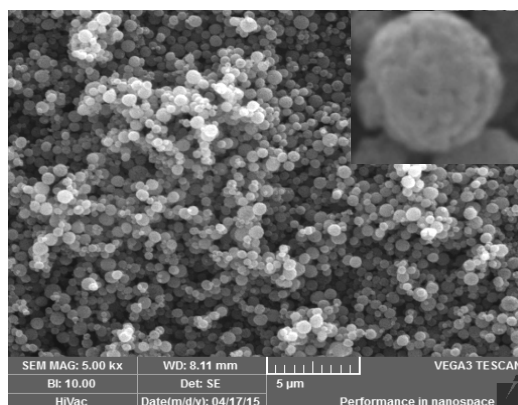


Fig. 4 SEM result of ZnO

Through Fig. 4, we can conclude that we have synthesized sphere-like ZnO features diameter between 400nm to 600nm and showed good dispersity which were surely met the requirements of core layer materials, synthesize of ZnO was very successful.

### Characterization of core-shell material

Based on the above discussion, we choose a relatively good sample SSS-1 to perform coating experiment of which SEM results represent initial coating and secondary growth were shown in Fig. 5 and EDS results were shown in Fig. 6.

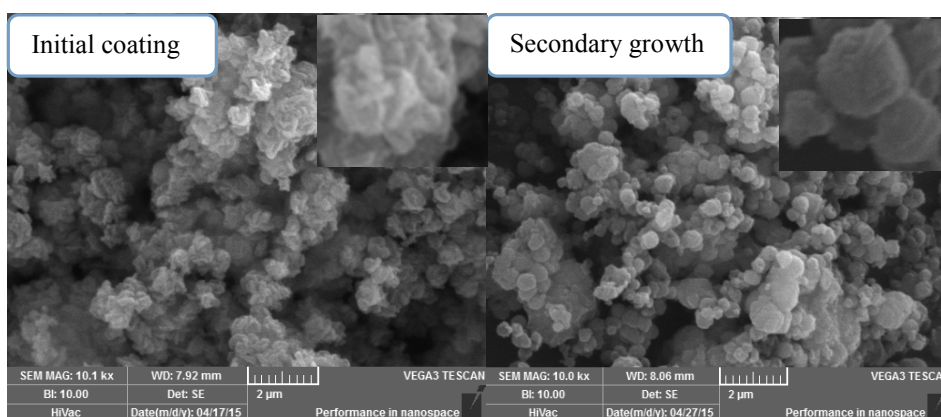


Fig. 5 SEM results for initial coating and secondary growth

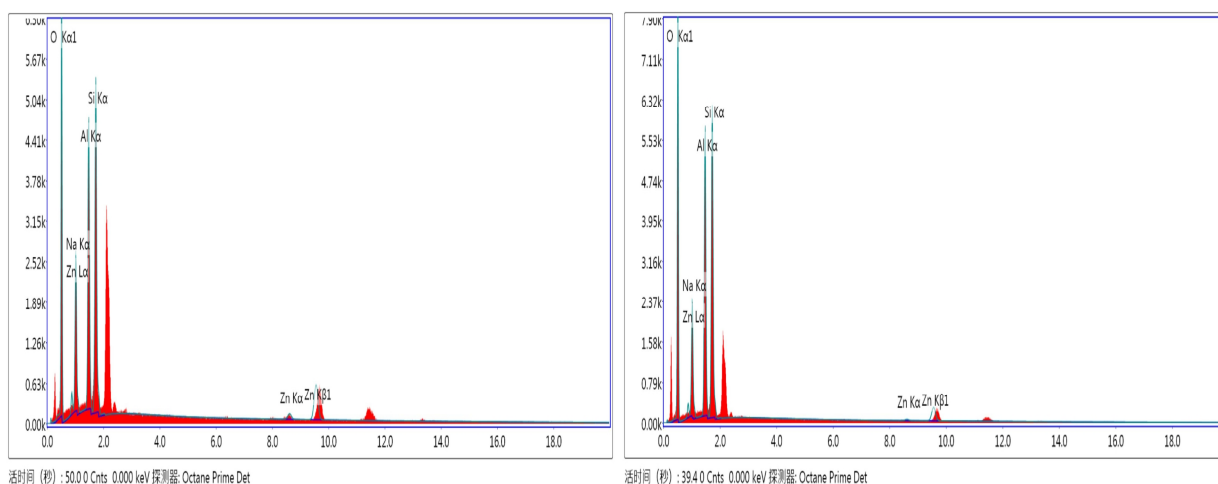


Fig. 6 EDS results for initial coating and secondary growth

The graph in Fig. 5 showed a great agglomeration phenomenon which indicated initial coating and secondary growth were successfully or not was not for sure, so EDS was carried out to figure out its surface elemental compositions shows in Fig. 6 and it can be found that there is a slightly decrease in Zn content which maybe accountable to the relatively increase in 4A on the ZnO surface that reduces decrease in Zn content, however, from Fig. 6, in a certain way, we can not identify we have synthesized ZnO@4A materials successfully. In order to make a further confirmation, we introduced XRD and the results was shown in Fig. 7.

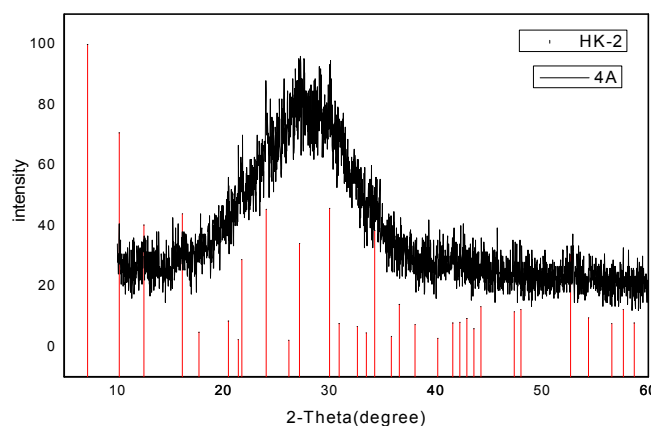


Fig. 7 XRD results of the secondary growth sample

Fig. 7 shows a little crystal peak both 4A sieve and ZnO which may go with its standard not well, indicating we have successfully complete coating procedure to obtain ZnO@4A materials to a certain extent, in order to double check its results, we repeated warping experiment 3 times and its results remain the same. To further study on this similar research, there might another way to cop with it in the purpose of getting ZnO@4A materials completely success.

## Conclusion

- (1) Using guiding agent method, 4A molecular sieve was synthesize at the best condition of experimental aging time at 12h, template agent dosage at 6. 8992g, crystallization time at 4h upon which sample shows a certain size at 200-300nm but a little morphology.
- (2) Through ways of two-step method, sphere-like ZnO with uniform particle size was formed which features size at 400-600nm.
- (3) To ensuring a good warp procedure proceed, a good control of Zeta Electric Potential is a must before coating or after.
- (4) All the warp works we did were turn out to be a little success to some extend but, to some degree, some reference maybe cited for other researchers in our work in order to proceed further study in the future.

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