

## Preparation and characterization of TMA-A zeolite incorporated with ZnO nanocrystals

Chang Sung Lim\*, Seok Ju Lee, Won-Chun Oh and Ik Jin Kim

\*Department of Advanced Materials Science and Engineering, Hanseo University, Seosan 356-706, South Korea

Nano-sized ZnO crystals were successfully incorporated using an ion exchange method in TMA-A zeolite synthesized by the hydrothermal method. The optimal composition for the synthesis of TMA-A zeolite resulted from a solution of Al(i-pro)<sub>3</sub> : 2.2 TEOS : 2.4 TMAOH : 0.3 NaOH : 200 H<sub>2</sub>O. 0.3 g of TMA-A zeolite and a 5 mol of ZnCl<sub>2</sub> solution was employed for the preparation of ZnO incorporated TMA-A zeolite. The crystallization process and bonding structures of ZnO incorporated TMA-A zeolites were analyzed by XRD and FT-IR. The morphology and the particle size dependence on the temperature and time were observed using a particle size analyzer and SEM. The nano-sized ZnO crystals incorporated and the crystallinity of the TMA-A zeolite were evaluated by HRTEM. Subsequently, the ZnO incorporated TMA-A zeolite showed photoluminescent characteristics in the wavelengths of 330-260 nm and 260-230 nm using a UV spectrophotometer.

**Key words:** TMA-A zeolite, ZnO, Nano size, Incorporation.

### Introduction

Zeolite materials are microporous aluminosilicates with cavities or channels, allowing application as a host of novel composite material synthesis [1, 2]. It is possible to generate well-defined nanoclusters in zeolite pores, which provide fine tuning of electronic properties using a large variety of zeolites with different cage sizes if the zeolite pores are successfully filled with semiconductor particles [2]. Zeolites find widespread issue both in separation processes as sorbents and as heterogeneous catalysis [3]. The presence of micropores (diameter < 2.0 nm) with a well-defined pore size and pore geometry is of major importance in these industrial applications [4]. The pore size and pore geometry is determined by the crystal structure of the zeolite and today a wide range of zeolites with different crystal structures are available [5]. However, in several applications it has been shown that the presence of larger pores, micropores, is desirable in order to increase the rate of diffusion in the zeolite crystals [6].

The preparation of low-dimensional materials, in particular semiconductors, has been widely studied since it is well-known that their optical properties can be tuned by the size of the semiconductor material due to the quantum size effect [7]. In particular, zinc oxide, a wide band-gap II-VI semiconductor (gap = 3.37 eV, 298 K), shows a significant quantum confinement effect when its size reaches the Bohr radius, 1.8 nm. Moreover, ZnO is an interesting material due to its many applications such as in varistors, gas sensors,

electrical and optical devices [8, 9]. Both chemical and physical methods have been employed to synthesize semiconducting nanocrystals but their aggregation remains very often unavoidable. A simple way to solve this problem is to incorporate nanocrystals inside a porous matrix [10, 11] which can limit the crystal growth.

Since ZnO nanoclusters are so small and unstable, many materials, such as glass, polymers and zeolites, have been used as supports or stabilizers in the various preparation methods of them [12]. Using mesoporous zeolites as a host, they provide well-defined and well-ordered pores to confine the ZnO clusters. Thus, the size and configuration of ZnO nanoclusters can be tailored using different mesoporous zeolites. On the other hand, ZnO nanoclusters encapsulated in the zeolites have shown catalytic activities for some reactions [13]. In this study, ZnO nanocrystals were successfully encapsulated in TMA-A zeolites using an ion exchange method followed by a hydrothermal route. The crystallization process and bonding structures of ZnO nanocrystals incorporated TMA-A (ZnO/TMA-A) zeolites were investigated by XRD, SEM, TEM and optical spectroscopies in detail.

### Experimental

TMA-A zeolite nanocrystals of a uniform particle size between 60 - 150 nm were synthesized by a hydrothermal method in a mother solution having a composition of Al(i-pro)<sub>3</sub> : 2.2 TEOS : 2.4 TMAOH : 0.3 NaOH : 200 H<sub>2</sub>O at 100 + C for three days. The reactant materials used were aluminum isopropoxide Al(i-pro)<sub>3</sub>, tetra-ethyl-orthosilicate (TEOS), tetra-methyl-ammonium hydroxide (TMAOH), and sodium hydroxide (NaOH). The autoclave was removed at predetermined times from the oven to

\*Corresponding author:  
Tel : +82-41-660-1445  
Fax: +82-41-660-1445  
E-mail: cslim@hanseo.co.kr

arrest the reactions. The crystallized TMA-A zeolites were collected and separated by centrifugation. The TMA-A zeolite products were repeatedly dispersed in distilled water using centrifugation to remove the remaining mother solution until the pH of the dispersion was close to 7. The TMA-A zeolites were obtained by drying at 80 °C for 4 h.

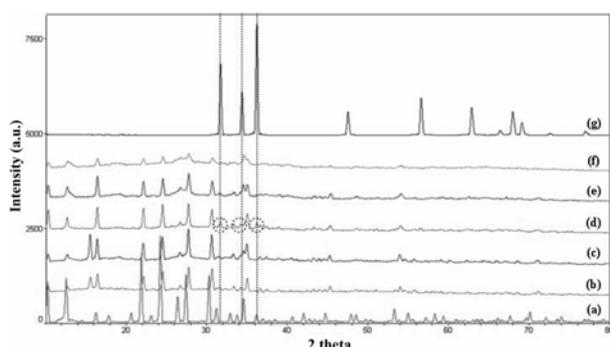
The incorporation of ZnO nanoparticles was performed by impregnation of 0.3 g TMA-A zeolite into 20 ml of a 5 mol ZnCl<sub>2</sub> aqueous solution over 3 hours. The powder was separated by centrifugation and dried at 100 °C for one day. The ZnO/TMA-A zeolite powders were heat-treated from 400 to 600 °C for 3 hours. The initial and the final products of ZnO/TMA-A zeolite obtained after heat treatments were characterized by X-ray diffraction (XRD, D/MAX 2200 + ULTIMA, Rigaku, Japan) with Cu K<sub>α</sub> radiation, scanning electron microscopy (SEM, JSM-5600, JEOL, Japan), high resolution transmission

electron microscopy (HRTEM, Tecnai G2, STEM), Fourier transform infrared (FT-IR, Magna-IR 760, Nicolet) spectroscopy and UV spectroscopy.

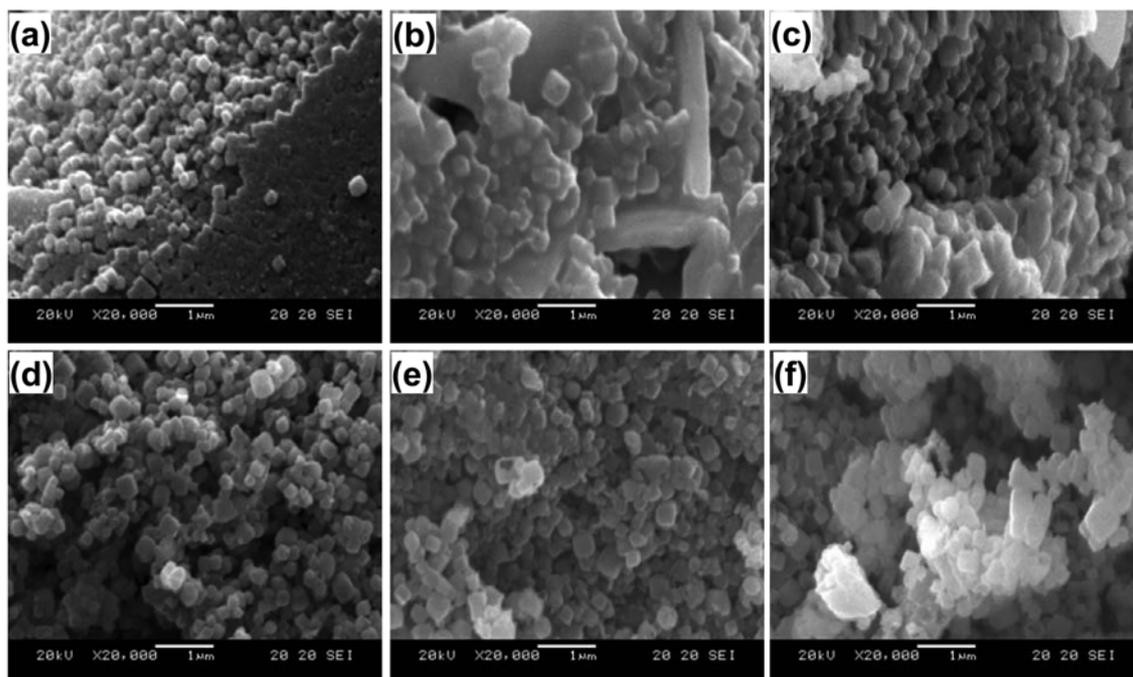
## Results and discussion

Fig. 1 shows XRD patterns of the ZnO/TMA-A zeolite nanocrystals (a) and heat treated at (b) 400, (c) 450, (d) 500, (e) 550 and (f) 600 °C for 3 hours. For a better understanding, XRD patterns of Zn ion unchanged TMA-A zeolite (a) and wurzite structured ZnO crystals (b), respectively are included. It can be clearly be seen that the patterns of ZnO/TMA-A are somewhat different thus indicating some changes in the crystallite structure of TMA-A zeolite with heat treatment temperature. It is assumed that the changes of the relative peak intensities and small shift of the diffraction angles to the higher values are induced by the compression of the TMA-A crystallite structure due to the crystal growth of the ZnO nanocrystals. At low heat treatment temperatures of 400 and 450 °C, no diffraction peaks of crystalline ZnO exists. At higher heat treatment temperatures from 500 to 550 °C, the diffraction peaks of ZnO with the wurzite structure appear and develop with increasing heat treatment temperature. However, from 600 °C, the diffraction intensity of TMA-A zeolite decreases significantly accompanying the disappeared crystalline peaks of ZnO. Consequently, it is realized that the optimum heat treatment condition of ZnO/TMA-A is in the range from 500 to 550 °C.

Fig. 2 shows SEM images for (a) ZnO/TMA-A zeolite at 25 °C, and heat treated at (b) 400, (c) 450, (d) 500, (e) 550, (f) 600 °C, respectively. For comparison, Fig. 2(a) shows an unheated ZnO/TMA-A zeolite, which represents cubic



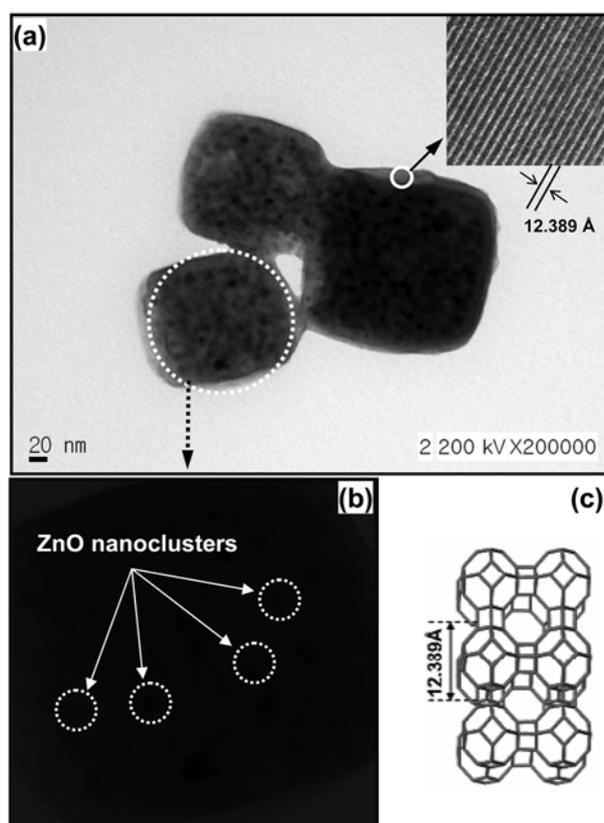
**Fig. 1.** XRD patterns for (a) TMA-A zeolite, and ZnO/TMA-A zeolite heat treated at (b) 400, (c) 450, (d) 500, (e) 550, (f) 600 °C, respectively. XRD peaks for wurzite structured ZnO is represented in (g).



**Fig. 2.** SEM images for (a) ZnO/TMA-A zeolite at 25 °C, and heat treated at (b) 400, (c) 450, (d) 500, (e) 550, (f) 600 °C, respectively.

shaped particles with a well-controlled crystal size distribution between 100 to 150 nm. The cube or hexahedron is composed of six perfect square faces that have  $90^\circ$  angles. When heated at 400 and 450 °C, the ZnO/TMA-A zeolite showed agglomerated and rounded crystal morphology, including elongated crystals as shown in Fig. 2(b) and (c). At 500 and 550 °C in Fig. 2 (d) and (e), the ZnO/TMA-A zeolite presents a well-dispersed cubic morphology. However, at the higher temperature of 600 °C in as shown in Fig. 2(f), the ZnO/TMA-A zeolite revealed an overgrown and re-agglomerated crystal shape mixed with irregular particles. Therefore, the microstructural changes showed that the optimum heat treatment condition for ZnO/TMA-A zeolite was in a temperature range from 500 to 550 °C, which is consistent with above XRD results.

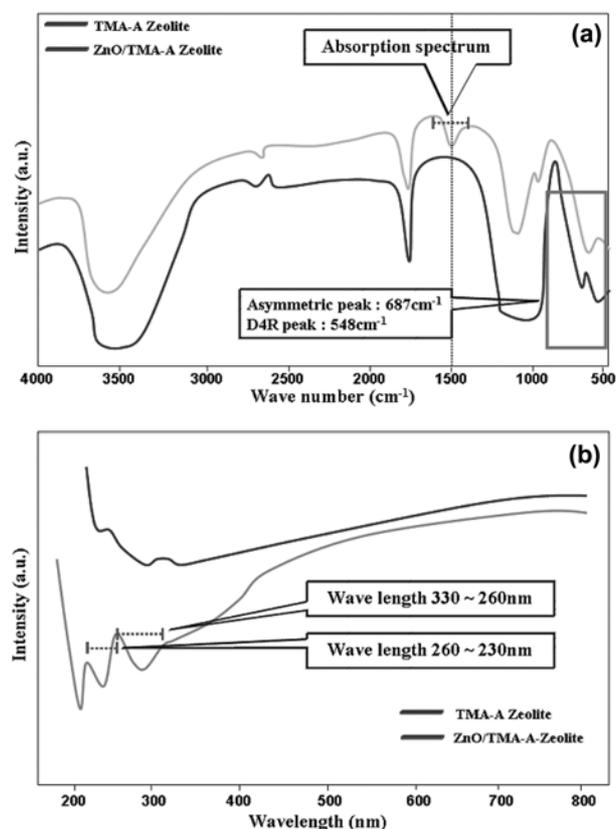
Fig. 3 shows HRTEM images of the ZnO/TMA-A zeolite nanocrystals heat treated at 500 °C. The images show a high degree of structural order leading to a perfect crystalline morphology. It is proposed that the crystals have a typical cubic form with a uniform crystal size between 100 and 150 nm. The ZnO nanoclusters located inside the TMA-A zeolite are marked with arrows in Fig. 3(b). It can be confirmed that ZnO nanoclusters are incorporated very homogeneously inside the TMA-A zeolite structure.



**Fig. 3.** The (a) HRTEM image of ZnO/TMA-A zeolite, (b) magnified region of the marked area in (a) showing the homogeneously distributed ZnO nanocrystals inside the TMA-A zeolite, and (c) a typical zeolite structure showing well-developed crystallinity with a length of 12.389 Å for the sodalite cage.

No other ZnO particles are found on the outside or at the zeolite surface. In general, the framework of a TMA-A zeolite can be described in terms of two types of polyhedra; one has a simple cubic arrangement of eight tetrahedra, which is termed D4R, and the other is a truncated octahedron of 24 tetrahedra or cages. It is well known that a TMA-A zeolite is generated by placing the cubic D4R units in the center of the edges of a cube with an edge length of 12.3 Å [14] and these nanostructured zeolite materials are applied as host materials for nanocluster materials [15, 16]. The lattice image in the inset of Fig. 3(a) indicates that the size of the sodalite cage is 12.389 Å as depicted in Fig. 3(c), which consists well with the reported value [14].

Fig. 4(a) shows the FT-IR curves of TMA-A zeolite and a ZnO/TMA-A zeolite heat treated at 500 °C, respectively. A strong OH stretching vibration region of the bridged Si(OH)Al is observed around  $3,600\text{ cm}^{-1}$  [17], and another strong vibration at  $1,100\text{ cm}^{-1}$  is assigned to a T-O stretching mode. Fig. 4(a) and (b) give an asymmetric vibration mode at  $687\text{ cm}^{-1}$  and a D4R peak at  $548\text{ cm}^{-1}$ , which means bonding structures were not changed after incorporation of ZnO nanoclusters. However, in the



**Fig. 4.** The (a) FT-IR curves of the TMA-A zeolite and a ZnO/TMA-A sample heat treated at 550 °C showing the asymmetric peak on at  $687\text{ cm}^{-1}$ , a D4R at  $548\text{ cm}^{-1}$  and an absorption spectrum of ZnO at  $1,500\text{ cm}^{-1}$ , and (b) UV-vis curves of TMA-A zeolite and a ZnO/TMA-A zeolite. The spectrum of the ZnO incorporated TMA-A zeolite shows typical peaks around 230-260 and  $260\text{--}330\text{ cm}^{-1}$ .

ZnO/TMA-A zeolite heat treated at 500 °C, a new absorption spectrum around 1,500 cm<sup>-1</sup> due to the bonding with TMA-A zeolite and incorporated ZnO nanoclusters was found. The UV-vis reflection spectra of Fig. 4(b) show the shape for the ZnO nanoclusters incorporated in the TMA-A zeolite. The absorption peaks around 330 and 240 nm can be assigned to ZnO nanoclusters [18]. These FT-IR and UV-vis spectroscopic results confirm that ZnO nanoclusters are incorporated the TMA-A zeolite structure very uniformly.

### Conclusions

Nano-sized ZnO crystals were successfully incorporated using an ion exchange method in TMA-A zeolites synthesized by a hydrothermal method. The optimum heat treatment condition for oxidation of zinc was in the range from 500 to 550 °C. The crystal morphology of ZnO/TMA-A zeolites showed a well-dispersed configuration having six perfect square planes. The crystalline and microstructural analyses indicated the successful incorporation of ZnO nanocrystals inside TMA-A zeolites. The ZnO/TMA-A zeolite heat treated at 500 °C had a sodalite cage size of 12.389 Å. The ZnO incorporated TMA-A zeolite showed photoluminescent characteristics at wavelengths of 330-260 nm and 260-230 nm.

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