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Synthesis of ZnO mesoporous powders and their application in dye photodegradation

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INTRODUCTION

ZnO materials have attracted considerable interest due to their large-scale potential applications for photodiodes, photocatalysis, sensing and others[1]. For photocatalytical application, ZnO is usually prepared with a mesoporous structure, providing a large surface area for enhancing the system performance. Nowadays, various methods have been explored to prepare ZnO porous powders and films. Among them, the most important and more common techniques to synthetize mesoporous ZnO particles are wet chemical methods, including precipitation from inorganic or organic solutions and sol-gel, owing to their simplicity and low cost. Herein, we studied ZnO mesoporous powder synthesis based on preparation and further thermal decomposition of zinc hydroxide chloride hydrate precursor. The attention was given to the role of reaction medium in the formation of final products and to the photocatalytic activity of the synthesized ZnO.

EXPERIMENTAL

In a typical procedure to produce $Zn_5(OH)_8Cl_2{\cdot}H_2O$ precursor, 29.7 g of $Zn(NO_3)_2$, 7.45 g of KCl and 10 g of polyvinylpyrrolidone were dissolved in 1 L of distilled water or water-ethanol mixture (50:50 by volume). The resulting solution was heated with stirring (the temperature was kept at 70 °C). Aqueous ammonia solution was added dropwise to reach a pH value of 7.0. The obtained precipitate was filtered, rinsed with water and dried at 50 °C in air. The materials were then characterized by XRD, SEM and N_2 adsorption.

RESULTS AND DISCUSSION

The XRD data indicate that a pure phase of $Zn_5(OH)_8Cl_2{\cdot}H_2O$ is formed during the hydrolysis of $Zn(NO_3)_2$ in KCl-containing water-ethanol solution with a final pH of 7.0. After annealing at 400 °C in air, the $Zn_5(OH)_8Cl_2$ precursor transforms into wurtzite ZnO as evidenced by XRD. The role of ethanol in solution was studied by replacement of water-ethanol mixture with aqueous solutions. Under the latter conditions, as-prepared precipitate consisted of pure ZnO.

SEM images show that the zinc hydroxide chloride precursor is constituted by microplates with a lateral size of 0.5–1.5 μm and a thickness of 100–200 nm. After annealing, the microplates exhibit the same shape, but are formed by loosely aggregated ZnO nanocrystallites having a size of appr. 20–40 nm. ZnO particles produced in aqueous solutions have a shape of hexagonal columns with an average diameter of 80 nm. The developed nanoporous structure of the ZnO powder obtained from water-ethanol mixture renders a high specific surface area. The adsorption–desorption isotherm of the ZnO powder belongs to IV type with a distinct hysteresis loop, which is characteristic of mesoporous materials.

According to the above presented results, we can conclude that the structure of the as-prepared precipitate strongly depends on the presence of ethanol in the solution. The influence of ethanol on the precursor formation can be explained by the interaction of Zn^{2+} and ethanol in the solution. Generally, ammonia reacts with water to form ammonia hydroxide, generating OH^- ions. Hydroxyl ions form complex with Zn^{2+} to produce hydroxide species, including $Zn(OH)^+(aq)$, $Zn(OH)_2(aq)$, $Zn(OH)_2(s)$, $Zn(OH)_3^-(aq)$, and $Zn(OH)_4^{2-}(aq)$. The nuclei of ZnO start growing by dehydration of these hydroxide species. However, when ethanol molecules were added into the solution, a new coordination complexes such as $[Zn(C_2H_5OH)_{4-n}(OH)_n]^{2-n}$ may be formed. As a result, the last ones mainly converted into $Zn_5(OH)_8Cl_2{\cdot}H_2O$.

Mesoporous ZnO particles show superior photocatalytic efficiency as compared with the commercial powders. Solution of Rhodamine B dye was efficiently discolored under UV irradiation in the presence of the ZnO powders.

CONCLUSION

The synthesis of mesoporous ZnO particles based on preparation and further thermal decomposition of $Zn_5(OH)_8Cl_2{\cdot}H_2O$ has been described. The presence of ethanol molecules in the solution strongly influences the structure of as-prepared precipitate. The effect of ethanol molecules was explained by formation of new complexes in solution. The resulting mesoporous ZnO exhibits a strong photocatalytic activity in photodegradation of Rhodamine B.

REFERENCES

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