Bulgarian Chemical Communications, Volume 49, Special Issue G (pp.172 –176) 2017

Investigation of photocatalytic properties of pure and Ln (La^{3+}, Eu^{3+}, Ce^{3+}) – modified ZnO powders synthesized by thermal method

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Received November 7, 2016; Revised January 4, 2017

Simple and fast thermal method is used to synthesize ZnO and Ln–modified (La^{3+}, Eu^{3+}, Ce^{3+}) ZnO powders. Nanocrystalline photocatalysts with 2.0 mol% concentration are annealed at 100°C for 1h. The pure and doped powders are characterized by a variety of characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM).

The photocatalytic action of the mixtures is tested in photocatalytic oxidation of ethylene as model air pollutant (5000 ppm feed concentration) in gas-phase flat-plate continuous flow photocatalytic reactor at maximum ethylene contact time of 4 min and optimal relative humidity 30%. The powder-form samples are suspended in water and after sonication (24 kHz) to disintegrate agglomerates the slurry was deposited by the capillary method on TLC sheets (Merck) to obtain 1 mg/cm^2 loading. The photoactivity testing was carried out using UV-A and UV-C illumination (0.014 W/cm^2). Sample 3 (Ce^{3+}-doped)/ZnO was superior to pure ZnO. It gave the highest conversion degrees both under UV-A and UV-C illumination, whereupon the latter yielded superior performance. There was no activity under visible light illumination due to the wide band gap.

Key words: *ZnO, rare earths, powders, photocatalysis*

INTRODUCTION

As a new-generation multifunctional II-VI semiconductor material, ZnO has received extensive attention in recent years. Due to the direct wide bandgap of 3.37 eV and a large exciton binding energy of 60meV at room temperature [1], zinc oxide combine interesting properties such as non-toxicity, good photocatalitc properties, high luminous transmittance, hardness, optical and piezoelectric behavior and its low price [2]. Therefore, it is not surprising that it has been under intensive investigation.

The dependence of the properties on the size of the ZnO has led to many interesting application of particles [3] especially by tuning the band gap of the semiconductors [4].

The investigation on the preparation and properties of ZnO has attracted a great deal of attention, and a variety of methods have been employed to fabricate this material, including sol–gel, precipitation, micro-emulsion, solvothermal, hydrothermal methods [5 – 9]. However, there are not many efforts regarding low temperature chemical techniques [10]. It has been demonstrated that the hydrothermal synthesis is a feasible route for the preparation of ZnO with controlled morphology, structure and surface area [11, 12]. For photocatalytic applications, the improvement of the photoactivity might be achieved by influencing those properties that control either the charge carrier dynamics (carrier generation, transfer and diffusion) or the surface catalytic process, which are the quality of the structure and the surface features. In this sense, it is widely reported that the hydrothermal synthesis would provide the adequate structural and surface properties for photocatalytic applications [13].

In the present study, we prepared for the first time high-quality ZnO materials using hydrothermal method. The photocatalytic activity of ZnO has been carried out in a gas-phase flat-plate continuous flow reactor using ethylene as model air contaminant under ultraviolet (UVA and UVC) and visible light. The improvement of the photocatalytic efficiency of ZnO might be achieved by modified with rare earths (La^{3+}, Ce^{3+}, Eu^{3+}). The nanosized pure and RE powders are characterized by X-ray diffraction and Scanning Electron Microscopy. We concluded that hydrothermal treatment of pure and doped ZnO grant the finest performance in the catalyst for photocatalytic application.

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EXPERIMENTAL

Commercial zinc oxide powder (>99.0%), Eu_2O_3 (>99.0%), $Ce(NO_3)_3.6H_2O$ (>99.0%), La_2O_3 (>99.0%) and absolute ethanol were obtained from Fluka.

Pure and modified ZnO powders were synthesized by green, simple and fast hydrothermal method. La/ZnO photocatalysts were prepared using zinc oxide commercial powder and La_2O_3. The substances were mixed in a glass vessel, and then ethanol was added as a mixing medium. The resultant clear solution was sonicated for additional 30 min and dried at 100°C for 1 h in order to obtain the ZnO/La powders for photocatalytic tests. In our previous work, we experimentally found that the optimal RE concentration is 2 mol% [14]. The remaining catalysts (Ce/ZnO and Eu/ZnO) were prepared at the same conditions and optimal concentration of 2 mol% of RE ions (Ce^{3+} and Eu^{3+}).

The as-obtained nanosized powders (pure ZnO and RE–modified ZnO were first imaged by Scanning Electron Microscope (SEM) JSM-5510 (JEOL), operated at 10 kV of acceleration voltage. The investigated samples were coated with gold by JFC-1200 fine coater (JEOL) before observation. The X-ray diffraction (XRD) was recorded at room temperature on a powder diffractometer (Siemens D500 with CuK_α radiation within 2θ range 30–70° at a step of 0.05° 2θ and counting time 2 s/step). The average crystallite sizes were estimated according to the Scherrer’s equation [15]:

$$d_{hkl} = k\lambda / \beta \cos(2\theta) \qquad (1)$$

where d_{hkl} is the average crystallite size (nm), λ is the wavelength of CuKα radiation (λ = 0.154056 nm), θ is the Bragg’s angle of diffraction, β is the full-width at half maximum intensity of the peak observed at 2θ = 25.20° (converted to radian) and k is a constant usually applied as ~0.9.

The photocatalytic activities of the 4 powder – form samples (pure ZnO and 3 modified samples) has been carried out in a gas-phase flat-plate continuous flow reactor using ethylene as model air contaminant. The course of the photocatalytic reaction of complete oxidation of ethylene is monitored using a gas-analyzer (LANCOM III, Land Instruments Co., England), equipped with chemisorption sensor for total hydrocarbons content in the gaseous mixture (ppm CxHy). The feed composition at the reactor inlet was 0.5% (5000 ppm) C_2H_4, 10% O_2, 89.5% N_2 (four–channel mass flow controller Matheson model 8249). Two of the channels were feeding nitrogen – dry N_2 flow directly into the reactor, and moisturized N_2 (after passing first through a water vapor saturator). The use of two channels enables varying the water vapor content in the feed mixture. Our previous experiments established 30% Relative Humidity (RH), to be the optimum [16, 17]:

$$RH = [F_{N2}moist/(F_{N2}dry + F_{N2}moits + F_{O2} + F_{C2H4})].100(\%) \qquad (2)$$

where F_i denotes the various feed flow rates (ml/min). The feed H_2O molecules are needed to photogenerate the highly active hydroxyl radicals °OH, capable of destroying various classes of organic compounds. Feeding ethylene and oxygen by two different channels, regulated independently of each other, enables varying the C_2H_4:O_2 ratio (large stoichiometric excess of oxygen with respect to C_2H_4 in all our experimental runs). In this case we can accept that O_2 concentration is practically unchanged in our experiments, so its value can be included in the value of the efficient rate constant k_{eff} in the kinetic equation:

$$R_{C2H4} = k_{eff}.C_{C2H4}/(1 + K_{O2}.C_{O2} + K_{C2H4}.C_{C2H4}) \qquad (3)$$

The equation (3) includes the rate of ethylene consumption R_{C2H4} (mol/h.g-cat), C_{C2H4} is the outlet concentration (mol/cm^3), while K_{O2} and K_{C2H4} are the adsorption-desorption equilibrium constants i.e. Langmuir-Hinshelwood type of mechanism with both reactants in adsorbed state on the surface. The rate limiting step is the interaction between the two adsorbed molecules. No inhibiting effect of the reaction products CO_2 and H_2O is observed. The use of k_{eff} means that the applied approach is “formal kinetics”, in which the efficient rate constant k_{eff} has complex physical meaning, comprising rate constant, adsorption equilibrium constant and reactant concentration. The ethylene contact time τ_e was 4 min i.e. the maximal possible contact time at the lowest inlet flow rate of ethylene that the ethylene channel can allow. At this maximal τ_e we achieved the maximal conversion degree of ethylene photocatalytic oxidation.

The dimensions of the flat plate quartz window were 5 cm width x 15 cm length, allowing simultaneous accommodation of 2 lamps Philips TL4W/08 F4T5/BLB of total light power 8 Watts, placed on top of the window (distance of illumination 0 cm) supplying light intensity of 0.014 W/cm^2 polychromatic illumination of wave length range 320-400 nm (λ_{max} = 365 nm).

Two lamps Philips TUV 4W/G4 T5 (monochromatic illumination λ = 254 nm) (total light power 8 Watts), at 0 cm distance, the same illumination intensity of 0.014 W/cm^2, but much higher energy of the photons. The visible light irradiation was accomplished by linear halogen lamp

Tungsram 500 Watts K1R7s supplying illumination intensity 8.9 mW/cm^2 (9700 Lm) at 50 cm distance of illumination to avoid overheating of the explosive C_2H_4-O_2 mixture [16, 17].

Thin layer chromatography (TLC) sheet (Merck Art.5554 Kieselgel 60 F254) pre-coated with SiO_2 was used to deposit the ZnO slurry by capillary method. The sheet had dimensions 4.2 cm x 13.4 cm of total geometric surface area 56 cm^2. To obtain 1mg/cm^2 coating 56 mg of the powder-form sample were weighed, suspended and then sonicated (Hielscher UP 200S, 24 kHz). Then the so obtained suspension was deposited drop-by-drop by capillary using directing air stream to obtain a uniform thin film on the SiO_2 coating.

RESULTS AND DISCUSSION

The SEM images of the as-prepared ZnO and RE–modified (La^{3+}, Eu^{3+} or Ce^{3+}) ZnO powders are shown in Fig. 1. As seen, the morphology of all samples is well ordered. ZnO/Ln powders are flowerlike in shape with average diameter size of about 0.4–0.45 μm (determined from the SEM images). An average particle size of 0.25 μm for ZnO nanocomposite. The surface of the pure and RE–modified ZnO samples does not show any changes. So, the type of rare earths does not influence the morphology. The SEM images of the four powders are similar.

X-ray diffractogram of the powders is analyzed to obtain information about various crystalline aspects. Fig. 2 shows that XRD patterns of synthesized pure ZnO. The sharp and intense peaks indicate that ZnO have high crystallinity and polycrystalline structure. The XRD peaks for (100), (002) and (101) planes of pure ZnO correspond to hexagonal wurtzite crystalline phase. The high intensity of (101) peak suggests that the growth of nanoparticles has taken place along this direction of crystallization of ZnO. No characteristic peaks of impurity phases such as Zn or $Zn(OH)_2$ are observed for all samples. The XRD spectras of the RE–modified ZnO powders are almost similar to that of ZnO [18], which can be due to their low concentration (2 mol%) in the ZnO nanocomposite. There is no change in the crystal structure. This also indicates that Ln^{3+} is uniformly dispersed between ZnO nanoparticles in the form of small Ln_2O_3 clusters. The crystallite average size of pure ZnO is found to be 36.68 nm, calculated by Sherrer's formula (Eq. 1).

In order to determine the photocatalytic activity of ZnO and RE-modified ZnO powders, a series of experiments are carried out with ethylene as model air pollutant in gas-phase flat-plate continuous flow photocatalytic reactor.

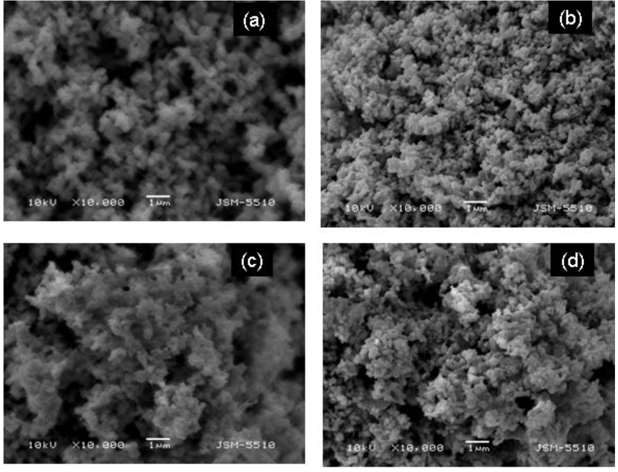

Fig. 1. SEM images of pure (a) and Eu^{3+} (b), La^{3+} (c), Ce^{3+} (d) – modified ZnO powders.

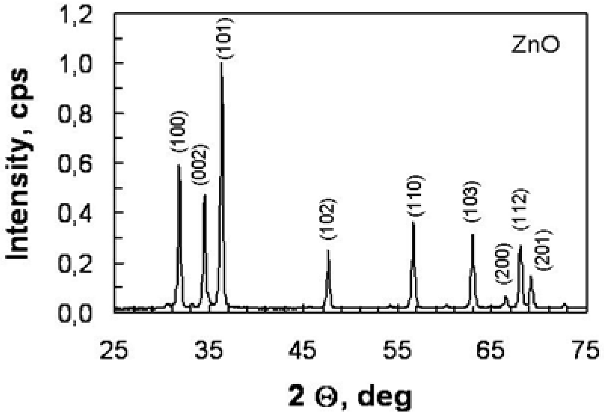

Fig. 2. XRD spectra of pure ZnO powder

The experiments carried out with UV-C illumination show higher degrees of photooxidation of ethylene in comparison with the experiments with UV-A light illumination (Fig. 3). The photocatalytic tests under visible light (intensity – 0.89 W/cm^2) did not show reduced conversion of ethylene for the same reaction time.

As seen from Fig. 3, the photocatalytic efficiency is highest for the modified ZnO powders with Eu^{3+} (C_2H_4 conversion (%) – 5.1 and 8.2, under UV-A and UV-C irradiation). The modified samples with lanthanum oxide have a higher activity and faster degrade the pollutant (C_2H_4 conversion (%) – 4.6 and 7.8, under UV-A and UV-C irradiation) in comparison with the pure ZnO nanocomposite (C_2H_4 conversion (%) – 3.9 and 7.4, under UV-A and UV-C irradiation). The lowest photocatalytic properties have Ce – modified ZnO powders.

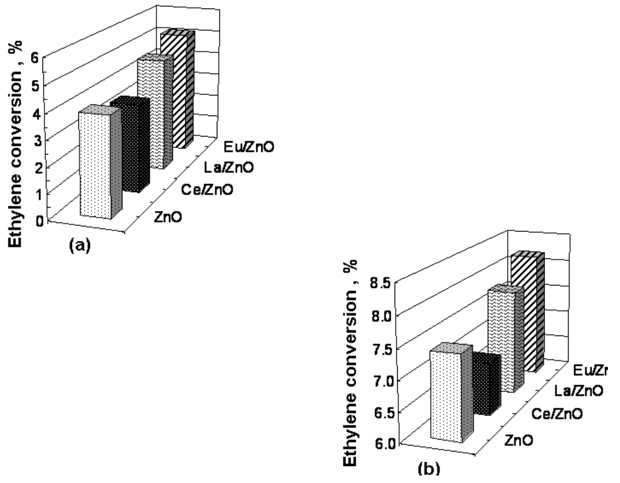

Fig. 3. Degrees of photooxidation of C_2H_4 under (a) UV-A and (b) UV-C irradiation with intensity 0.014 W/cm^2, τ_e = 4 min, 30% RH and O_2 excess over 4 ZnO photocatalysts (1 mg/cm^2)

CONCLUSIONS

We are prepared pure and rare earth modified ZnO samples by hydrothermal method. The nanosized powders are characterized by Scanning Electron Microscopy and X-ray diffraction. The powders (pure and modified) are spherical in shape belonging to hexagonal wurtzite structures, which demonstrates that the RE^{3+} ions have no effect on the crystal structure. There is no photocatalytic activity under visible light due to the wide band gap of ZnO. UV-C light gives higher conversion degree owing to the higher photon energy than UV-A light. The experimental result shows that the nanosized Eu–modified powders have highest activity and fastest photocatalytic degradation the ethylene as model air pollutant. The photocatalytic efficiency of pure ZnO particles is lower than the activity achieved by La modified sample under UV-light irradiation. All these observations prove that RE-modified ZnO is a potential candidate for the practical application in photocatalytic degradation of organic contaminants.

Acknowledgements: *This research is financially supported by the Russian Ministry of Education as part of the base portion of the state task № 2014/151 (Project Code 117), DFNI-T02/16 (№2742) and FP7 Horizon 2020.*

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ИЗСЛЕДВАНЕ ФОТОКАТАЛИТИЧНИТЕ СВОЙСТВА НА ЧИСТИ И Ln (La^{3+}, Eu^{3+}, Ce^{3+}) – МОДИФИЦИРАНИ ZnO ПРАХОВЕ, СИНТЕЗИРАНИ ЧРЕЗ ТЕРМАЛЕН МЕТОД

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Постъпила на 7 ноември 2016 г.; приета на 4 януари 2017 г.

(Резюме)

Прост и бърз термален метод е използван за синтезирането на ZnO и Ln–модифицирани (La^{3+}, Eu^{3+}, Ce^{3+}) ZnO прахове. Нанокристалните фотокатализатори с концентрация 2.0 мол% са накалени при 100°C за 1 час. Чистите и модифицираните прахове са характеризирани с различни техники, такива като Рентгенова дифракция, Сканиращ електронен микроскоп.

Фотокаталитичното действие на смесите е тествано за фотокаталитично окисление на етилен (замърсител на въздух) в газова фаза, използвайки фотокаталитичен реактор – скорост 5000 ppm, максимално контактно време на етилен 4 мин и оптимална относителна влажност 30%. Пробите от прах се суспендират във вода и се подлагат на ултразвук (24 kHz) с цел раздробяване на големите агломерати в разтвора. За експериментите се използва TLC капиляpен метод. Фотокаталитичните тестове са проведени в присъствие на UV-A и UV-C светлина (0.014 W/cm^2). Проба 3 (Ce^{3+}-модифициран)/ZnO притежава най-висока ефективност при облъчване с UV-A и UV-C светлина, превъзхождайки чистият ZnO. Модифицираният фотокатализатор не е активен в присъствие на видима светлина, което се дължи на ширината на забранената му зона.

Ключови думи: *ZnO, редкоземни елементи, прахове, фотокатализа*