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PHOTOCATALYTIC TESTING OF MECHANOCHEMICALLY-SYNTHESIZED CADMIUM SELENIDE

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ABSTRACT

Spectroscopic and optical properties of highly luminescent II–VI semiconductor CdSe nanocrystals have been extensively studied due to their application in electrical and opto-electrical devices. CdSe nanocrystals are prepared by chemical wet process mainly. However, mechanochemical synthesis in planetary ball mill produces surface clean semiconductor nanoparticles without the influence of organic ligands coming from chemical process and such nanoparticles can be investigated as photocatalyst.

The aim of the present investigation was to test the photocatalytic activity of mechanochemically synthesized CdSe semiconductor with UV-C (monochromatic λ=254 nm) light and to compare this activity with the activity of the standard reference photocatalyst TiO_2 Degussa P25 (75% anatase + 25% rutile, average anatase particle size 25 nm). The second aim of the study was to test the photocatalytic activity of CdSe with visible light. The photocatalytic activity of the samples was tested in a batch reactor with Chromium Acidic Black Diazo Dye (Colour Index

Acid Black 194), which is used for colouring textiles. It appears in waste waters from textile factories and the new environmental regulations have forbidden discharging it into the waterways strictly.

The relatively low conversion degrees over CdSe, compared to the TiO_2 Degussa P25, can be explained by the low specific surface area of the CdSe sample. In order to increase the conversion degree sonication pretreatment of the CdSe is required as it falls at the bottom of the reactor as sediment, probably due to formation of agglomerates of large size. The sonication, prior to the photocatalytic activity test improves considerably the performance of the CdSe semiconductor. The result with model waste water is encouraging and the investigation could be extended to monitor the performance of CdSe for contaminated air purification in a gas-phase flat-sheet continuous flow steady state photocatalytic reactor. In view of the band gap of CdSe ($\Delta E = 1.7$ eV corresponding to band gap absorption edge wavelength of 730 nm) the investigation can be extended also in the direction of photocatalytic performance of CdSe with visible light to test the photonic efficiency (quantum yield) of this nanosized semiconductor material.

Key words: *Photocatalysis, mechanochemistry, Cadmium selenide*

INTRODUCTION

Cadmium selenide belongs to the group of metal chalcogenides $A^{II}B^{VI}$. CdSe is an n-type semiconductor and due to its band gap energy from 1.65 to 1.8 eV it can be used for various optoelectronic applications. According to Frame and Osterloh metal chalcogenides are promising as catalysts for photocatalytic water reduction because their bandgaps allow absorption in the visible region of the spectrum [1]. Many other metal chalcogenides can be used as photocatalysts for hydrogen evolution from water or water solutions by using solar light or UV-Vis irradiation [2–5]. CdSe nanocrystals are prepared by chemical wet process mainly [6–9]. However, recently Tan and co-authors synthesized CdSe nanocrystals by mechanical alloying process that is a safe, low cost and easy way to fabricate semiconductor nanocrystals, and can be easily extended to mass production [10]. Mechanochemical synthesis in planetary ball mill also produces surface clean semiconductor nanoparticles without the influence of organic ligands coming from chemical process and such nanoparticles can be investigated as photocatalyst.

Verifying of photocatalytic activity of selenide semiconductor is possible by testing with the various dyes and the pollutants that are appearing in waste waters especially from textile factories. Song and co-authors [11] have tested

photocatalytic activity of S-doped BiSe photocatalyst by photocatalytic oxidation of methylene blue under visible-light irradiation ($\lambda > 400$ nm). Photocatalysis is so called Advanced Oxidation Process (AOP) whose a main feature is the generation of reactive hydroxyl radicals (OH•), which are the precursors of degradation of any organic or inorganic compound. These hydroxyl species possess a higher oxidation potential (2.80V) compared to the other common oxidants like atomic oxygen (2.42 V), O_3 (2.07 V), H_2O_2 (1.78 V), hydroperoxy radicals (1.70 V) and chlorine dioxide (1.57 V) [12]. TiO_2 with wide band gap energy 3.2 eV is generally used for photocatalytic degradation reactions in UV light range because of non-toxic nature, simple synthesis, low costs, and can be used for comparative study.

In this paper we report the photocatalytic activity testing of mechanochemically synthesized CdSe with UV-light and visible light. The results are compared with photocatalytic activity of the standard reference photocatalyts TiO_2 (Degussa P25).

EXPERIMENTAL

Mechanochemical synthesis of cadmium selenide was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany) by high-energy milling of cadmium powder (99 %, Aldrich, Germany) and selenium powder (99.5 %, Aldrich, Germany) in argon atmosphere according to the reaction

$$Cd + Se \rightarrow CdSe \qquad \Delta H^0_{298} = -144.7\, kJ.mol^{-1} \qquad (1)$$

which is thermodynamically possible due to the negative values of enthalpy change, $\triangle H^{\circ}_{298}$. The following experimental conditions were used for the mechanochemical synthesis: loading of the mill, 50 balls of 10 mm in diameter; material of milling chamber and balls, tungsten carbide; volume of milling chamber, 250 mL; mass of Cd and Se for reaction (1), 2.94 g and 2.06 g, respectively; ball-to-powder ratio, 73:1; room temperature; rotational speed of the mill planet carrier, 500 min^{-1} (8 Hz); milling time, 30 min.

X-ray diffraction measurements were carried out using a D8 Advance diffractometer (Bruker, Germany) equipped with a Θ/Θ goniometer, Cu K_α radiation (40 kV, 40 mA), a secondary graphite monochromator, and a scintillation detector. The diffraction data were collected over an angular range $20<2\Theta<70°$ with steps 0,03° and a counting time of 5 s/step.

The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

Specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

The photocatalytic aktivity of TiO_2 (Degussa P25) and mechanochemically synthesized CdSe was tested with Chromium Acidic Black Diazo Dye (Colour Index Acid Black 194) which is known to be especially stable to UV-light and with 4-chlorophenol that is also common pollutant of waste waters. The UV--light source was Phillips lamp TUV 4W/G4 T5 (UV-C light monochromatic, λ=254 nm) and the intensity of illumination of the water surface was 0.05 Watts/ cm^2. The distance of illumination (between the lamp and the water surface of the reactor was 1.5 cm. The batch reactor contains 200 ml of the aqueous solution of Acid Black 194 – 20 ml of the stock standard solution (0.001 M) were diluted to obtain 0.0001M solution. The batch reactor was equipped with a magnetic stirrer (400 rpm). The diameter of the reactor is 10 cm and the water surface area is 78.5 cm^2. The air flow was bubbled through the solution passing through 2 frits to scatter the air in tiny bubbles to saturate the solution in oxygen. At the same time the stirrer and the tiny air bubbles prevented agglomeration of the nanosized semiconductor particles resulting in ideal mixing slurry reactor without any need of ultrasonic treatment in advance. Prior to the photocatalytic activity measurement the photocatalyst sample was stirred for 30 min in the dark in air flow in order to reach the adsorption-desorption equilibrium of the dye on the photocatalyst sample surface before switching on the illumination. Ultrasonic pretreatment of the selenide suspension was carried out for 5 min with Ultrasonic Processor UP200S (Hielscher, Germany) immersing the sonotrode directly in the photocatalytic reactor.

The conversion degree (degree of decoloration) is calculated on the basis of the formula:

$$X_3 = (C_o - C_3).100/C_o \qquad (2)$$

where C_0 corresponds to initial concentration based on the calibration curve, initial extinction (absorbance) at λ_{max} = 570 nm corresponds to E_o, C_3 correspond to concentration after 3 hours of illumination (extintion (absorbance) after 3 hours of illumination = E_3.

The concentration of the working solution is checked spectrophotometrically by a single beam CamSpec M501 spectrophotometer at wavelength of the maximum λ_{max} =570 nm – the extinction (absorbance) should be E_o=1.091 Abs corresponding to initial concentration C_o=0.0001M.

The analysis was carried out by a Total Organic Analyzer (TOC Shimadzu VCSH), based on total combustion of organics in a quartz reactor at 680°C and

detection of CO_2 by non-dispersive infrared gas analyzers. The result is given in mg of carbon per liter of water.

RESULTS AND DISSCUSSION

The X-ray diffraction pattern of mechanochemically synthesized CdSe is shown in Fig. 1. The XRD peaks were identified based on the JCPDS card 19–191 and correspond to cubic cadmium selenide – CdSe phase. The large broadening of X-ray diffraction reflections also confirms the nanocrystalline nature of the cadmium selenide prepared by mechanochemical synthesis. The value of specific surface area, S_A of mechanochemically synthesized CdSe is also displayed in Fig. 1. The specific surface area value of TiO_2 is 50 m^2g^{-1}.

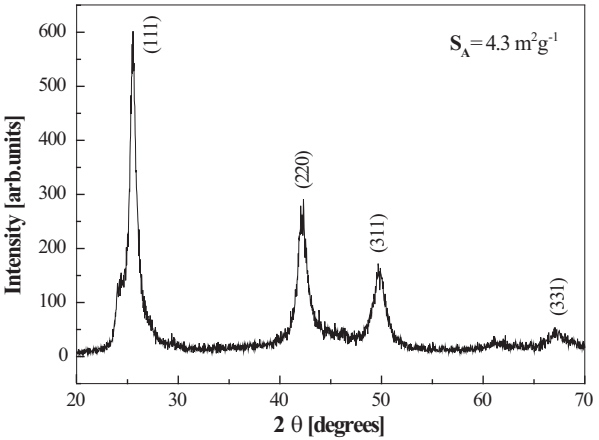

Figure 1. *X-ray diffraction pattern of CdSe mechanochemically synthesized for 30 min.*

TiO_2 and CdSe samples were tested with Chromium Acidic Black Diazo Dye (Colour Index Acid Black 194), which is used for colouring textiles and 4-Chlorophenol that was chosen as a model pollutant of waste waters as it is used for the synthesis of azodyes and it always appears in wastewaters from azodyes production. They appear in waste waters from textile factories and the new environmental regulations have forbidden them strictly. The dye is manufactured by the BULCOLOR Co. in the town Kostenetz, which is known to be especially stable to UV-light. The chemical structures of the dye and chlorophenol are shown in Fig. 2.

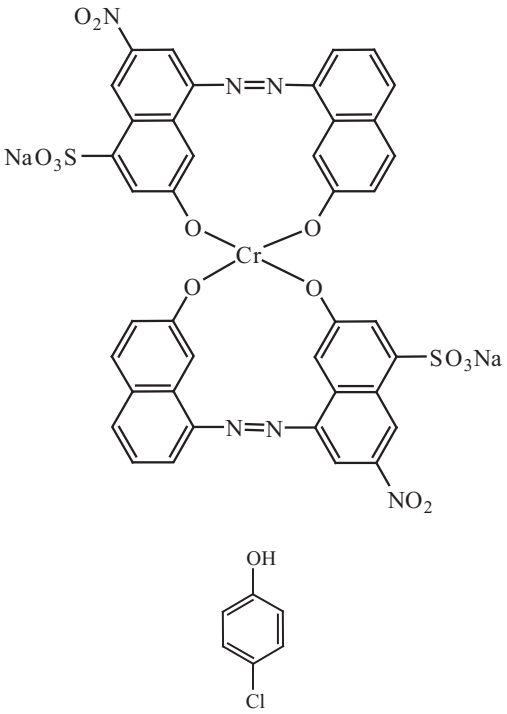

Figure 2. *Structural formulae of Chromium Acidic Black Diazodye (Colour Index C.I. Acid Black 194) and 4-Chlorophenol.*

Table 1. *Comparison of conversion degrees of wastewater model pollutants Acid Black 194 (A) and 4-Chlorophenol (C) in aqueous solutions over nanosized TiO_2 Degussa P25 and mechano-chemically prepared CdSe in a batch photocatalytic reactor under UV-C irradiation (λ=254 nm) at illumination intensity 0.05 W/cm^2.*

Type of photocatalyst	**TiO_2**	**CdSe**
Photocatalyst amount [mg]	200	400
Initial absorbance – E_0 [Abs]	1.200	1.833
Initial concentration – $C_0(A)$ [M]	0.0001083	0.0001679
Initial concentration – $C_0(C)$ [mgC/L]	1285	1 333
Absorbance after 3 h of illumination – E_3 [Abs]	0.533	1.245

Concentration after 3 h of illumination – $C_3(A)$ [M]	0.0000488	0.000114
Concentration after 3 h of illumination – $C_3(C)$[mgC/L]	470	745
Conversion degree X_3 of *(A)* [%]	55.0	32.1
Conversion degree X_3 of *(C)* [%]	63.4	44.1

The conditions and the results of photocatalytic activity testing of TiO_2 Degussa P25 and mechanochemically synthesized CdSe are shown in Table 1. The relatively low conversion degrees over CdSe, compared to the TiO_2 Degussa P25, can be explained by the low specific surface area of the CdSe sample. In order to increase the conversion degree sonication of the CdSe is required as it falls at the bottom of the reactor as sediment, probably due to formation of agglomerates of large size. The sonication, prior to the photocatalytic activity test improves considerably the performance of the CdSe semiconductor.

The experimental runs with visible light (8.9 Watts/cm^2 illumination intensity) showed zero activity of TiO_2, which should be expected in advance in view of the wide band gap of TiO_2 (3.2 eV). However the CdSe semiconductor sample gave some moderate activities – 9% conversion of Acid Black 194 and 13.5% conversion of 4-chlorophenol preserving the rest of the experimental conditions the same as those shown in Table 1.

CONCLUSIONS

The result with model waste water is encouraging and the investigation could be extended to monitor the performance of CdSe for contaminated air purification in a gas-phase flat-sheet continuous flow steady state photocatalytic reactor. The nanosized CdSe semiconductor photocatalytic material displays some moderate activities in regard to Acid Black 194 and 4-Chlorophenol decontanation in model wastewaters, being superior in this respect to the TiO_2 photocatalyst. Future research work should be focused on composite CdSe-TiO_2 photocatalytic materials to utilize both the UV and the visible light components of the solar spectrum.

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