

## BIOTEMPLATED SYNTHESIS OF NANOSTRUCTURED ZnO WITH ENHANCED VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY

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### Abstract

Cotton wool was used as a biotemplate for the synthesis of nanostructured ZnO with enhanced visible light photocatalytic activity. Zn<sup>(II+)</sup> complexes were introduced into the structure of cotton fibers via evaporation of ammonia solution containing dissolved ZnO powder. Thermal decomposition of Zn<sup>(II+)</sup> impregnated biotemplate at 500 °C, 600 °C and 700 °C provides yellowish ZnO fine powder which retains the morphology of cotton wool fibers. The photocatalytic activities of both starting and biotemplated ZnO powders were evaluated from the time dependency of degradation of Methyl Violet 2B under the UV ( $\lambda \sim 365$  nm) and visible light ( $\lambda \sim 400$  nm and  $\lambda \sim 425$  nm) irradiation. Measurements were carried out online in UV-Vis spectrometer using a homemade cuvette holder housing equipped with an LED diode. The degradation rate constant for biotemplated ZnO under visible light irradiation was 8 times higher than that of the starting ZnO. The significantly enhanced photocatalytic activity of biotemplated ZnO under visible light irradiation can be attributed to the intimate contact of the ZnO crystalline phase with residual carbonaceous species.

**Keywords:** Photocatalysis, semiconductor, LED diode, photocatalytic reactor, powder material

### 1. INTRODUCTION

Semiconductor-driven photocatalysis is a well-established and growing scientific field with great innovation and commercialisation potential. It underpins many current and emerging technologies in diverse applications, such as water and air purification, self-cleaning and antibacterial surfaces, water splitting, energy conversion and many others (Hashimoto, Irie et al. 2005). Among many semiconducting materials, TiO<sub>2</sub> is undoubtedly the material of the first choice because of its high photocatalytic activity, chemical stability, low toxicity, and price. On the other hand, ZnO has been reported to exhibit photocatalytic activity comparable to or even better than that of TiO<sub>2</sub>. It possesses a similar band gap (E<sub>g</sub> 3.37 eV for bulk) and, as a cheap, non-toxic and bio-safe material with excellent thermal and chemical stability, it is often considered as a promising alternative to TiO<sub>2</sub> (Sakthivel, Neppolian et al. 2003, Han, Liu et al. 2012). Furthermore, the inherent features of ZnO wurtzite structure allows the synthesis of various morphologies possible which is of significant importance as the photocatalytic activity generally depends on the size, specific surface area, crystals perfection, presence of defects, or on the ratio between the surface areas of differently oriented crystalline facets (Djurisic, Leung et al. 2014, Jang, Won et al. 2006). In this light, ZnO is often regarded as model semiconductor material (for studying the relationship between material properties, crystal structure, and photocatalytic activity) in the research field of photocatalysis (Samadi, Zirak et al. 2016, Marschall 2014). Although significant progress has been achieved, the ideal photocatalysts which combine high quantum yield and high efficiency of solar conversion (incident sunlight) are still out of sight. Overall, the quantum yield of the photosensitized reaction is substantially reduced by fast trapping or recombination of photo-generated charge carriers, either on the surface or in bulk. Moreover, the portion of incident sunlight which can generate charge carriers is restricted by the wide band gap of ZnO (or both ZnO and TiO<sub>2</sub>) to photons with energies corresponding to the wavelength  $\lambda \leq 390$  nm, so only a small fraction of incoming energy is harvested. Thus, many attempts have been done to address these issues to explore fully the application potential of semiconductor driven photocatalysis in emerging green technologies (to meet the practical requirement for application in). Among them, the creation of two- or more phase semiconductor heterojunctions, loading photocatalysts surface by noble metals or metal oxide nanoparticles, doping by metal and non-metal elements or dye sensitization are highlighted in literature.

In this paper, we demonstrate the synthesis of visible light photocatalytic active ZnO nanocrystals assembly via a biotemplated method. Cotton wool was impregnated by a solution containing dissolved starting pure ZnO powder in a mixture of ammonia/hydrogen peroxide. Ammonia evaporated quickly, leaving Zn<sup>(II+)</sup> species inside the cotton fibers. Calcination of cotton fibers soaked by Zn<sup>(II+)</sup> species nanocrystals deposited onto the cotton wool surface at 500 °C, 600 °C and 700 °C results in yellowish powders consisting of nanostructured ZnO with the morphology of biotemplate (Dong, Su et al. 2007, Oudhia, Sharma et al. 2016).

## 2. EXPERIMENTAL SECTION

### 2.1. Synthesis of starting material and biotemplated ZnO

All chemicals were used as received without further purification, namely: zinc acetate dihydrate (Penta, purity 99.5%, Czech Republic), oxalic acid dihydrate (Penta, purity 99.2%, Czech Republic), ammonia solution (mikroCHEMO, p.a. NH<sub>3</sub> ca 26% in H<sub>2</sub>O), hydrogen peroxide solution (Penta, p.a. H<sub>2</sub>O<sub>2</sub> ca 30% in H<sub>2</sub>O). Folded cotton wool (BATIST, Czech Republic) was used as a biotemplate. Starting ZnO powder was prepared via thermal decomposition of the ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursor at 500 °C obtained originally by a room temperature precipitation of zinc acetate solution by oxalic acid for 2 hours. Thermal decomposition of the ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is a common method for preparation of high purity ZnO. Biotemplated ZnO was prepared as follows; 0.6 g of starting ZnO powder was dissolved in a 50 mL of ammonia solution with the aid of 4 mL of hydrogen peroxide. After that, 3 g of folded cotton wool spread uniformly on a Petri dish with the diameter of 12 cm were sprinkled dropwise with 5 mL of prepared solution. Soaked cotton wool was left to dry in a ducted laboratory fume hood. Ammonia was quickly evaporated from the zinc impregnated cotton wool in the dish. Then the treated cotton wool was placed into a porcelain crucible with a porcelain cap and calcined in a muffle furnace at 500 °C, 600 °C, and 700 °C. Finally, the obtained fragile materials were disintegrated manually to powder by gentle pressure in a storage bottle.

### 2.2. Characterization methods

The crystalline phase compositions of prepared materials were identified by using X-ray diffractometer MiniFlex 600 (RIGAKU, Japan) equipped with Co X-ray source; operation voltage and current being 40 kV and 15 mA, respectively. The particle size and morphology of prepared materials were characterized by scanning electron microscope Nova NanoSEM (FEI, the Czech Republic). The UV-VIS-NIR spectrophotometer Lambda 1050 (PerkinElmer, USA) was used for the photocatalytic activity measurements. LED diodes VL425-5-15, VL400-5-15 and XSL-365-5E (Roithner LaserTechnik, Austria) were used as light sources for photocatalysis experiments.

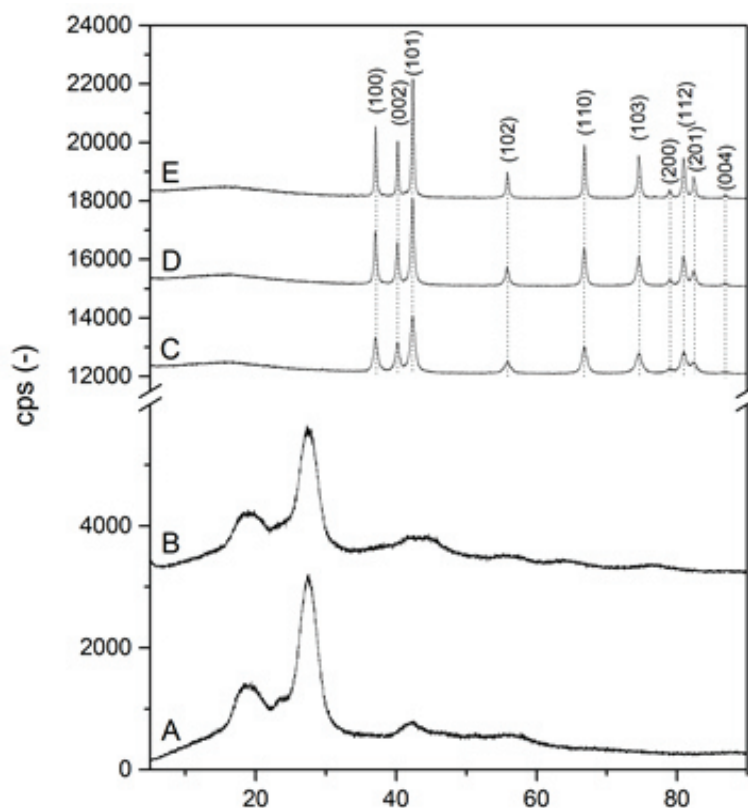
### 2.3. Photocatalysis experiments

The photocatalytic activity of prepared materials was evaluated by means of degradation of Methyl Violet 2B at concentration 3.5 mg.L<sup>-1</sup> under UV and visible light. A novel method based on the use of the homemade board equipped with LED diode for measurement of photocatalytic activity. Moreover, LED diodes can be easily changed, making an experimental set up suitable for assessment of photocatalytic activity over a broad spectrum of wavelengths ranging from 365 to 700 nm. The degradation reaction of model dye and UV-VIS measurements are performed separately.

In a typical experiment, the beaker containing 10 mg of photocatalysts and 10 mL of model dye solution was inserted into the special holder, covered by the board with LED diodes and stirred in the dark for 1 hour in order to reach adsorption/desorption equilibrium. After that, a LED diode illumination was switched on while further stirred. Degradation of model dye was monitored in 60 minutes intervals. Photocatalytic experiments were performed under UV light ( $\lambda \sim 365$  nm) and visible light ( $\lambda \sim 400$  nm and  $\lambda \sim 425$  nm) illumination

### 3. RESULTS AND DISCUSSION

Powder X-ray diffractograms of raw cotton wool, impregnated cotton wool and biotemplated ZnO (annealed at 500 °C, 600 °C and 700 °C) are shown in **Figure 1**. The cotton wool diffraction peaks were indexed to the standard data of the Cellulose (PDF Card No.: 4114994 Quality:C).



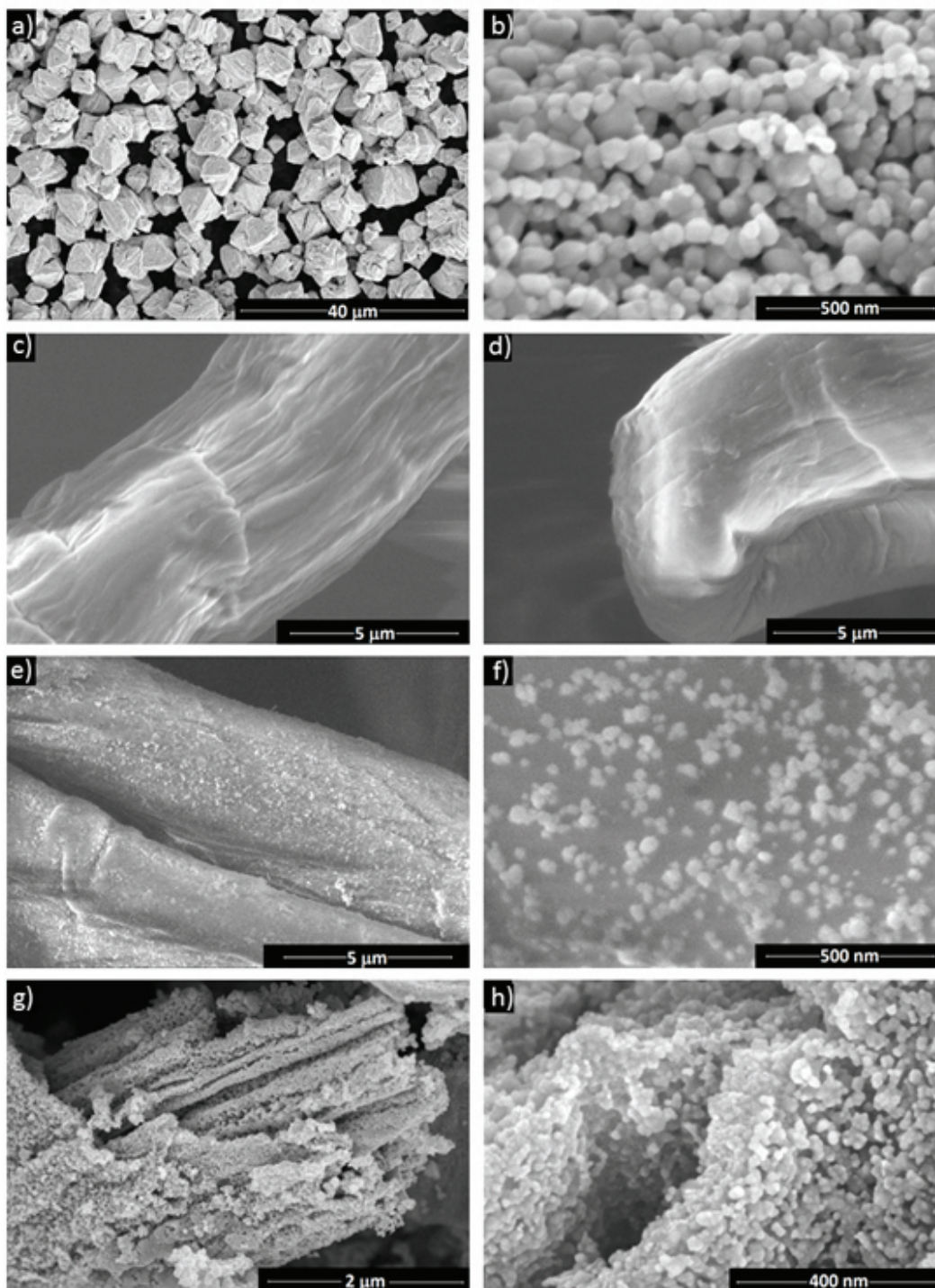
**Figure 1** X-ray diffraction (XRD) patterns of cotton wool (A), impregnated cotton wool (B), biotemplated ZnO-500C (C), biotemplated ZnO-600C (D), biotemplated ZnO-700C (E)

There is no obvious difference in the XRD pattern of impregnated and raw cotton wool in **Figure 1**. Even the FWHM of the main peak (122) did not change by the impregnation process which indicates no or only a negligible change of the crystalline cellulose phase. Besides peaks associated with cellulose substrate, there are no other diffraction lines observable in the diffractogram (B) which indicates that particles deposited onto its surface (clearly seen in **Figure 2.D**) are amorphous by XRD. Diffraction patterns recorded for the product obtained by calcination of Zn<sup>(+II)</sup> impregnated biotemplate (**Figure 1C, D and E**) matched well to the standard data of ZnO powder (PDF Card No.: 10 Quality:C). Obviously, are revealed no cellulose diffraction lines and a negligible peak at 28.2° which can be attributed to carbonaceous residuum after cellulose burning.

The morphologies of starting ZnO material, impregnated cotton wool and bio template ZnO obtained by its calcining are shown in **Figure 2**. Starting ZnO powder formed large aggregates (**Figure 2a**) composed of nanocrystals with size around 60 nm (**Figure 2b**). Morphology observations of impregnated cotton wool at the low and high resolution in **Figure 2c, d** reveals that the surface of cotton fibers is covered uniformly by ZnO<sub>2</sub> nanoparticles of about 40 nm in diameter. Although the crystalline phase structure of these nanoparticles was not confirmed by XRD analysis, amorphous ZnO<sub>2</sub> particles are expected to be present. Low magnification image in **Figure 2e** shows the morphology of impregnated cotton wool calcined at 500 °C for 1 hour and 2g shows the morphology of impregnated cotton wool calcined at 700 °C. There can be clearly seen that the resulting bio template ZnO retains the morphology of cotton wool fibres. On the other hand, the product has not hollow fibre morphology or reasonably thinner fibres, hence it can be considered, that the cotton wool fibres



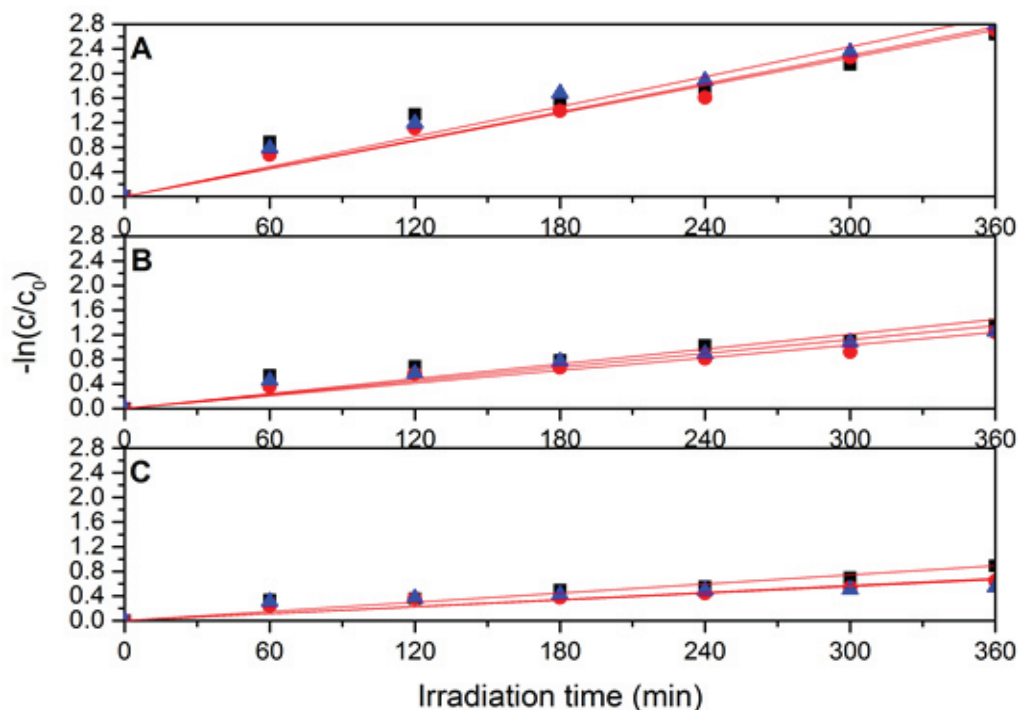
were fully soaked by the caustic oxidative solution during the impregnation procedure. Indeed, no macroscopic shrinking of the wool in the crucible was experienced after calcining.



**Figure 2** SEM images of starting ZnO (a,b), ZnO<sub>2</sub> impregnated cotton wool (c,d), biotemplated ZnO after calcination 500C (e,f), and biotemplated ZnO after calcination 700C (g,h)

Degradation rates of Methyl Violet 2B under UV ( $\lambda \sim 365$  nm) and visible light ( $\lambda \sim 400$  nm;  $\lambda \sim 425$  nm) for both samples, starting and biotemplated ZnO powders were measured. Experiments were carried out also in dark

in order to extract a decrease in dye concentration due to its absorption onto the photocatalyst surface. The plot of  $-\ln(c/c_0)$  versus irradiation time of all samples shows a linear trend which suggests that photocatalytic driven decomposition of dye follows pseudo-first order kinetics.



**Figure 3** Photocatalytic experiment measured under various irradiation wavelengths: **A** 365 nm; **B** 400 nm; **C** 425 nm

The photocatalytic activity was measured as a methylene blue 2B solution bleaching under exposure to light of selected wavelengths. The results of photocatalytic experiments are shown in **Figure 3**. All samples are marked as follow: biotemplated ZnO-700C (blue triangle), biotemplated ZnO-600C (black squares) and biotemplated ZnO-500C (red circles). The overall efficiency of these materials decreases with increasing wavelength of used photo-degradation light. Such a dramatic change and superiority of the biotemplated ZnO material in visible light photocatalytic activity can be assigned to the absorption of photons due to tail-forming states in the bandgap resulting in to the formation of active species involved in the photocatalytic reaction pathway although the precise mechanism remains unclear.

#### 4. CONCLUSION

Nanostructured ZnO with enhanced visible light photocatalytic activity was designed via templated synthesis utilizing cotton wool as a template. Photocatalytic activity of these materials was performed by online measurement of degradation reaction, in the meaning of no sample collecting. It was found that the rate constants for bio template ZnO samples under visible light irradiation were 2 times lower than that of under the UV light irradiation. This ability can be assigned especially to the increased concentration of oxygen vacancies in prepared nanostructured ZnO material. This approach provides a simple and efficient route to prepare hollow fibers and it shows a prospect to prepare a large variety of composite materials using the abundant biological materials as templates.

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