

## Abstract

In the doctoral thesis, two areas of the use of ZnO-based catalysts are presented. The first area involves the preparation of modified ZnO-based materials that have proven to be rather effective photocatalysts, with the ability to photoelectrochemically (PEC) split H<sub>2</sub>O. The second part of the doctoral thesis involves the preparation of the modified Cu-Zn oxide catalysts for ammonia decomposition reaction. Properties of photocatalytic and catalytic materials were investigated using spectroscopic and microscopic methods. Photocatalytic and catalytic activities were then tested with photocatalytic and catalytic measurements. The main focus was to differentiate between the pristine and modified photocatalyst/catalysts regarding their photocatalytic/catalytic activities, and to check the stability of the prepared photocatalytic/catalytic materials.

The first part of the research work describes the preparation of modified photocatalytic materials ZnO with graphitic carbon structures containing nitrogen (hereinafter referred to as g-C<sub>x</sub>N<sub>y</sub>). The prepared photocatalysts were efficiently involved in the production of O<sub>2</sub> with PEC water splitting. Photocatalysts (also referred to as PEC cells), which were modified by the dip-coating method and prepared by the immersion of the electrode into the aqueous dispersions of the precursor CM-complex (CM – cyanuric acid–melamine), showed the highest PEC activity. Namely, the materials retained their porous structure which, during PEC testing, allowed penetration of the electrolyte and simulated solar light to the active sites on the surface of the photocatalysts. The sample synthesised by the powder deposition method, showed the lowest PEC activity, in fact even significantly lower than the PEC activity of the pristine ZnO, which had the morphology of nanowires. This could be interpreted by assuming that the excessive g-C<sub>x</sub>N<sub>y</sub> layer blocked the electrolyte from entering the volume between the ZnO nanowires. With a detailed PEC characterisation, it was shown that the g-C<sub>x</sub>N<sub>y</sub> layer has the ability to effectively extract electronic holes, which are the active sites in the process of H<sub>2</sub>O oxidation. Consequently, this leads to a major improvement in PEC activity - with respect to the photocatalyst ZnO. The optimal sample, which is synthesised by the dip-coating method (when compared to a ZnO photocatalyst without a g-C<sub>x</sub>N<sub>y</sub> layer), shows a 3.5-times higher photocurrent density at a potential of 1.23 V, measured relative to the reversible hydrogen electrode (RHE). Good stability is also confirmed in a strongly alkaline solution.

In the second part of the study, the main focus is on the preparation of Cu-Zn oxide catalysts synthesised by a modified citrate method. The catalysts are further modified with Al<sub>2</sub>O<sub>3</sub> with two synthetic methods, i.e. sol-gel and wet-impregnation techniques. The catalysts were tested for NH<sub>3</sub> decomposition reaction and the production of high purity H<sub>2</sub> for fuel cells. The catalyst prepared using a wet-impregnation technique, having  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a catalyst support, show an improved dispersion of copper-containing species on the catalyst surface, when compared to the catalysts without catalyst support. The analysis of the mentioned catalysts using scanning electron microscopy (SEM) shows a uniform distribution of Cu-species and ZnO particles, and a similar morphology, regardless of the Cu/Zn ratio. Catalysts prepared by the wet-impregnation method, show a superior catalytic activity, compared to catalysts prepared by the modified sol-gel method. This could be attributed to the content of Cu<sup>0</sup> nanoparticles on the catalyst surface and the synergistic effect of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous support. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support helps in distributing the active sites on the surface of catalysts, and significantly increases their specific surface area.

**Keywords:** ZnO, catalyst, O<sub>2</sub> production, H<sub>2</sub> production, activity