

Abstract

Nowadays, the use of carbon dioxide becomes an important economic and environmental problem. Development of techniques allowing for the transformation of this gas in the atmosphere is necessary to achieve closed-loop carbon economy and to prevent any further rise of CO₂ levels. Photocatalysis, which is a promising method, might allow to solve this problem and to efficiently use the energy from sunlight. Titanium dioxide (TiO₂) is a commonly used semiconductor photocatalyst. Unfortunately, this material does not exhibit good activity in photocatalytic CO₂ reduction, especially when water is used as the ecological electron donor. Water oxidation, as an accompanying process to CO₂ reduction, is the least harmful to the environment. In this work, the composites of TiO₂ with other semiconductor photocatalysts were studied in order to obtain a system with enhanced activity in the photocatalytic process. The composites were studied in a gas phase reactor, since such systems may use as feed gas the air and thus might be cheap and easy to produce, which may encourage their wide adaptation.

Materials such as tin-iron, zinc-iron, cobalt, zinc-cobalt spinels, cadmium, copper and copper-cadmium sulfides, copper, tin, cerium and tungsten oxides, and cobalt and copper tungstates were characterized in this work, and tested in the photocatalytic CO₂ reduction, alone and in combination with TiO₂. No activity was found for cerium, tin, tungsten oxides, and cobalt, zinc-cobalt spinels, both alone and in composite. Attempts were made to activate these materials by deposition of nanoparticles of platinum or palladium cocatalyst, however, to no avail. For the composites that did exhibit the activity in photocatalytic CO₂ reduction, further experiments were performed to study the mechanisms governing these processes by employing the spectroelectrochemical techniques (in order to establish the electronic structure of the materials), photocurrent measurements (to determine the interfacial charge transfer and electrical contact between the materials in the composites) surface photovoltage measurements (to check the electrons flow between composite constituents and its direction), and testing the complementary oxidation process with the use of terephthalic acid as the probe.

One of the research questions of this work was the possibility of achieving the improvement in the efficiency of photocatalytic activity of individual materials by combining them into two component systems. Another hypothesis was the question whether combining two semiconductors – one of *n*-type, another of *p*-type – would allow to obtain systems with S-Scheme electron transfer and whether they would exhibit better activity. Next question, which regarded the stability of multicomponent systems, was whether the obtained composites would retain constant activity in the photocatalytic CO₂ reduction process.

The studies demonstrated a substantial improvement of photocatalytic activity of some of the composites relative to individual constituents. For total of 10 different materials, for which the substantial improvement in photocatalytic CO₂ reduction activity was found, the characterization, photocatalytic tests were performed and the mechanisms were studied. It was demonstrated that different mechanisms of photoactivity may exist in the composites of TiO₂ with other semiconductors. The occurrence of heterojunctions, S-Schemes and sensitization of TiO₂ was confirmed. It was demonstrated that the efficiency of the materials in the photocatalytic CO₂ reduction may arise both from the combination of *p*-type with *n*-type semiconductors, as well as the two *n*-type semiconductors. Furthermore, the example of

CuO/TiO₂ (where beneficial energetically relative positions of band edges were observed) demonstrated that the attempts of combining *p*-type and *n*-type semiconductors not always result in a S-Scheme, nor do they always exhibit higher activity in photocatalytic processes. However, it was shown that it is more important for the development of S-Schemes to appropriately select materials with suitable Fermi levels. For the activity in the photocatalytic CO₂ reduction, equally important are other properties of the materials and composites such as electrical contact between the semiconductors, or the engineering of the surface or defects of the materials. The studies of the stability of the photocatalytic activity of the materials shown that some of the materials over the course of the process loose some of the activity. These materials were composites of TiO₂ with zinc-iron spinel, copper and copper-cadmium sulfides, copper and cobalt tungstates. It was observed that because of the photocorrosion and/or the poisoning of the active centres on the surface with strongly adsorbed CO₂ reduction products the activity deteriorated with subsequent runs.