Do we know how to design efficient photocatalysts?

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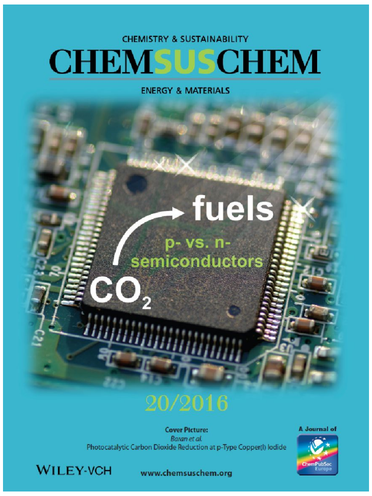
The photocatalytic carbon dioxide reduction is a challenging process in which, similarly to photosynthesis, light can be converted to a chemical energy. The energetics of this reaction is very different from the most commonly studied photocatalytic reactions in which pollutants are photooxidized to CO_2. Although these two processes are, in principle, opposite to each other, usually the same photocatalysts (mainly oxides, including TiO_2) are considered in both cases. Most of metal oxides, being *n*-type semiconductors, upon excitation offer strong oxidation properties, but at the same time they are relatively mild reductants. We propose another approach to a photocatalytic CO_2 reduction, involving application of *p*-type semiconductors, offering, in comparison to *n*-semiconductors, better reduction and worse oxidation properties. As an example, the photocatalytic activity of *p*-CuI towards carbon dioxide photoreduction (mainly to CO and HCOOH) can be compared to that of TiO_2 (P-25).[1] The applicability of *p*-type semiconductors, including g-C_3N_4, for carbon dioxide valorization will be discussed.[1,2]

Other important parameters influencing the photocatalytic CO_2 reduction process encompass: redox properties of the material, adsorption of reactants, number of electrons participating in the reduction reaction, the oxidation counterpart of the reaction, and several others. Redox properties of the photocatalysts can be easily determined using spectroelectrochemical methods developed recently in our laboratories.[3] Recognition of density of electronic states appears fundamental in understanding and predicting applicability of a photocatalyst for carbon dioxide reduction. The number of electrons participating in reduction reactions should also be taken into account. Methane formation requires eight electrons in total,[4] but carboxylic acids can be synthesized in the process of $CO_2^{\bullet-}$ (one-electron reduction of CO_2) and $R^{\bullet}$ radicals (one-hole oxidation of RH) coupling.[5,6]



The spectroelectrochemical approach to characterize redox properties of semiconductors helped us also to understand the differences between the activity of various titanium dioxide materials usually used to photooxidize organic pollutants.[7] Rutile-TiO_2 and anatase-TiO_2 offer various activity in water oxidation and O_2 reduction.

Do we know how to design photocatalysts for CO_2 reduction or water oxidation? Can we control the redox properties of photocatalysts? How can we improve the photocatalytic activity of photocatalysts? These questions will be answered during the presentation.

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[1] T. Baran, S. Wojtyła, A. Dibenedetto, M. Aresta, W. Macyk, *ChemSusChem* **2016**, *9*, 2933-2938.
[2] S. Ye, R. Wanga, M.-Z. Wu, Y.-P. Yuan, *Appl. Surf. Sci.* **2015**, *358*, 15–27.
[3] E. Świętek, K. Pilarczyk, J. Derdzińska, K. Szaciłowski, W. Macyk, *Phys. Chem. Chem. Phys.* **2013**, *15*, 14256-14261.
[4] T. Baran, S. Wojtyła, A. Dibenedetto, M. Aresta, W. Macyk, *Appl. Catal. B: Environ.* **2015**, *178*, 170-176.
[5] T. Baran, A. Dibenedetto, M. Aresta, K. Kruczała, W. Macyk, *ChemPlusChem* **2014**, *79*, 708-715.
[6] M. Aresta, A. Dibenedetto, T. Baran, S. Wojtyła, W. Macyk, *Faraday Discuss.* **2015**, *183*, 413-427.
[7] M. Buchalska, M. Kobielusz, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, *ACS Catalysis* **2015**, *5*, 7424.