

Effect of metal ions on photoelectrochemical oxidation of methanol and formic acid at nanoporous TiO₂ electrodes.

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Metal ions are known to affect rates of photooxidation of various organic molecules at semiconductor photocatalysts such as TiO₂.⁽¹⁻⁵⁾ The actual effect of the metal depends strongly on the chosen organic molecule and the conditions of the experiment. In fact, the influence of the metal ions can vary from enhancing the photooxidation process to virtually suppressing it. Although various mechanisms trying to explain such behaviour have been proposed, certain aspects of the role played by the metal ions present in the reaction medium are still not clear.

In this work the effect of two selected metal ions upon photooxidation of small organic molecules (methanol and formic acid) at nanoporous TiO₂ electrodes is re-examined. Behaviour of such films under band-gap illumination is to a large extent similar to that of TiO₂ suspensions and, in addition, their use allows one to conduct in parallel photoelectrochemical and microgravimetric experiments. Combination of these techniques allows following simultaneously the photooxidation of organic species and the deposition of metal ions since the beginning of the photocatalytic process.

For these experiments nanoporous TiO₂ film electrodes of different thickness immersed in carefully deaerated acidic solutions containing methanol or formic acid and various amounts of metal ions, expected to act as hole, respectively, electron scavengers have been employed. It is shown that, under specific conditions, the photooxidation of methanol and formic acid under applied anodic bias exhibits an important current increase in the presence of Cu²⁺ ions in solution (Fig. 1). Such photocurrent increase occurs for copper ion concentration up to 1 mM and under relatively low intensity incident illumination. On the other hand, under similar conditions, Hg²⁺ ions act simply as electron scavengers leading to a decrease in the net photocurrent. The raise of the photooxidation current in the presence of Cu²⁺ ions was less pronounced when thin (less than 1 μm thick) TiO₂ films were replaced by thicker (ca. 3 μm) electrodes.

As already mentioned, the increase of the photocurrent in the presence of copper (II) ions was observed only under relatively low intensity illumination. Increasing the light intensity (using a full output of a 150 W Xe lamp) lead to a dominant copper deposition and the corresponding decrease of the photocurrent.

As expected, results of microgravimetric measurements performed in the course of methanol photooxidation in the solution containing simultaneously copper (II) ions are consistent with a continuous, rapid metal deposition occurring at open circuit potential (Fig. 2). However, a slower copper deposition was still

observed at the illuminated TiO₂ electrode subjected to a large anodic bias.

Possible ways in which the Cu²⁺ ions can affect photooxidation of small organic molecules on nanostructured TiO₂ electrodes are discussed.

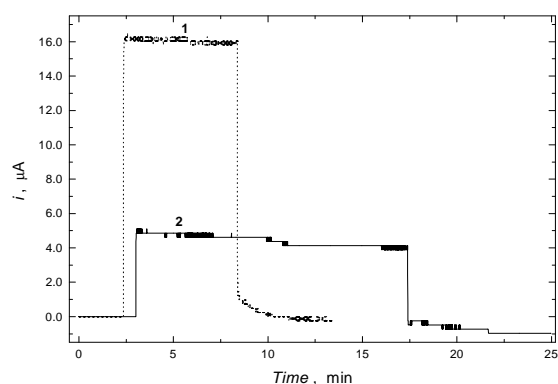


Fig. 1 Photooxidation of 0.11 M methanol from a solution containing 0.01 M HClO₄ and 0.1 M NaClO₄ on a ca. 0.5 μm thick mesoporous TiO₂ layer under monochromatic illumination (360 nm) in the presence (1) and absence (2) of 1 mM Cu²⁺. Applied anodic potential: 0.997 V vs. NHE.

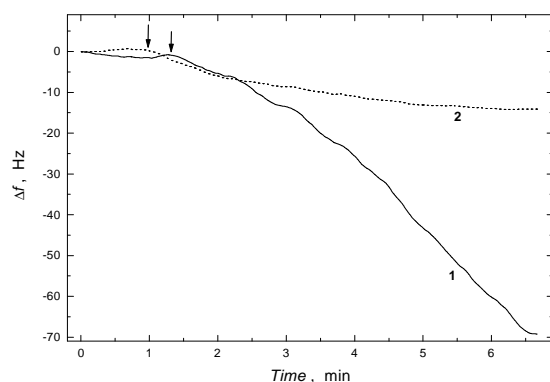


Fig. 2 Frequency changes during photooxidation of 0.11 M methanol in a solution containing 1 mM Cu²⁺, 0.01 M HClO₄ and 0.1 M NaClO₄ on a ca. 0.9 μm thick mesoporous TiO₂ layer deposited on 5 MHz Ti-coated quartz crystal under monochromatic illumination (360 nm) at open circuit (1) and under a large anodic bias (0.997 V vs. NHE (2)).

References

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