

Nanocrystalline Binary Oxide Composites for Photoelectrochemistry and Photocatalysis

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At present, photoelectrochemical and photochemical properties of wide-bandgap semiconductors (TiO_2 , ZnO , WO_3 , Fe_2O_3 , etc.) are rather well understood in the commercially useful processes of water photodecomposition as well as in the processes of photodegradation of organic pollutants [1-4].

In the present work, we have studied the properties of binary semiconductor oxide systems (TiO_2 - In_2O_3 , TiO_2 - WO_3 , TiO_2 - Bi_2O_3 , etc.) [5,6] prepared in the form of both nanostructured composites and two-layered thin film electrodes.

The detailed investigation of nanostructured TiO_2 - In_2O_3 composite has revealed that there exists a strong mutual influence of the components of the binary oxide system during the thermal treatment of TiO_2 - In_2O_3 composite xerogels which manifests itself in a marked suppression of the TiO_2 crystallite growth and in an increase in temperature at which anatase begins to transform to rutile in the composites in the presence of indium dioxide. In the case of the pure titanium dioxide xerogels, TiO_2 crystallites grow from 4.5 to 34 nm as the annealing temperature increases from 200 to 600 °C, whereas for the $\text{TiO}_2(0.91)$ - $\text{In}_2\text{O}_3(0.09)$ composite heated at 600°C, the average diameter of anatase crystallites does not exceed 7 nm, and rutile traces appear only at a temperature of 700 °C.

Optical and PEC spectroscopy measurements have shown that the bandgap edge of the composite films is blue-shifted as compared with that of single-component films. The energy of direct and indirect transitions passes through a maximum as the In_2O_3 content increases. The enhanced effective bandgaps of the composites have been assigned to a combination of possible quantum size and quasi size effects and interface phenomena. It is significant that the distinction of the composite properties from those of the individual oxides does not result from the chemical interaction of the composite components. No evidence for indium titanate formation has been found in the composite system by XRD, XPS, IR-spectroscopy and thermogravimetric analysis, at least in the temperature range investigated (up to 800 °C).

From the dark conductivity, photo-conductivity and photoelectrochemical measurements, it follows that the charge transport in the TiO_2 - In_2O_3 composite films occurs mainly through interconnected In_2O_3 particles and drastically facilitates when 3D infinity clusters of In_2O_3

nanoparticles form. The efficient separation of photogenerated charge carriers takes place in the interconnected TiO_2 and In_2O_3 particles due to the favorable energetics of the conduction bands of these oxides.

The distinctions of the photoelectrochemical and photocatalytical properties of the composites from those of the individual oxides revealed in a variety of processes (photoelectrolysis of water, photodecomposition of dichloroacetate, o-chlorophenol and Methyl Orange) is probably associated not only with the specific interface interaction of the particles, but also with the change in their properties arising during the thermal treatment of the composite. So, the treatment of $\text{TiO}_2\text{-In}_2\text{O}_3$ (1:0.25) composite with 1 N H_2SO_4 for 2 h gives rise to dissolution of In_2O_3 leaving only TiO_2 which was a constituent of the composite. The distinctive feature of this new- TiO_2 is a small average size of its particles (less than 7 nm) in spite of a rather high annealing temperature (400). It should be noted that its photocatalytic activity in Methyl Orange photodegradation is two times higher than that of the individual TiO_2 xerogel annealed at the same temperature and 40 times higher than that of $\text{TiO}_2\text{-In}_2\text{O}_3$ (1:0.25) xerogel from which this new- TiO_2 was produced. It was shown, the photocatalytic reactivity of the new- TiO_2 , $\text{TiO}_2\text{-In}_2\text{O}_3$ composite and individual In_2O_3 in the process of DCA photodegradation is markedly lower than that in Methyl Orange photodegradation. Commercially available TiO_2 photocatalysts (Degussa P-25, Hombikat) demonstrate a higher photoactivity in the former process. In contrast, the new- TiO_2 is the most efficient catalyst of the o-chlorophenol photodegradation. When applied to this process, it does not cause the formation of extremely undesirable products of o-chlorophenol photopolymerization, which are formed in the similar experiments involving Degussa or Hombikat as a photocatalyst.

References

1. Poznyak S.K., Kokorin A.I., Kulak A.I. J.Electroanal.Chem., 1998, V. 442, 99-105.
2. Poznyak S.K., Kulak A.I. Electrochimica Acta, 2000, V. 45, 1595-1605.
3. Poznyak S.K., Golubev A.N., Kulak A.I. Surf. Sci., 2000, V. 454-456, 396-401.
4. Poznyak S.K., Sviridov V.V, Kulak A.I., Samtsov M.P. J. Electroanal. Chem., 1992, V. 340, 73-97.
5. Sviridov V.V, Kulak A.I. Elektrokhimiya, 1986, V. 22, 83-89.
6. Kulak A.I. Electrochemistry of semiconductor heterostructures. Minsk, "Univ.", 1986.