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Nanosized WO_3 thin film as a multifunctional hydrogen material for achieving photolysis in CuCl films via hydrogen photosensitization

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ABSTRACT

The paper highlights less-common properties of nanosized WO_3 thin films which make it possible to achieve photolysis in CuCl films via the use of a CuCl–WO_3 double-layer structure. The WO_3 film provides first photoinduced detachment of hydrogen atoms from organic molecules adsorbed on the oxide surface; the hydrogen atoms, being transferred into WO_3, turn into electrons and protons which migrate then to the CuCl film forming sensitizing centres on the halide surface being illuminated simultaneously with the illumination of the WO_3 surface. This in turn gives rise to photolysis in the CuCl films, which does not occur without the hydrogen sensitization. The nanosized WO_3 film makes it possible to trigger two famous surface photochemical reactions, first proton-coupled electron transfer between the hydrogen-donor molecules and the oxide surface, and then the photolysis of the halide, which radically changes the optical parameters of both the WO_3 and the CuCl films.

1. Introduction

The interest in WO_3 thin films increased with the pioneering work by Deb [1], which initiated intensive investigations of electrochromism and photochromism in this oxide [2–5].

WO_3 thin films can also play other important roles, which can be employed for achieving new processes in well-studied materials.

First WO_3 can play the role of a catalyst in photoinduced hydrogen transfer, if specially selected organic molecules (hydrogen donors) are adsorbed on the WO_3 film surface; hydrogen atoms being detached from the adsorbed molecules as the result of excitation of the WO_3 film surface by photons with the energy exceeding the oxide forbidden energy gap and transfer of surface excitation to the adsorbed molecules [6–10].

When the WO_3 surface absorbs n photons with energy exceeding the oxide band gap n electron–hole pairs are generated in the oxide

$$WO_3 + n(h\nu) \rightarrow WO_3 + n(h^+ + e^-) \quad (1)$$

Very often, methanol is used as a hydrogen donor, like in this study, and for the one of the photogenerated holes, according to [9,10], it is possible to write

$$h^+ + (CH_3OH)_{ads} \rightarrow H^+ + (\dot{C}H_2OH)_{ads} \quad (2)$$

The hydrogen transfer between the donor molecule and the oxide surface yielded a scavenge of the hole and formation of a $\dot{C}H_2OH$ radical, which in fact is an exchange of the photogenerated hole for a proton. This in turn makes the life-time of an electron, photogenerated together with the hole, indefinitely long, since scavenging of the hole makes recombination impossible. This electron is localized at a W atom giving rise to the formation of a lower-valency cation

$$W^{6+} + e^- \rightarrow W^{5+} \quad (3)$$

The number of the photogenetrated electrons and protons continuously grows under illumination and hydrogen tungsten bronzes are formed

$$WO_3(RH_n)_{ads} + h\nu \rightarrow H_xWO_3(RH_{n-x})_{ads} \quad (4)$$

where $(RH_n)_{ads}$ is an adsorbed molecule (hydrogen donor), and H_xWO_3 is a hydrogen tungsten bronze [2].

Under illumination the concentration of the injected particles grows and the electron–proton plasma front moves from the film surface into the film depth, which implies the possibility of transporting of the electron–proton excitation to some other materials that could be in contact with the WO_3 films, see Fig. 1.

For this purpose double-layer structures can be prepared; WO_3 being the upper layer of the double-layer structure, whereas the other layer is a hydrogen acceptor material whose doping with hydrogen atoms should be carried out. Demands of compatibility predetermine the regime of deposition for the WO_3 layer: namely,

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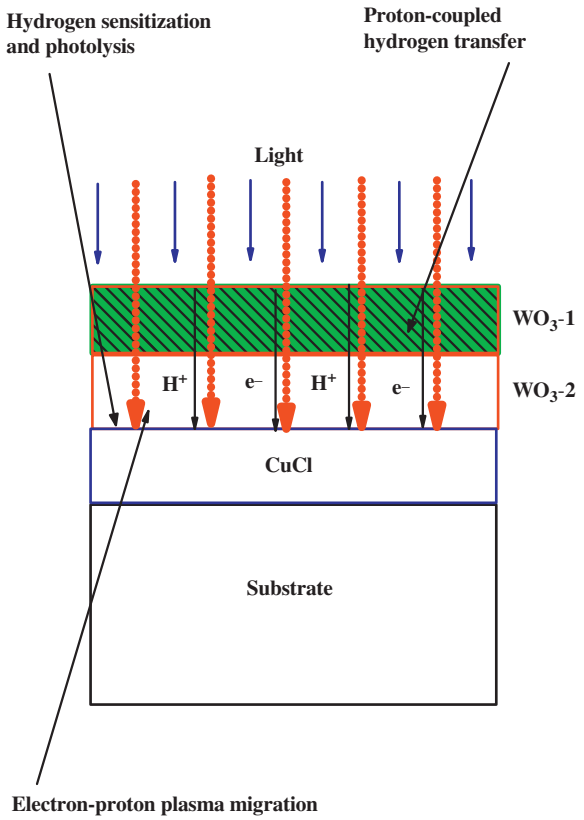

Fig. 1. Schematic of the processes arising in the CuCl–WO_3 structure under illumination. WO_3-1 is an upper layer of the WO_3 film where the reaction of the proton-coupled electron transfer is effective, WO_3-2 is a layer through which the photogenerated protons and electrons migrate to the CuCl surface. Solid lines denote the photons absorbed in the WO_3 film, whereas dotted lines denote the photons absorbed in the CuCl film (colour on line).

it must be deposited onto the hydrogen acceptor at room temperature.

There are various technologies of WO_3 thin film preparation, but the films prepared by evaporating WO_3 powder onto unheated substrate possess many interesting specific properties, which is worthwhile to elucidate. In the next section the properties of the nanosized WO_3 films are considered to demonstrate why and how these films successfully perform several functions which yield the photo-initiated supply of the CuCl surface with atomic photochemical hydrogen.

1.1. Properties of WO_3 disordered films

In the present research highly disordered WO_3 were employed. There properties have been widely investigated. For this reason, only a short summary concerning the film characterization is given here which is necessary for understanding of the performance of the double-layer structure.

The atomic force microscope investigations showed that the WO_3 films deposited onto unheated substrates were be nanocomposites [9,11], whereas the absence of long-range order was confirmed by X-ray analyses. For this reason, the films can be characterized as "quasi-amorphous".

The films possess a friable structure with the grains of ~50 nm average size and a high porosity with an average of ~50 nm pore diameter and ~100 nm depths, where the adsorbed molecules can be arranged freely. The surface is essentially heterogeneous with exceptionally high chemical reactivity for some surface centres [9,11]. These films have ~0.8 of WO_3 bulk density [1]. The same tendency is observed for the refractive index n which is n=2.2 versus n=2.5 for bulk WO_3[1]. The rough and highly disordered fractal surface with macropores provides high adsorption capacity. Investigations of adsorption of methanol on the WO_3 film surface, carried out with the help of the resonance nuclear reaction $^3He(^2D, p)a$, gave the number of adsorbed CH_3OH molecules > 0.2 per one W cation [12].

The WO_3 films have high efficiency in the photoinduced hydrogen transfer between hydrogen-containing molecules and the oxide surface, which enables to carry out this process even at very low temperatures. The mechanism was described in detail elsewhere [9,10]. The reaction was determined as tunnelling proton-coupled electron transfer (PCET) [13].

The WO_3 films have very small electron mobility μ which ranges within between 0.03 and 0.2 $cm^2\,V^{-1}\,s^{-1}$[14]; the electron diffusion coefficient is determined as $D=0.0025\pm0.0006$ $cm^2\,s^{-1}$[15]. The photogenerated electrons have great inclination to localization via Anderson, electron–phonon, and electron–electron mechanisms of localization [14].

The electron work function for the WO_3 films being j=4.3–4.9 eV [16–21], which is a relatively low value as compared with many other materials. The typical schematic of the electron energy band diagram, which is valid also in the present case, is presented in [11].

The electron flow occurs from the WO_3 layer to the hydrogen acceptor after preparation of the double-layer structure if a partner material has a higher value of ϕ; the surface of the hydrogen acceptor being negatively charged. The charging prevents injection of the photogenerated electrons into the partner material since they have a very small probability to reach the hydrogen acceptor surface. The overwhelming majority of the photogenerated electron–hole pairs recombine; only small number of the phogenerated holes reaches the surface where they can be scavenged by the adsorbed organic molecules (hydrogen donors) and exchanged for protons. The electron conduction in the WO_3 films is variable range hopping [15]. Under illumination, the concentration of the electrons and protons on the WO_3 surface increases, which drives the electron–proton plasma to migrate towards the hydrogen acceptor surface; the rate of transfer being determined by a chemical diffusion coefficient D of the slowest particle, that is by the proton diffusion constant D_H^+, which for the WO_3 films is $\sim10^{-11}$ $cm^2\,s^{-1}$[22]. Below it will be shown that due to the high absorption coefficient, it is obvious that the photoreaction is efficient within the upper layer of ~0.1 μm thick [9,11]. If the WO_3 film is ~1 μm thick, the plasma front reaches the hydrogen acceptor surface approximately in a time

$$t=d^2/4D \tag{5}$$

where d is the film thickness. The plasma front reaches the partner surface several minutes after the illumination has started.

From what is said above we learn that the WO_3 films have a number of exceptional qualities which make it possible to use them for in situ hydrogen doping of materials. The WO_3 films provide the adsorption of the hydrogen donors, the detachment of hydrogen atoms, and their migration to the surface of a partner material.

One can easily notice that the process described has much common with the hydrogen spillover, see, e.g., [23] and references therein. Like for the common hydrogen spillover, hydrogen atoms are released and transferred to the surface of another material. The difference is that here hydrogen atoms are released under the action of light. At first the photoinduced hydrogen spillover (photospillover) was used to achieve the hydrogen doping of other transition oxide films such as VO_2 films [24], polycrystalline