

Hydrogen activation at TiO₂ anatase nanocrystals

Thomas Berger^a, Oliver Diwald^{a,*}, Erich Knözinger^a, Francesco Napoli^b, Mario Chiesa^b,
Elio Giamello^b

^a Institute of Materials Chemistry, Vienna University of Technology, Veterinärplatz 1/Trakt GA, 1210 Vienna, Austria

^b Dipartimento di Chimica IFM, Università di Torino, NIS Centre of Excellence, Via P. Giuria 7, 10125 Torino, Italy

Received 16 March 2007; accepted 6 June 2007

Available online 22 June 2007

Abstract

The chemical activation of small molecules like hydrogen or oxygen at the surface of UV excited nanocrystals can provide valuable insights into the solid's photoactivity. We investigated the interaction of dehydroxylated TiO₂ anatase nanocrystals with atomic as well as molecular hydrogen using electron paramagnetic resonance spectroscopy. Electron transfer from atomic hydrogen occurs spontaneously at $T = 77$ K and produces a charge separation state which is characterized by surface adsorbed protons and trapped electrons forming paramagnetic Ti³⁺ (d¹) states. While there is no significant activation of molecular H₂ at the surface of dehydroxylated particles in the absence of UV light, H₂ acts as an efficient scavenger of photogenerated hole centers. These reactions are compared with charge carrier trapping at $p < 10^{-5}$ mbar and discussed in the light of experiments which were carried out on frozen colloidal nanoparticle suspensions as described in the literature.

© 2007 Elsevier B.V. All rights reserved.

Keywords: TiO₂ nanocrystals; Atomic hydrogen; Trapped hole centers; Hole scavenging; Electron paramagnetic resonance; Ti³⁺ ions

1. Introduction

Oxide semiconductors keep playing a prominent role in the present search for new synthetic strategies to design nanostructure architectures for solar energy conversion [1–4]. The efficient use of light which corresponds to the conversion of photon energy into electricity requires the spatial separation of charge carriers in the solid until they can undergo interfacial transfer steps. Due to the confined volume of a nanometer-sized crystal charge carriers in the bulk can significantly interact with those trapped at the surface. If their concentration is too high and the spatial separation of holes and electrons is insufficient, charge carrier recombination leads to substantial dissipation of photon energy into heat. In this context, the chemical condition of the surface is of particular importance since sites capable of charge carrier trapping are expected to be there [5–7].

However, little information about nature and location of trapping and recombination sites is available for photoactive materials in polycrystalline form [8,9].

On TiO₂-based materials localized charges in form of paramagnetic Ti³⁺ (d¹) ions were investigated on a variety of colloidal TiO₂ nanoparticle samples at cryogenic temperatures [10–14]. Such investigations usually involve suspended slurry samples which are frozen in liquid nitrogen to form a water glass. Whereas it has been found that the concentration of trapped holes is sensitive to hydration and total surface area, specific electron centers on TiO₂ behave rather invariant with respect to the chemical condition of the surface. For colloidal samples it was found that at temperatures above 10 K electrons localized in the TiO₂ lattice, i.e. Ti³⁺ (d¹) ions migrate to the surface where they become trapped and can react with adsorbates [15–18]. An interesting experiment in this context has revealed that all localized electrons are converted into surface trapped electrons when specific molecules such as methanol were employed as hole scavengers [17].

* Corresponding author. Fax: +43 1 250773890.

E-mail address: odiwald@mail.zserv.tuwien.ac.at (O. Diwald).

There is general agreement about the fact that the physical properties of nanometer-sized oxide semiconductors are subject to the coordination state of surface ions and for this reason critically depend on the size of the particles as well as on the surrounding phase. As an example, it was found for TiO₂ nanocrystals that the presence of adsorbed solvent molecules, capping agents or contaminants can lead to positive excess specific heats that are not observable on dehydrated nanoparticles [19]. OH groups localized at the surface of alkaline-earth oxides have been found to drastically modify the electron trapping properties of the solid [20]. Very important for photocatalytical applications it has been shown by means of time-resolved two-photon photoemission spectroscopy that the propensity of water to hydroxylate metal oxide surfaces [21,22] can give rise to “wet electron” states that are associated with low energy pathways for transfer of photogenerated electrons [23,24]. Therefore, the investigation of trapping and recombination of charge carriers carried out in the absence of adsorbates and intergranular contacts [25] is needed as a point of reference in order to rationalize more complex systems [26,3,27]. In addition, the dependence of characteristic figures – such as the concentration of trapped charges per crystallite – on the inherent materials properties, e.g. size, morphology of the polycrystals and degree of electrical insulation between them, is a critical requirement in order to make observations obtained on powdered materials transferable to surface science studies on single crystals [28–30].

In previous studies, we have shown that when isolated and essentially dehydroxylated TiO₂ nanocrystals are subjected to UV light under high vacuum conditions (HV, $p < 10^{-5}$ mbar), the surface trapping process of photogenerated hole centers can be tracked by electron paramagnetic resonance (EPR) spectroscopy [31]. For anatase particles with an average size of 13 nm and a photon flux below $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, we found that the maximum concentration of trapped charges amounts to one separated electron–hole pair per particle [32]. However, if the photon flux lies considerably above $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ a local temperature rise that is caused by the nonradiative recombination of charge carriers is detectable by EPR spectroscopy [33]. Specific for dehydroxylated TiO₂ nanocrystals which were previously activated under high vacuum conditions and oxidized thereafter we found that the majority of trapped electrons escape EPR detection and, as indicated by a continuous MIR absorption, remain in the conduction band, i.e. delocalized over the lattice of the crystallite [5,34]. The limit of one electron–hole pair that can be kept persistently separated per nanocrystal can be exceeded when scavengers for photogenerated charges are present (Eq. (1))



Using molecular oxygen as an electron acceptor, photogenerated electrons become localized at adsorbate molecules O₂[−] and the negative charge is screened more efficiently from other charge carriers [32]. Consequently,

Coulomb repulsion as well as charge carrier recombination are diminished and approximately 10 electron hole pairs can be separated persistently.

Photogenerated holes – on the other hand – oxidize electron donor molecules that act as hole scavengers. Although there is a rich body of spectroscopic evidence related to the hole scavenging ability of reagents like alcohols or inorganic ions [35,36] only few informations exist for the activity of more simple H-containing molecules like molecular hydrogen or water in trapping photogenerated charges. This topic is very important in the light of the fact that water electrolysis is an active area of research in photoelectrochemistry reasoned by its potential to generate molecular hydrogen as a fuel.

Apart from photocatalytical and photoelectrochemical applications, the interaction of H atoms with oxide host materials has attracted increasing scientific interest [37–39]. In the case of simple insulating oxides such as MgO, H atoms undergo spontaneous ionization at the surface forming surface excess electron species, which provide opportunities for the design of new materials with precisely tuned electronic and magnetic properties [40]. For complex oxides such as nanoporous crystals of 12CaO:7Al₂O₃ the interconversion of hydrogen species in different charge states (hydride ions, neutrals and protons) provide novel photoelectronic functions to the host material [41,42]. Furthermore, intentional intercalation of hydrogen into oxide materials represents a promising approach for the storage of environmentally harmless fuels [43]. For powdered TiO₂, it was reported very recently that reaction with atomic hydrogen gives rise to a charge separation state where the H atom derived electrons enter shallow trap states. Up to now, such an n-type doping procedure was only investigated by transmission IR spectroscopy [44,45].

The purpose of the present paper is to report on the interaction of hydrogen with isolated TiO₂ nanocrystals in the dark as well as under the influence of UV excitation. In this context EPR spectroscopy is extremely useful since it is the method of choice for the detection of localized charges such as trapped electron states (Ti³⁺) or surface trapped hole centers (O[−]) [10–12,46]. By using well-defined environment conditions such as vacuum or hydrogen gas it is possible to single out reaction channels which involve the chemical reactivity of specific bulk and surface sites. With regard to colloidal nanocrystals that are photoexcited in a frozen matrix [11–13] the results presented in this paper should also contribute to a deeper understanding of effects that occur at the gas–solid or gas–liquid interface in the course of photochemical reactions [47].

2. Experimental

Nanocrystalline anatase TiO₂ particles were synthesized by means of thermal decomposition of titanium isopropoxide vapor in a flow reactor system by the metal organic chemical vapor deposition (MOCVD) method [48]. The product powder was then gradually annealed (10 K/min)

Download English Version:

<https://daneshyari.com/en/article/5376327>

Download Persian Version:

<https://daneshyari.com/article/5376327>

[Daneshyari.com](https://daneshyari.com)