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Photocatalysis

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Tuning the Selectivity of Photocatalytic Synthetic Reactions Using Modified TiO_2 Nanotubes**

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Abstract: *Differently modified TiO_2 nanotubes were used to achieve a drastic change in the selectivity of a photocatalytic reaction. For the photocatalytic oxidation of toluene, depending on the electronic properties of TiO_2 (anatase, rutile, Ru-doped), a strong change in the main reaction product (namely benzoic acid versus benzaldehyde) can be achieved, and certain undesired reaction pathways can be completely shut down.*

Photocatalytic reactions on semiconductive TiO_2 are widely used and investigated for 1) water splitting in view of H_2 production, and 2) the destruction of environmental pollutants from water and air.[1–8] A much less explored application is the use of the photogenerated electron–hole pairs in redox or radical based organic synthetic reactions. In comparison with the large potential of this approach, only a small number of successful attempts have been reported.[9,10] The main reason that photocatalytic synthesis is still in its infancy may, to a large extent, be ascribed to the fact that a multitude of reaction pathways become accessible when a photoinduced electron or hole transfer from TiO_2 to an organic species occurs. For example, a wide range of radical species can be initiated at the TiO_2 valence or conduction band, which generally leads to a high degree of non-selectivity and thus a wide product distribution. For the majority of photocatalytic experiments, commercial TiO_2 nanoparticles such as P25 are used as suspensions, not only for photocatalytic decontamination reactions (pollutant degradation) but also for constructive organic synthesis. In the latter case, the main approaches to enhance the reaction selectivity are based on optimizing solvents to steer lifetime and speciation of radicals. Nevertheless, examples where a high selectivity in organic synthesis is reached are relatively scarce.[9–11]

A conceptually entirely different approach to shift the reaction selectivity is altering the photocatalyst, namely its electronic properties and its nanoscopic geometry. Geometry control seems particularly crucial, as recent work by Bahnemann et al.[12] demonstrated that for practical nanoparticle-based photocatalysts the real aggregate size in solution is of a very critical role. In the present work, to circumvent the aggregate issue, we use self-organized TiO_2 nanotube layers fixed on their substrate as a highly geometry defined photocatalyst. Such anodic nanotube layers additionally allow an easy and straightforward modification of the electronic properties of the photocatalyst. This is important as the electronic properties of the semiconductor, namely its band-edge position and the presence and position of carrier trapping states relative to the environment directly determine the thermodynamic feasibility of reactions.[3,13,14] Additionally, kinetic effects of the catalyst and its selectivity can strongly be altered by “adding” charge transfer co-catalysts or by introducing charge carrier recombination or trapping centers. In the present work, we use nanotube layers and show that in these systems, modification of structure (rutile vs. anatase) or even more the incorporation of a doping element such as ruthenium can have an extreme effect on the selectivity of a photocatalytic synthesis reaction. As an example we use the photocatalytic oxidation of toluene to carbonyl and carboxyl compounds. This toluene photocatalytic oxidation is known to yield a wide range of reaction products.[15–18] Oxidation approaches of toluene using a range of classical routes,[19] as well as some photocatalytic attempts, typically lead to a mixture of compounds such as benzyl alcohol, benzaldehyde, benzoic acid, and carbon dioxide; additionally, if benzoic acid and benzyl alchohol are simultaneously formed they may react to benzyl benzoate (Supporting Information, Scheme S1). Usually the target product in toluene oxidation is either benzaldehyde or benzoic acid; both are used in the pharmaceutical, agricultural, and industrial applications.

Herein we report the use of TiO_2 nanotubes for the photocatalytic oxidation of toluene, and demonstrate how specific modification of the tubes electronic properties leads to a significant change in selectivity (Figure 1).

Ordered Ti-oxide based nanotubes were grown on their metallic substrates by self-organizing anodization to a length of 1–2 μm (as shown in Figure 2a) and then crystallized by an adequate heat treatment. In our work we annealed the nanotube layers in air to a partially crystalline anatase at 300 °C, to fully crystallized anatase at 450 °C, and rutile-rich nanotubes at 650 °C and full rutile tubes (see XRD in Figure 2b; Supporting Information, Figure S1d). Additionally we used Ru-doped TiO_2 nanotubes produced as described in previous work[20] (compositional information is also given in the Supporting Information, Section S1l). To distinguish effects distinct to Ru from other metal addition, reference experiments were carried out with TiO_2-Pt and TiO_2-Pd tubes produced (see the Supporting Information).

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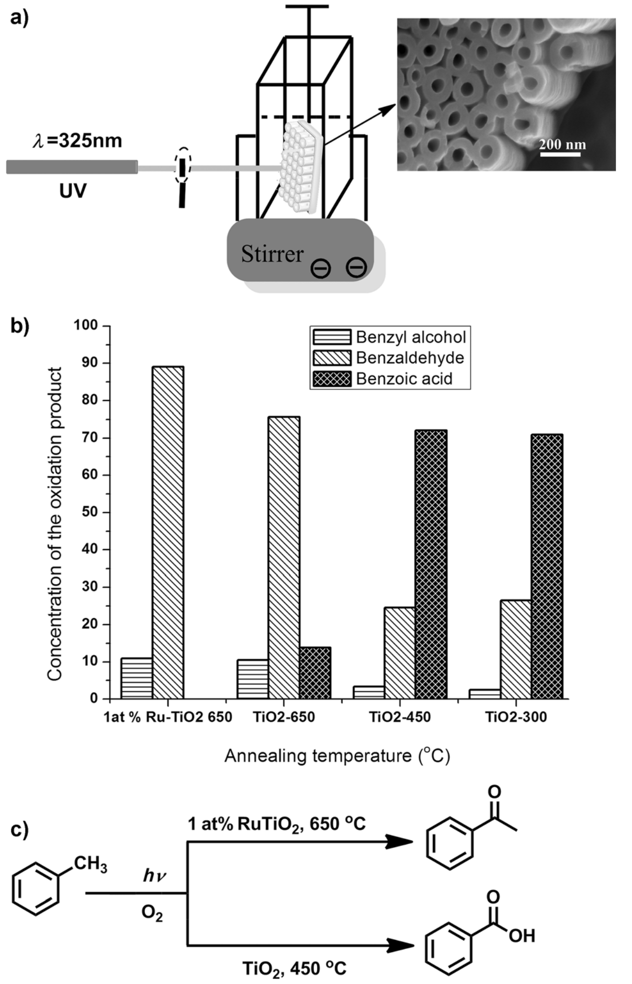

Figure 1. a) Illustration of the toluene oxidation experiment, which is carried out in a cuvette in the presence of oxygen and under UV irradiation (UV laser $\lambda = 325$ nm, 50 mW cm^{-2}). b) Distribution of the products from toluene oxidation after 4 h UV exposure of different annealed TiO_2 nanotubes or Ru-TiO_2 nanotubes. c) Illustration of the different pathways on two catalysts leading to benzaldehyde or benzoic acid formation.

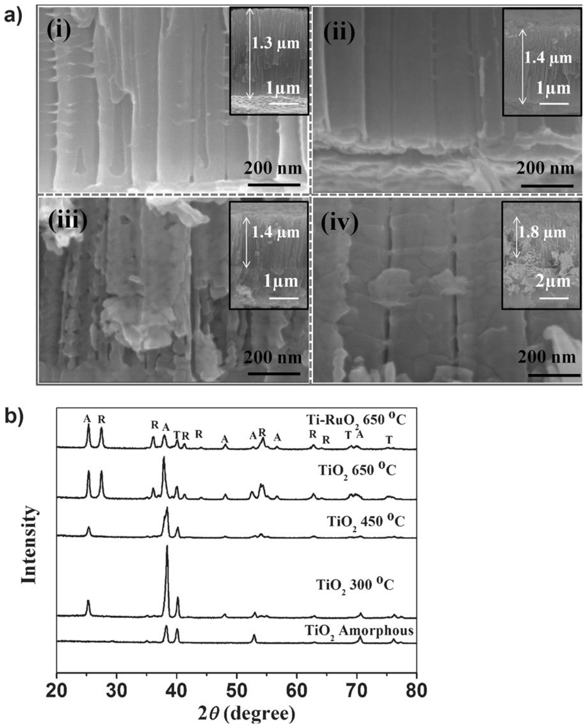

Figure 2. a) SEM images of self-organized TiO_2 nanotubes and ruthenium-doped TiO_2 nanotubes formed by electrochemical anodization and annealed for 1 h at i) 300 °C, ii) 450 °C, iii) 650 °C, and iv) Ru-TiO_2 at 650 °C. b) X-ray diffraction patterns for TiO_2 nanotubes and Ru-doped TiO_2 nanotubes of (a) after some annealing treatments. T = Ti substrate, A = anatase, R = rutile.

For photocatalytic synthesis, the nanotube samples were inserted into a cuvette and reactions were carried out using monochromatic UV light provided by a 50 mW 325 nm CW-HeCd laser. Figure 1 a shows the set-up used for the photocatalytic experiments (for details, see the Experimental Section in the Supporting Information). After UV light exposure for different times, the solution was analyzed and the reaction products quantified using GC-MS. Figure 1 b shows the reaction product distribution for different modifications of the TiO_2 nanotubes after 4 h of illumination. Clearly, nanotubes that are annealed to anatase at 300 °C and 450 °C lead to a distribution of products with benzoic acid as the main product (for 300 °C: 70.95 % benzoic acid, 26.55 % benzaldehyde, and 2.50 % benzyl alcohol; for 450 °C: 72.36, 24.55, and 3.39 %, respectively). Remarkably, for tube layers annealed at a higher temperature to rutile (650 °C; see the XRD in Figure 2 b), a significant change in the product distribution is observed; now the main reaction product is benzaldehyde with 75.66 %, while benzoic acid and benzyl alcohol are only present at 13.84 % and 10.50 %, respectively. For pure rutile and pure anatase titania nanotubes, the product distribution is given in the Supporting Information.

Even more drastic changes are observed for Ru-doped tubes after annealing at 650 °C. In this case also the main reaction product is benzaldehyde (89.07 %), but the formation of benzoic acid is completely suppressed. Up to 4 h illumination, the distribution of reaction products is maintained (Supporting Information, Figure S1). Nevertheless, in cases where a detectable amount of benzoic acid is formed, extended reaction times lead to a substantial formation of benzyl benzoate. This presumably occurs by a reaction of benzyl alcohol and benzoic acid. The relative amount of benzyl benzoate present in the reaction chamber after 10 h of illumination is shown in the Supporting Information, Figure S1 a,b. These results clearly show that benzyl benzoate is formed in cases where benzoic acid can be formed. In the case of the Ru-doped sample, the formation of this side product is thus also prevented. This is contrast to reference experiment carried out with TiO_2-Pt and TiO_2-Pd (see the Supporting Information). These catalysts also lead to wide product distribution. A compilation of results is given in Supporting Information, Figure S1 k.

Some other experimental details are worth mentioning: For non-annealed amorphous titania nanotubes, a mixture of benzyl alcohol, benzaldehyde, and benzoic acid was obtained with a very poor selectivity and conversion. Additionally we explored different solvents such as water and acetonitrile. Although the reaction rates could be increased to some degree for both cases, only a very poor selectivity was observed. As a result all experiments were carried out under solvent-free conditions using O_2 (bubbling). If instead of a nanotube film a nanoparticle layer (produced as in the Supporting Information) is used, an even wider spread of products is obtained than for nanotubes (Supporting Information), which may reflect the advantage of using a highly ordered substrate in view of selectivity.

Overall, the strongest shift in selectivity is obtained by doping of the tubes with Ru. In fact, in photocatalysis, some studies have been reported on TiO_2 decorated with RuO_2 nanoparticles; however, in contrast to the in situ Ru incorporation used herein, particle decoration in general was much less successful in view of selectivity.[20–22] This may be ascribed to the fact that Ru can have different effects on the photocatalytic activity of TiO_2. It may act as a hole transfer promoter at the valence band or as a doping species in TiO_2,[20,23] but also, and very importantly, it acts as a recombination center that may drastically suppress $O_2^{\bullet-}$ formation at the conduction band of TiO_2 (Figure 3 a). It has been reported that $Ru^{3+/4+}$ states in TiO_2 are situated 0.4 eV below the conduction band of anatase, that is, electrons trapped on these states have an energy not sufficient to create $O_2/O_2^{\bullet-}$.[24] We confirmed the role of Ru on the formation $O_2^{\bullet-}$ species by a luminol test[25] (Supporting Information). Figure 3 b shows the relative amount of $O_2^{\bullet-}$ species generated on the three main modification used in the present work. Clearly for anatase tubes the generation of $O_2^{\bullet-}$ species is highest followed by rutile, whereas for the Ru-doped material $O_2^{\bullet-}$ species is not detectable.

Therefore, reasoning for the change in selectivity can be given by the different reactivity of anatase, rutile, and Ru-doped material to form $O_2^{\bullet-}$. The difference observed between anatase and rutile is in line with previous reports for the photocatalytic activity of the two polymorphs, namely their ability to form $O_2^{\bullet-}$.[26–28] The effect of Ru doping can be described by considering the relevant energy levels in the semiconductor and the solution (Figure 3 a). In principle, TiO_2 photocatalysis can be dominated by a valence or a conduction band mechanism. In our case it may be assumed that hole transfer at the valence band forms a benzyl radical, which is then further oxidized (using O-species) to benzyl alcohol, aldehyde, or acid (Figure 3 c). For selectivity, most relevant is the speciation of the oxidizer, that is, the conduction band electron transfer to O_2 and the formation (or not) of activated dioxygen species $O_2^{\bullet-}$. That is, if electrons transfer via surface states in energy lower than the $O_2/O_2^{\bullet-}$ couple, this reaction path may be shut down. This is suggested to be the role of additionally introduced Ru levels[24] (Figure 3 a). Excited electrons are fast trapped on the Ru levels and owing to their lower energy do not have sufficient oxidative power to create $O_2^{\bullet-}$ (this in accordance with literature [24]). In view of the reaction given in Figure 3 c, it is thus proposed that suppression of $O_2^{\bullet-}$ formation prevents oxidation step 3, and therefore the formation of benzoic acid.

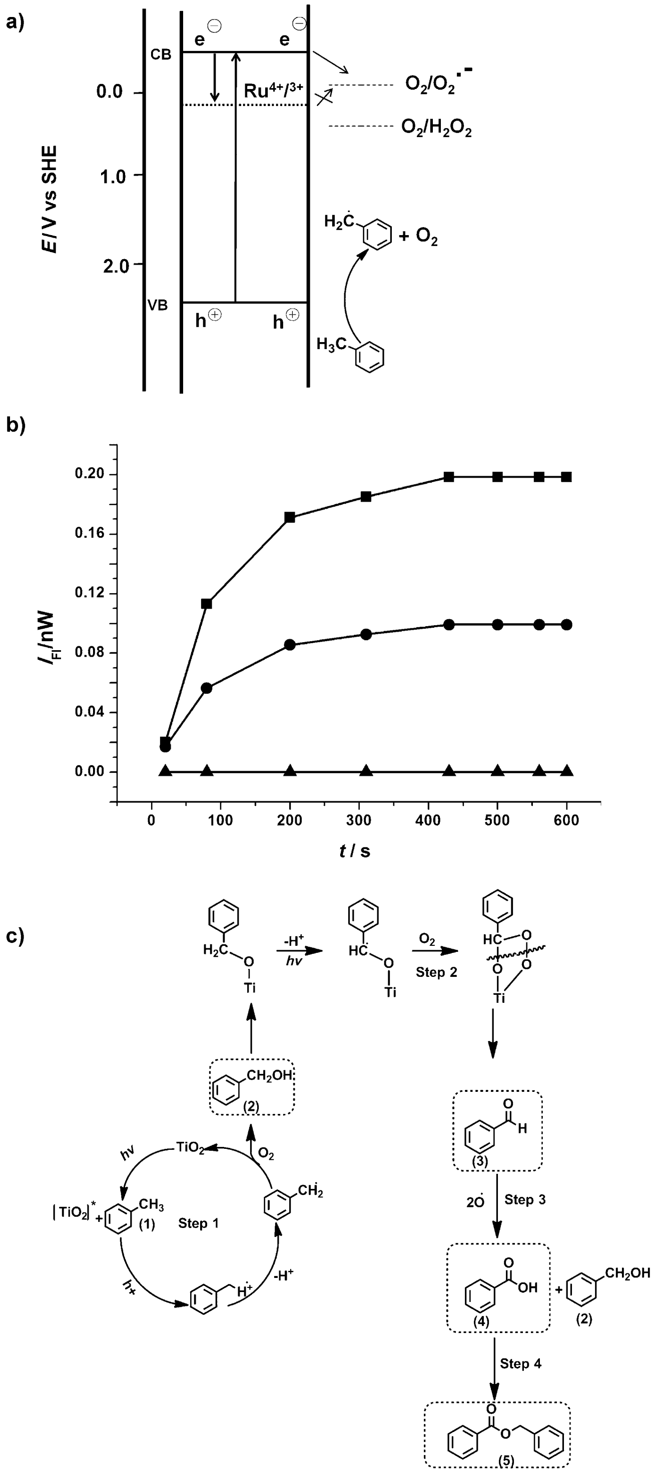

Figure 3. a) Illustration of the band position during toluene oxidation on TiO_2 (anatase and rutile) and ruthenium-doped TiO_2 nanotubes under UV irradiation. CB = conduction band, VB = valence band. b) Fluorescence intensity as a function of time at different samples. ■ anatase TiO_2, ● rutile TiO_2, ▲ Ru-rutile TiO_2. c) The proposed reaction pathways during photocatalytic toluene oxidation.

In summary, the present work demonstrates how the selectivity of synthetic photocatalytic reactions can be significantly altered by suitable band-gap engineering approaches of the TiO_2 photocatalyst. Namely, we show how the introduced electronic states can strongly determine photocatalytic reaction pathways. We believe the principles demonstrated in this work (that is in general terms to tailor the exit energy of electron and hole to facilitate or suppress a reaction) has wide potential as a concept to achieve a much higher selectivity in photocatalytic reactions.

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