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Effects of Sn^{4+} dopant ions located either in the bulk or at crystallite surfaces on the ultraviolet photocatalytic activity of anatase

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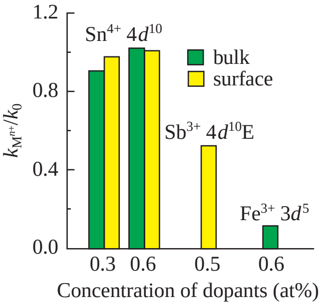
Isovalent Sn^{4+} dopant cations do not have a significant effect on the ultraviolet photocatalytic activity of anatase (TiO_2) regardless of their location in the bulk or at the surfaces of crystallites. This is due to the formation of no charge balance oxygen vacancies V_O acting as (e^-,h^+) recombination centers towards photogenerated electrons and holes upon doping with Sn^{4+}. Nevertheless, the analysis of a sample containing surface-located heterovalent Sb^{3+} ions (isoelectronic with Sn^{2+}) revealed a significant weakening of the negative effect of V_O, which can be accounted for by the presence of a stereochemically active lone pair E of 5*s* electrons in the nearest vicinity of V_O.



Keywords: Sn^{4+}-doped anatase TiO_2, bulk and surface sites, photocatalytic activity, decolorization of methyl orange, ^{119}Sn and ^{121}Sb Mössbauer spectroscopy, stereochemically active lone pair.

Earlier, we used ^{119}Sn Mössbauer spectroscopy[1] to study the stabilization of tin dopant ions at uppermost surface layers of anatase crystallites and physicochemical processes occurring at the $Ti_{1-x}Sn_xO_2$/gas interface. The samples were synthesized by the hydrogen annealing of polycrystalline $Ti_{1-x}Sn_xO_2$ obtained by the calcination of coprecipitated Ti^{IV} and Sn^{IV} hydroxides in air. Upon annealing, Sn^{4+} ions on crystallite surfaces were reduced to a divalent state and, owing to their stereochemically active electronic lone pair E, located on low coordination sites (CN < 6) energetically unfavorable for Ti^{4+}. The subsequent contact with ambient air resulted in the formation of isolated Sn^{4+} impurity centers, whose surface location was confirmed by both X-ray photoelectron spectroscopy (XPS) and an analysis of ^{119}Sn Mössbauer spectra recorded after exposure of H_2-annealed $Ti_{1-x}Sn_xO_2$ to various gases.[1] These $Ti_{1-x}Sn_xO_2$ powders are particularly suitable for comparing the effects of a dopant located at surface sites or in the bulk of TiO_2-based photocatalytic materials promising for solar energy conversion.[2–4] The advantage provided by the use of Sn^{4+} dopant ion, which is isovalent with the host Ti^{4+}, is due to the fact that its presence in TiO_2 does not involve the formation of interfering charge-balance defects, in contrast to heterovalent additive ions.[5] Moreover, the investigation of $Ti_{1-x}Sn_xO_2$ may provide some insight into the effects related to intermediately formed Sn^{2+} ions. Thus, we studied the photocatalytic activity of $Ti_{1-x}Sn_xO_2$ powders in the decolorization reaction of methyl orange (MO), which was recently used[6] to compare the modifying actions of bulk-located Cr^{3+} and Fe^{3+}.

The single-phase anatase TiO_2 powders were irradiated using a LED ($\lambda = 370$ nm, $P = 3$ W). Optical density was determined at $\lambda = 460$ nm, and the values of k were calculated using a linear equation of first-order reactions.

Samples containing Sn^{4+} ions located in the bulk of crystallites were obtained by the annealing of a coprecipitated $Ti_{1-x}Sn_x(OH)_4$ precursor ($x = 0.003$ or 0.006) in air at 500 °C for 2 h. To obtain the samples containing Sn^{4+} at surface sites, the same precursor was annealed in a hydrogen atmosphere at 500 °C for 2 h. To prepare the hydroxide precursors $Ti_{1-x}Sn_x(OH)_4$, a stannic chloride solution enriched in the Mössbauer isotope ^{119}Sn to 92% was used. Figure 1(*a*) shows the Mössbauer spectrum of the air-annealed sample (material 1, see Online Supplementary Materials). The spectral parameters (the isomer shift $\delta_1 = 0.01 \pm 0.01$ mm s^{-1}, the quadrupole splitting $\Delta E_{Q1} = 0.41 \pm 0.01$ mm s^{-1}, the full width at half maximum of each doublet component $\Gamma_1 = 0.88$ mm s^{-1}, and the spectral contribution $A_1 = 100\%$) evidenced the presence of tetravalent tin on a site of unique type assignable to a distorted oxygen octahedron of the anatase structure. Moreover, the above

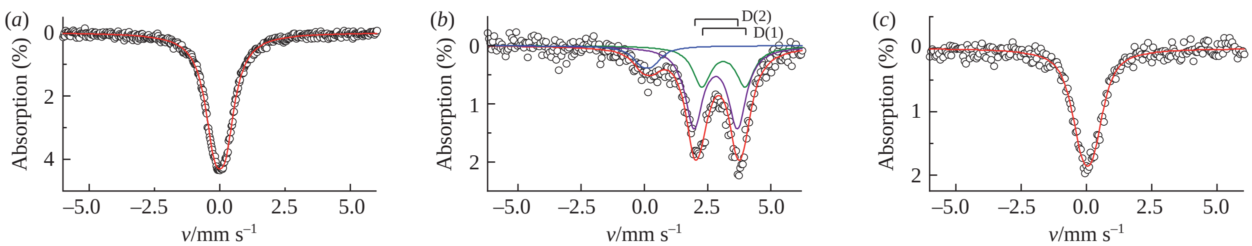


Figure 1 ^{119}Sn Mössbauer spectra (recorded at 100 K) of 0.6 at% Sn/TiO_2 samples obtained by the annealing of a coprecipitated precursor (*a*) in air (2 h at 500 °C) and (*b*) in H_2 (2 h at 400 °C, *in situ* measurements) and (*c*) after exposure of the hydrogen-annealed sample to ambient air.

values are consistent with those reported earlier for a similar sample annealed in air at 650 °C, which were ascribed to the bulk-located Sn^{4+}. To determine the valence state of tin upon the hydrogen annealing of $Ti_{1-x}Sn_x(OH)_4$ (hydrogen-annealed material 2, see Online Supplementary Materials), we performed *in situ* Mössbauer measurements at 100 K in the reactor used for hydrogen annealing, which was equipped with a lateral thin-window quartz sample cell to avoid the contact of a test sample with ambient air [Figure 1(*b*)]. As can be seen, the majority of the Sn^{4+} was reduced to a divalent state, revealed by the appearance of an asymmetric doublet at positive Doppler velocities. This new spectral component is a superposition of two quadrupole doublets D1 and D2, either being imputable to Sn^{II} species possessing a lone pair E but located at nonequivalent sites with CN < 6. Their spectral parameters are $\delta_{2(1)}$ = 3.18 ± 0.04 mm s^{-1}, $\Delta E_{Q2(1)}$ = 1.71 ± 0.11 mm s^{-1}, $\Gamma_{2(1)}$ = 0.85 ± 0.03 mm s^{-1}, and $A_{2(1)}$ = 30%; $\delta_{2(2)}$ = 2.82 ± 0.04 mm s^{-1}, $\Delta E_{Q2(2)}$ = 1.72 ± 0.11 mm s^{-1}, $\Gamma_{2(2)}$ = 0.85 ± 0.03 mm s^{-1}, and $A_{2(2)}$ = 59%. They are consistent with those previously assigned to Sn^{2+} ions on the surfaces of anatase TiO_2 crystallites.[1] As for the minor third spectral component, its parameters (δ_m = 0.07 ± 0.05 mm s^{-1}, ΔE_{Qm} = 0.44 ± 0.13 mm s^{-1}, Γ_m = 0.85 ± 0.03 mm s^{-1}, and A_m = 11%) are assignable to pristine Sn^{4+} ions still remaining in the bulk positions.

Figure 1(*c*) shows the ^{119}Sn Mössbauer spectrum recorded after contact of material 2 cooled to room temperature with ambient air. This spectrum revealed the reoxidation of Sn^{2+} ions and, consequently, their easy accessibility to oxygen molecules, as expected for a surface-located species (material 3, see Online Supplementary Materials). Thus, we used materials 1 (bulk) and 3 (surface) to compare the photocatalytic activities of anatase containing Sn^{4+} in the bulk and on surface sites. The subsequent photocatalytic experiments were carried out at the concentrations [Sn] of 0.3 and 0.6 at% for both materials 1 and 3. The former value corresponds to the highest concentration of tin utilized in ref. 1 while the latter is the lowest concentration of antimony, still allowing to determine its virtual valence state by means of ^{121}Sb Mössbauer spectroscopy. Figure 2 shows that, in both cases, the location of Sn^{4+} ions did not significantly affect the kinetics, in contrast to a drastic decrease in the activity of the sample doped with Fe^{3+} ions proven to create V_O. Thus, it would be tempting to consider the kinetics in the presence of TiO_2 doped with surface-located Sn^{2+} ions exhibiting a positive charge deficiency like Fe^{3+}. Unfortunately, this could not be done because of their fast oxidation under ambient air. For this reason, we studied the kinetics in the presence of TiO_2 powders doped with surface-located Sb^{3+} ions, which possess a lone pair E like Sn^{2+} and are stable in air at room temperature. A sample containing ~0.6 at% Sb^{3+} was prepared using a published procedure[7] involving dropwise deposition of a $SbCl_5$ solution on a TiO_2 powder wetted with an ammonia solution. The relevant ^{121}Sb Mössbauer spectrum (Figure 3) evidenced that the majority of Sb^{5+} ions (δ^* = –0.01 ± 0.1 mm s^{-1}, the quadrupole coupling constant $e^2qQ_{5/2}^*$ = 2 ± 2 mm s^{-1}, Γ^*= 2.55 ± 0.15 mm s^{-1}, and A^* = 22%) was reduced upon the subsequent hydrogen annealing to a trivalent state (δ^{**} = –12.3 ± 0.2 mm s^{-1}, $e^2qQ_{5/2}^{**}$ = 17.7 ± 1.1 mm s^{-1}, Γ^{**} = 2.8 ± 0.2 mm s^{-1}, and A^{**} = 78%). The virtual concentration of Sb^{3+} ions, whose spectral parameters are typical of cations possessing a lone pair E, reflecting the hybridization of their 5*s* and 5*p* electronic orbitals,[8–10] in this sample amounted to nearly 0.5 at%.[†] The photocatalytic measurements revealed a significant decrease in the activity of Sb^{3+}-doped TiO_2 ($k_{Sb^{3+}}/k_0$ = 0.56), as compared to that observed in the presence of surface-located Sn^{4+} ions creating no V_O (material 3, $k_{Sn^{4+}}/k_0$ = 1.16). However, the slowing of the kinetics induced by Sb^{3+} ions is obviously much weaker than that observed in the presence of 0.6 at% Fe^{3+} ($k_{Fe^{3+}}/k_0$ = 0.13), the trivalent dopant having no E. These results allowed us to suggest that the moving of the negative charge density of Sb^{3+} lone pair E towards the nearest vacancy V_O diminishes its efficiency as an (e^-,h^+) recombination center.

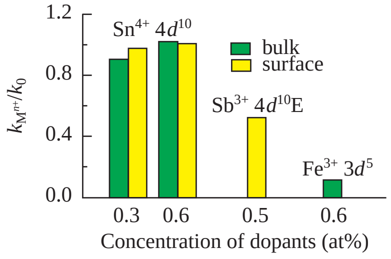


Figure 2 Kinetics of the ultraviolet photocatalytic decolorization of MO in the presence of TiO_2 powder containing Sn^{4+} dopant ions in the bulk or on the surface of crystallites (k_0 is the rate constant in the presence of undoped TiO_2). For comparison, the results obtained for a sample containing ~0.5 at% surface-located Sb^{3+} along with the earlier reported data for a TiO_2 sample containing 0.6 at% Fe^{3+} in the bulk of crystallites are also shown.

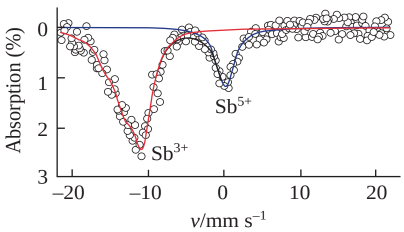


Figure 3 ^{121}Sb Mössbauer spectrum of the hydrogen-annealed 0.6 at% Sb^{5+}/TiO_2 sample recorded at 100 K.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.045.

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[†] Taking into account that the surface-located Sb^{3+} ions may exhibit a somewhat lower value of the recoil-free fraction *f* at 100 K than that of the bulk-located Sb^{5+} ions, the spectral contribution of the former ions presumably provides an underestimated value of their abundance.