Mendeleev Communications

Mendeleev Commun., 2025, **35**, 696–698

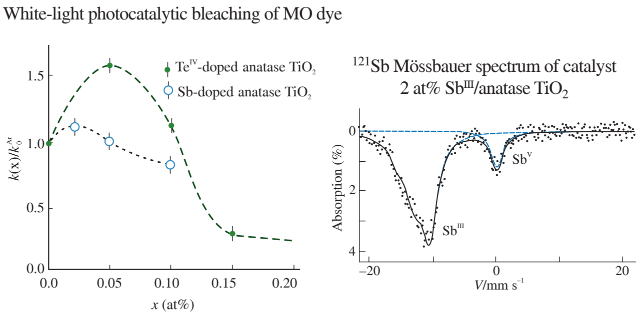
^{121}Sb Mössbauer spectroscopic insight into the puzzling persistence of photocatalytic activity exhibited by Sb-doped anatase TiO_2

Mikhail V. Korolenko, Denis A. Pankratov, Iraida M. Buntseva and Pavel B. Fabritchnyi*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: pf@radio.chem.msu.ru

DOI: 10.71267/mencom.7784

The unexpected behavior of Sb-doped anatase TiO_2 photocatalysts can be accounted for by their synthesis procedure involving thermal decomposition of a co-precipitated hydroxide precursor. This treatment results in the formation of titanium vacancies V_{Ti} which balance the excessive positive charge of Sb^V atoms in a way not affecting the wide-gap nature of anatase TiO_2 semiconductor. Nevertheless, V_{Ti} vacancies can also reduce its photocatalytic efficiency acting along with the oxygen ones V_O as supplementary recombination centers of photogenerated electrons and holes.



Keywords: Sb-doped TiO_2, photocatalytic bleaching, methyl orange, ^{121}Sb Mössbauer spectroscopy, Sb^V charge balance mechanism.

Antimony was among the elements which were first tested as single metal ion dopants with a view to enhance the efficiency of titania-based photocatalysts. To reach this goal, the dopant should both narrow the energy gap of the concerned wide-gap semiconductor oxide ($E_g \approx 3$ eV) and reduce the probability of recombination of photogenerated electrons and holes. In the study,[1] performed to assess the effect of antimony additives, a series of anatase TiO_2 samples containing Sb^V bulk doped crystallites has been investigated. The samples were obtained by annealing in air the precursors Sb^V_x:$Ti_{1-x}(OH)_{4+x}$ precipitated by adding NH_4OH in a mixture of acidified chloride solutions of both metals. It was found that the presence of Sb^V atoms (at their concentrations in the range 0.5–5 at%) in the solution used to obtain the precursor, resulted, independently of the antimony content, in some increase in the activity of the synthesized photocatalysts Sb_x:$Ti_{1-x}O_{2+x}$. Nevertheless, the improvement achieved was considered to be insufficient to justify further experiments with Sb^V dopant. A similar rather disappointing conclusion was drawn for many other dopants tested.[2] Later, however, antimony has again attracted attention, but this time to the atoms Sb^{III} containing a stereochemically active lone pair of electrons E in their valence shell (hereafter named E Sb^{III}). The interest in elucidating the effect of E Sb^{III} species was promoted by the theoretical work[3] implemented to analyze the changes in photocatalytic properties induced by the atoms Sn^{II} (hereafter named E Sn^{II}) which are isoelectronic with the E Sb^{III}. The authors have suggested that photocatalytic properties of anatase TiO_2 could be significantly improved by supporting small $(SnO)_n$ nanoclusters on one of anatase particle surfaces. The expected positive effect was ascribed to the presence of a lone pair of electrons in the Sn^{II} valence shell. By that time, ^{119}Sn Mössbauer spectroscopic studies[4] have already evidenced that hydrogen annealing Sn^{IV}_x:$Ti_{1-x}(OH)_4$ precursors allows one to easily stabilize the dopant as an E Sn^{II} species formed on surfaces of anatase TiO_2 particles. Accordingly, to experimentally verify that promising theoretical assumption,[3] at first glance, it may seem sufficient to determine the rate constant value of an appropriate photocatalytic reaction studied in the presence of anatase TiO_2 containing E Sn^{II} atoms. However, the relevant experiments, quite routine themselves, were not feasible due to the rapid oxidation of the surface-located divalent tin atoms in ambient air, that was found by ^{119}Sn Mössbauer spectroscopic investigation.[4,5,†]

Nevertheless, a similar experiment could be *a priori* implemented with atoms E Sb^{III} known to be both successfully located on surface sites of anatase TiO_2 and resistant to oxidation in air at room temperature.[6] In fact, the study of the photocatalytic activity of titania doped with surface-located E Sb^{III} atoms, revealed a spectacular 14-fold increase in the value of a test reaction rate constant.[7] Thus, this finding was qualitatively consistent with the effect theoretically predicted for E Sn^{II}/anatase TiO_2. However, in the above work the main constituent of the investigated catalyst was rutile TiO_2, instead of anatase TiO_2 polymorph. The former was chosen because of concerns that Sb^V species, which were expected to be formed along with Sb^{III} atoms upon synthesis of antimony-doped anatase TiO_2, could act as one-electron donors. This polymorph thus could lose its nonconducting properties necessary to exhibit photocatalytic activity. By contrast, in rutile TiO_2, the excessive positive charge of Sb^V is balanced by the cationic vacancies V_{Ti} which do not affect the wide-gap semiconductor nature of this polymorph.[8,9] However, in many cases, it was found that incorporation of Sb^V into anatase TiO_2, instead of deactivating this photocatalyst, caused a certain increase

---

[†] The location of Sn^{IV} dopant species and their stabilization in the reduced E Sn^{II} state immediately on surfaces of oxide particles were for the first time evidenced by ^{119}Sn Mössbauer spectroscopy applied to investigate[5] transformations occurring upon hydrogen annealing of amorphous tin-doped paramagnetic chromium hydroxides Sn^{IV}_x:$Cr_{1-x}(OH)_{3+x}$ into antiferromagnetic crystallites of Sn^{II}_x/$Cr_{2-x}O_{3-x}$.

in its reactivity.[1,10–12] Moreover, to interpret the positive effect reported earlier,[7] it was necessary to clarify its dependence on the experimental conditions of the synthesis of the relevant catalyst. For instance, the applied doping procedure has involved a long-term annealing at a temperature as high as 1000 °C, that has not only reduced the total amount of antimony doped but has also resulted in its simultaneous presence in two different valence states as E $\mathrm{Sb^{III}}$ and $\mathrm{Sb^{V}}$. This uncertainty could not be resolved by testing the catalyst by X-ray photoelectron spectroscopy: despite the multifold enrichment with antimony of the catalyst surface-adjacent layers, which was consistent with the presence of antimony as E $\mathrm{Sb^{III}}$ species, the binding energy value characterizing the Sb $3d_{3/2}$ analytical peak did not allow the authors to determine the antimony oxidation state and, consequently, to clarify whether the increase in the photocatalytic activity was an individual effect of the E $\mathrm{Sb^{III}}$ species or the synergistic one of both E $\mathrm{Sb^{III}}$ and $\mathrm{Sb^{V}}$. In this connection it is worthy to note that the latter possibility was already suggested in an earlier paper devoted to studying the photocatalytic activity of Sb-doped anatase $\mathrm{TiO_2}$.[12]

To elucidate this issue, which is of particular importance for the strategy of further development of $\mathrm{TiO_2}$-based photocatalysts, it is still necessary to investigate a series of anatase $\mathrm{TiO_2}$ samples containing known variable percentage of E $\mathrm{Sb^{III}}$. However, this is a difficult task which implies time-expensive low-temperature ^{121}Sb Mössbaur spectroscopic measurements to be performed for each sample selected for further comparing the relevant photocatalytic activities. Therefore, in the present work we at first attempted to get new information on E $\mathrm{Sb^{III}}$ surface-located atoms by comparing their photocatalytic impact with that of isoelectronic atoms $\mathrm{Te^{IV}}$ (hereafter named E $\mathrm{Te^{IV}}$) we have recently investigated.[13] For this purpose, a test reaction of visible-light bleaching methyl orange (MO) solutions was again used. The rate constant k was calculated *via* the kinetic equation of first-order reactions (information on the performed photocatalytic measurements can be found in the Online Supplementary Materials). The kinetic experiments were implemented with three antimony-doped anatase $\mathrm{TiO_2}$ samples, synthesized by annealing, under argon at 500 °C for 2 h, the relevant titanium hydroxide precursors co-precipitated with 0.02, 0.05 or 0.10 at% $\mathrm{Sb^{III}}$. All three antimony-doped photocatalysts were found to be single-phase anatase crystallites, as evidenced by their X-ray diffraction pattern (see Figure S1 in Online Supplementary Materials). Their photocatalytic activities were then compared with those of anatase $\mathrm{TiO_2}$ samples doped, in a similar way, with equivalent low amounts of $\mathrm{Te^{IV}}$. The mentioned study[13] of $\mathrm{Te^{IV}}$-doped anatase $\mathrm{TiO_2}$ has shown that whereas the presence of 2 at% E $\mathrm{Te^{IV}}$ has resulted in a drastic deactivation of this catalyst, at much lower $\mathrm{Te^{IV}}$ doping level, by contrast, an increase in the reaction kinetics was observed. The latter effect was ascribed to the neutralization, by the $\mathrm{Te^{IV}}$ lone pair of electrons, of the negative impact produced by the neighboring oxygen vacancy $\mathrm{V_O}$ acting as a recombination center of photogenerated electrons and holes. As the $\mathrm{Te^{IV}}$ dopant itself was found not to promote the studied test reaction, a much stronger increase in the bleaching kinetics thus should be anticipated for samples doped with comparable low amounts of photocatalytically active isoelectronic atoms E $\mathrm{Sb^{III}}$.

The k/k_0^{Ar} values determined in the presence of the relevant Sb-doped anatase $\mathrm{TiO_2}$ samples are shown in Figure 1. Thus, contrary to what could be expected, this figure revealed some slowdown of the test reaction kinetics. Moreover, these k/k_0^{Ar} values appear to be obviously inconsistent with the drastic enhancement of the photocatalytic activity previously observed in Sb-doped rutile $\mathrm{TiO_2}$.[7]

These results therefore allowed us to suggest that in the studied samples the dopant atoms were no longer present as pristine surface-located E $\mathrm{Sb^{III}}$ species but as the $\mathrm{Sb^{V}}$ ones oxidized by $\mathrm{O_2}$ traces that eventually available in argon used upon annealing the hydroxide precursors. As the very low antimony content does not allow one to obtain ^{121}Sb Mössbauer spectrum for either of these Sb-doped catalysts, we have studied a specially synthesized anatase $\mathrm{TiO_2}$ sample doped in a similar way with 2 at% $\mathrm{Sb^{III}}$ to verify the suggested oxidation of E $\mathrm{Sb^{III}}$. The much higher antimony content allowed us to determine the relative abundances of different valence states of antimony. In fact, the ^{121}Sb Mössbauer spectrum (see Figure 2) reveals the presence of two clearly discernable peaks of nuclear gamma resonance absorption: the predominant one (with a spectral contribution A = 85%), characterized by an isomer shift $\delta = -11 \pm 0.3$ mm s^{-1} and a quadrupole coupling constant $eV_{zz}Q_{5/2} = 18.9 \pm 1.5$ mm s^{-1}, on the one hand, and a much narrower peak with A = 15%, characterized by $\delta = 0.2 \pm 0.15$ mm s^{-1} and $eV_{zz}Q_{5/2} = 0.9 \pm 1.5$ mm s^{-1}, on the other hand.These peaks are typical of E $\mathrm{Sb^{III}}$, located on the surface of anatase $\mathrm{TiO_2}$ crystallites, and $\mathrm{Sb^{V}}$ located in somewhat distorted octahedral $[\mathrm{SbO_6}]$ groups, respectively.[6,12,14] The large value of the electric field gradient (EFG) eV_{zz}, characterizing atoms E $\mathrm{Sb^{III}}$, is in agreement with the strong distortion of local atomic environment created by the lone pair E whose presence also causes a drastic increase in the value of electronic density $|\Psi(0)|^2$ at the $\mathrm{Sb^{III}}$ nucleus, as attested by the large negative value of the isomer shift defining the relevant spectral component. Thus, this spectrum has clearly shown that annealing the hydroxide precursor under 'inert argon atmosphere' has nevertheless resulted in the oxidation of *ca.* 0.3 at% $\mathrm{Sb^{III}}$.

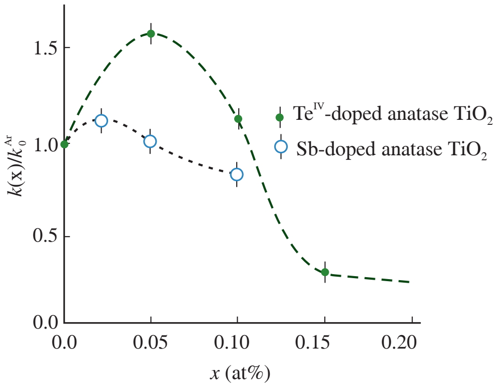


Figure 1 Kinetics curves of white-light photocatalytic bleaching of MO dye in the presence of Sb-doped anatase $\mathrm{TiO_2}$ and recently investigated samples $x\mathrm{Te^{IV}}$/anatase $\mathrm{TiO_2}$;[13] k_0^{Ar} is the rate constant determined in the presence of dopant-free reference anatase $\mathrm{TiO_2}$ synthesized under argon atmosphere.

Accordingly, the amount of oxidized $\mathrm{Sb^{III}}$ species in this sample was found to be much higher than that of pristine trivalent antimony atoms which were introduced into any of precursors used to synthesize the considered photocatalysts. This finding thus pointed to possible oxidation of the totality of $\mathrm{Sb^{III}}$ atoms doped. To get further information about the peculiarities of antimony dopant behavior, one of the studied catalysts (*i.e.*, 0.05 at% Sb/anatase $\mathrm{TiO_2}$) was again tested in

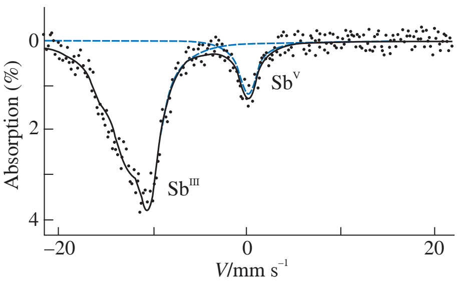


Figure 2 ^{121}Sb Mössbauer spectrum of catalyst 2 at% $\mathrm{Sb^{III}}$/anatase $\mathrm{TiO_2}$.

bleaching the same volume of fresh MO solution in order to compare the values of the rate constant k determined in two successive measurements. No significant difference was observed between the values of k (0.05 at% Sb)/k_0^{Ar}. Therefore, upon this supplementary bleaching, 0.05 at% Sb/anatase TiO_2 was found to retain its pristine photocatalytic characteristics.

Moreover, considering the reported results it should be taken into account that in the surface layers of oxide particles, formed upon decomposition of hydroxide precursors, apart from oxygen vacancies V_O, a large number of titanium vacancies V_{Ti} was also created. Thus, their formation could simultaneously balance the excessive positive charge of Sb^V species and, consequently, allowed anatase TiO_2 to preserve both its wide-gap semiconductor nature and inherent photocatalytic activity, same as it was the case in rutile TiO_2.

Another valuable insight provided by the Mössbauer spectrum of sample 2 at% Sb^{III}/anatase TiO_2 has evidenced that the large majority of its antimony atoms were present in the E Sb^{III} state. Therefore, according to the earlier results,[7] such a photocatalyst should provide exceptionally favorable conditions for an efficient space separation of photogenerated electrons and holes that should result in a record-breaking high photocatalytic activity. However, the value $k/k_0^{\mathrm{Ar}} = 4.6$, determined in the presence of catalyst 2 at% Sb^{III}/anatase TiO_2, was found, by contrast, to be 3 times smaller than $k/k_0 = 14$ earlier reported for Sb-doped rutile TiO_2.[7] This finding thus strongly suggests that decrease in the photocatalytic activity of sample 2 at% Sb^{III}/anatase TiO_2, also synthesized by annealing the relevant hydroxide precursor, is due, along with oxygen vacancies V_O, to the titanium vacancies V_{Ti}, acting as supplementary centers of (e^-, h^+)-recombination.

In conclusion, the reported results allow the unexpected behavior of Sb-doped anatase TiO_2 photocatalysts to be accounted for by their synthesis procedure involving thermal decomposition of a coprecipitated hydroxide precursor. This treatment implies the formation of titanium vacancies V_{Ti} which balance the excessive positive charge of Sb^V species in a way not affecting the wide-gap nature of anatase TiO_2 semiconductor. Nevertheless, the V_{Ti} vacancies can play, along with the oxygen ones, a negative role acting as supplementary recombination centers of photogenerated electrons and holes.

This work was carried out within the framework of the State Assignment of Lomonosov Moscow State University (project no. 122030200324-1). We are thankful to the Development Program of Lomonosov Moscow State University for the access to the cryogen-free closed cycle cryostat for Mössbauer spectroscopy CFHT-121-MESS.

Online Supplementary Materials:

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7784.

References

1 J. Moon, H. Takagi, Y. Fujishiro and M. Awano, *J. Mater. Sci.*, 2001, **36**, 949; https://doi.org/10.1023/A:1004819706292.

2 J. Choi, H. Park and M. R. Hoffmann, *J. Phys. Chem. C*, 2010, **114**, 783; https://doi.org/10.1021/jp908088x.

3 A. Iwaszuk and M. Nolan, *J. Mater. Chem. A*, 2013, **1**, 6670; https://doi.org/10.1039/C3TA10647K.

4 R. A. Astashkin, P. B. Fabritchnyi, M. I. Afanasov, M. V. Korolenko, A. Wattiaux, S. Bordère, C. Labrugère and C. Delmas, *Solid State Sci.*, 2013, **25**, 143; https://doi.org/10.1016/j.solidstatesciences.2013.09.006.

5 M. I. Afanasov, M. Danot, A. A. Ryabchikov, S. Maingaud, P. B. Fabritchnyi and J. Rouxel, *Mater. Res. Bull.*, 1996, **31**, 465; https://doi.org/10.1016/S0025-5408(96)00021-9.

6 M. V. Korolenko, P. B. Fabritchnyi, M. I. Afanasov and C. Labrugère, *Bull. Russ. Acad. Sci.: Phys.*, 2015, **79**, 1055; https://doi.org/10.3103/S1062873815080146.

7 M. Zimbone, G. Cacciato, L. Spitaleri, R. G. Egdell, M. G. Grimaldi and A. Gulino, *ACS Omega*, 2018, **3**, 11270; https://doi.org/10.1021/acsomega.8b01452.

8 D. S. Bhachu, R. G. Egdell, G. Sankar, C. J. Carmalt and I. P. Parkin, *J. Mater. Chem. C*, 2017, **5**, 9694; https://doi.org/10.1039/C6TC04462J.

9 A. Gulino, A. E. Taverner, S. Warren, P. Harris and R. G. Egdell, *Surf. Sci.*, 1994, **315**, 351; https://doi.org/10.1016/0039-6028(94)90138-4.

10 L. Luo, T. Li, X. Ran, P. Wang and L. Guo, *J. Nanomater.*, 2014, 947289; https://doi.org/10.1155/2014/947289.

11 H. Gandelman, A. L. da Silva, B. Ramos and D. Gouvêa, *Ceram. Int.*, 2021, **47**, 619; https://doi.org/10.1016/j.ceramint.2020.08.169.

12 A. L. Castro, M. R. Nunes, M. D. Carvalho, L. P. Ferreira, J.-C. Jumas, F. M. Costa and M. H. Florêncio, *J. Solid State Chem.*, 2009, **182**, 1838; https://doi.org/10.1016/j.jssc.2009.04.020.

13 M. V. Korolenko, P. B. Fabritchnyi, Yu. A. Teterin, K. I. Maslakov and M. I. Afanasov, *Mendeleev Commun.*, 2024, **34**, 440; https://doi.org/10.1016/j.mencom.2024.04.041.

14 P. E. Lippens, *Solid State Commun.*, 2000, **113**, 399; https://doi.org/10.1016/S0038-1098(99)00501-3.

Received: 1st April 2025; Com. 25/7784