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# A particular mechanism of the effect of lone pair E Te$^{IV}$ dopant atoms on visible-light photocatalytic activity of anatase TiO$_2$

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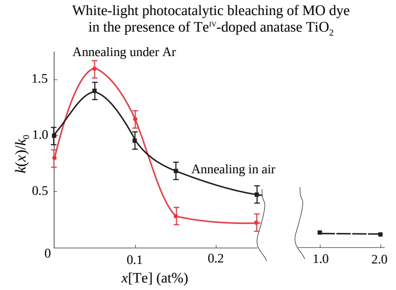
**It was found that small additives of E Te$^{IV}$ species (< 1 at%) notably enhance the visible-light photocatalytic activity of polycrystalline anatase TiO$_2$. This effect can tentatively be attributed to the neutralization of the neighboring surface-located oxygen vacancy, acting as a recombination center for photogenerated holes and electrons, by the dopant stereochemically active lone electron pair E.**



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For a long time, cationic doping has been extensively investigated to enhance the visible-light photocatalytic activity of titanium dioxide. However, despite both the wide variety of dopant elements tested (such as silver, rubidium, nickel, cobalt, vanadium, ruthenium, iron, chromium, osmium, lanthanum, *etc.*),[1] and the various methods of their introduction into TiO$_2$, empirical studies carried out so far have not led to the discovery of any sufficiently improved photocatalytic material. Moreover, cationic doping was found to be detrimental in several cases.[2]

Nevertheless, density functional theory (DFT) simulations performed in 2013 to explore the effect of lone pair electrons E led Iwaszuk and Nolan[3] to suggest that (SnO)$_n$ nanoclusters supported on the surface of anatase TiO$_2$ could provide an opportunity to develop, based on this wide bandgap polymorph ($E_g$ = 3.2 eV), photocatalysts that are highly active in the visible region of light. *A priori*, an experimental verification of this promising suggestion should include routine kinetic measurements using an appropriate chemical reaction to assess the virtual change in the reaction rate constant $k$ caused by the surface-located E Sn$^{II}$ centers. However, the implementation of such experiments for the theoretically considered model system turned out to be impossible due to the rapid oxidation of E Sn$^{II}$ species upon contact with air, as evidenced[4] by their $^{119}$Sn Mössbauer spectra. Thus, for this purpose, we were able to carry out only indirect experiments[5] with two samples containing, instead of E Sn$^{II}$, isoelectronic atoms E Sb$^{III}$ (2 at% Sb$^{III}$/TiO$_2$) or E Te$^{IV}$ (2 at% Te$^{IV}$/TiO$_2$), both of which are chemically stable in the ambient air. The activity of the catalysts was determined in a test reaction of bleaching methyl orange (MO) solutions under irradiation with visible light. The obtained results were found to be obviously conflicting. In the first case, a large increase in the $k_{2\%\ \mathrm{Sb^{III}}}$ value was observed compared to the $k_0$ value of the reaction in the presence of an undoped catalyst ($k_{2\%\ \mathrm{Sb^{III}}}/k_0$ = 5).[5] Accordingly, this result, as well as the result previously reported in the cited work,[6] was consistent with the theoretically predicted[3] positive effect of E Sn$^{II}$. By contrast, a drastic slowdown in the reaction was evidenced in the second case ($k_{2\%\ \mathrm{Te^{IV}}}/k_0$ = 0.1). To elucidate the peculiarities of the photocatalytic effect of E Te$^{IV}$ species, in this work we investigated the kinetics of visible-light bleaching of MO solutions in the presence of anatase crystallites containing smaller amounts of Te$^{IV}$.

The $x$ Te$^{IV}$/TiO$_2$ ($x$ = 0, 0.05, 0.15, 0.20, 0.25 and 1.0 at%) photocatalysts studied in this work[†] were all found to be single-phase anatase crystallites, as evidenced by their XRD pattern (Figure S1, see Online Supplementary Materials). Moreover, their analysis by X-ray photoelectron spectroscopy (Figure S2) reveals an almost 20-fold enrichment of the thin, about 5 nm-thick surface layers of crystallites in tellurium compared to the overall [Te] to [Ti] molar ratio defined by the amounts of tellurium and titanium, used in the synthesis of the relevant $x$ Te$^{IV}$/TiO$_2$ sample. The observed enrichment is consistent with previously reported[4,5,7] values for anatase TiO$_2$ doped with isoelectronic E Sn$^{II}$ or E Sb$^{III}$ species. Therefore, this finding indicates the presence of a stereochemically active lone electron pair in the tellurium valence shell, as expected for Te$^{IV}$.

To compare the photocatalytic activities,[‡] the rate constant $k$ was calculated using the kinetic equation of first-order reactions. The value of the ratio $k(x = 1\ \text{at\%})/k_0$ = 0.09, characterizing the

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[†] *Synthesis of photocatalysts.* To synthesize the relevant $x$ Te$^{IV}$/TiO$_2$ ($x$ = 0, 0.05, 0.15, 0.20, 0.25 and 1.0 at%) samples, we applied a procedure successfully used for the preparation of Sb$^{III}$/TiO$_2$ catalysts.[5] The procedure consisted of synthesizing a precursor by adding NH$_4$OH to a mixture of the required volumes of TiCl$_4$ and TeCl$_4$ solutions. The co-precipitated hydroxide was washed with deionized water and dried at 120 °C for 16 h. To convert the precursor into titanium dioxide, it was annealed either in air or in an argon atmosphere at a temperature of 500 °C for 2 h.

[‡] *Photocatalytic experiments.* Visible-light photocatalytic experiments were carried out using an appropriate LED (white light, color temperature $T_c$ = 6500 K, $P$ = 3 W). Optical density was determined at $\lambda$ = 460 nm in a cuvette used for irradiation.

air-annealed precursor with the highest $\text{Te}^{\text{IV}}$ concentration studied in this work (Figure 1, curve *1*) is consistent with the drastic slowdown of the reaction previously observed in the presence of 2 at% $\text{Te}^{\text{IV}}/\text{TiO}_2$. Thus, this finding evidences that the lone pair E $\text{Te}^{\text{IV}}$, in contrast to the lone pair E $\text{Sb}^{\text{III}}$, does not prevent the recombination of photogenerated holes with electrons. Moreover, curve *1* demonstrates the expected[5] negative effect on the reaction kinetics caused by the substitution of chemically inert $\text{Te}^{\text{IV}}$ atoms for available $\text{Ti}^{4+}$ active sites. However, these photocatalytic experiments unexpectedly revealed that the reaction rate constant $k$ in the presence of 0.05 at% $\text{Te}^{\text{IV}}/\text{TiO}_2$ is significantly higher than the rate constant $k_0$ measured using tellurium-free reference $\text{TiO}_2$.

In the case of photocatalysts $x$ $\text{Te}^{\text{IV}}/\text{TiO}_2$ obtained by annealing the hydroxide precursor in an argon atmosphere, the evolution of the $k(x)/k_0$ value (Figure 1, curve *2*) was very similar to that just considered (see Figure 1, curve *1*), and at the lowest tellurium concentrations, a comparable excess of the relevant $k_0$ value was again observed. Obviously, this effect cannot be accounted for by changes in the chemical properties of $\text{Te}^{\text{IV}}$. On the contrary, it can reasonably be imputed to changes, induced by the dopant susceptible to affect the state of the catalyst surface.[8,9] This suggestion is supported by comparing the kinetics of MO bleaching in the presence of two different tellurium-free reference $\text{TiO}_2$ samples. In the case of a sample annealed in an argon atmosphere, a notable decrease in photocatalytic activity was observed:

$$k(x = 0)_{\text{argon}}/k(x = 0)_{\text{air}} = 0.8.$$

To interpret the modifying effect of tellurium atoms, we reviewed the results of relevant studies aimed at elucidating the photocatalytic impact of oxygen vacancies $\text{V}_\text{O}$. A recently published study[10] investigating the influence of an annealing atmosphere on the photoelectrochemical response of $\text{TiO}_2$ nanotubes showed that thermal treatment performed in argon results in the formation of a greater number of surface-located vacancies $\text{V}_\text{O}$ than when the similar treatment was carried out in air. Thus, this finding makes it possible to account for the decrease in the photocatalytic activity of the tellurium-free sample annealed in an argon atmosphere by the negative effect of oxygen vacancies. In turn, experiments devoted to investigating the influence of trivalent dopant cations, such as $\text{Al}^{3+}$, $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$, also revealed[9–17] a decrease in the photocatalytic activity of $\text{TiO}_2$. Thus, those studies demonstrated that vacancies $\text{V}_\text{O}$ formed to compensate for the deficient positive charge of the mentioned cations actually play the role of effective $(\text{e}^-,\text{h}^+)$-recombination centers. In contrast, our study[18] of anatase $\text{TiO}_2$ crystallites doped with surface-located E $\text{Sb}^{\text{III}}$ species showed that the removal of their lone electron pair upon oxidation (leading to the filling of the facing vacancy with an oxygen anion) does not affect the rate constant of the photocatalytic reaction. This means that the removed neighboring vacancy $\text{V}_\text{O}$ no longer plays its negative role as an $(\text{e}^-,\text{h}^+)$-recombination center.

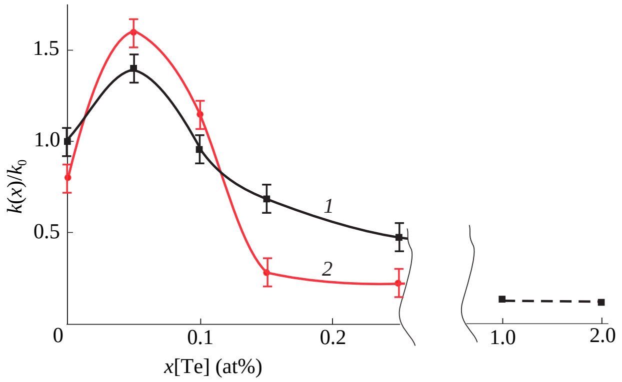

**Figure 1** Dependence of the ratio of rate constants $k(x)/k_0$ for the reaction of photocatalytic bleaching of MO dye in the presence of $x$ $\text{Te}^{\text{IV}}/\text{TiO}_2$ samples annealed either (*1*) in air or (*2*) in an argon atmosphere.

Thus, the above experimental results suggested that the increase in the activity of photocatalysts $x$ $\text{Te}^{\text{IV}}/\text{TiO}_2$ could also be due to the neutralization of the negative impact of $\text{V}_\text{O}$ vacancies formed on the surface of crystallites by the stereochemically active lone pair E $\text{Te}^{\text{IV}}$. The subsequent decrease in the photocatalytic activity observed with increasing tellurium concentration, in turn, can be accounted for by a negative effect reflecting the replacement of $\text{Ti}^{4+}$ active sites with inert $\text{Te}^{\text{IV}}$ atoms.

In conclusion, the present work allows us to suggest a novel mechanism for the positive photocatalytic impact of E $\text{Te}^{\text{IV}}$ dopant atoms. This mechanism is not related to the creation of new energy levels in the bandgap of $\text{TiO}_2$ or to a more efficient separation of photogenerated charges, but consists of suppressing the negative impact of oxygen vacancies already present on the surface of $\text{TiO}_2$ crystallites by the lone pair dopant E $\text{Te}^{\text{IV}}$.

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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.2024.04.041.

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