



Comments on the published article “Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO₂-film electrodes by J. Yang, J. Dai, Ch. Chen, J. Zhao; J. Photochem. Photobiol. A: Chem. 208 (2009) 66–77”^{☆,☆☆}

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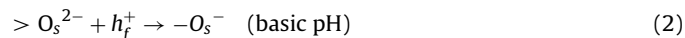
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On the basis of isotopic tracer experiments with ¹⁸OH₂, Yang et al. [1] have claimed recently that OH radicals appearing in the primary hydroxylated intermediates of the photoelectrocatalytic oxidation of 4-chlorophenol on TiO₂-thin film electrodes, are mainly generated via oxidation of water species adsorbed on the semiconductor surface with photogenerated valence band (VB) free holes, h_f^+ , according to reaction (1)



This claim is in contradiction with the evidence obtained from ultraviolet photoelectron spectra (UPS) that reaction (1) is hindered both thermodynamically and kinetically [2]. In order to avoid this contradiction, the following alternative mechanism for 4-chlorophenol photooxidation is proposed.

As indicated in ref. [2], energy levels of O:2p orbitals associated with 3-fold-coordinate bulk oxygen atoms compose the top of TiO₂ VB, while those associated with 2-fold-coordinated bridging oxygen atoms of the TiO₂ surface ($> \text{O}_s^{2+}$) should be located at the bottom of the bandgap region. Consequently, after thermalization, h_f^+ holes are inelastically trapped by $> \text{O}_s^{2-}$ surface oxygen atoms, giving rise to surface trapped holes, h_s^+ associated with either 1-fold coordinated bridging oxygen radicals ($-\text{O}_s^\bullet$) or bridging hydroxyl radicals $-\text{OH}_s^\bullet$, depending on the electrolyte pH. Therefore, instead of reaction (1), reactions (2) and (3) should be written

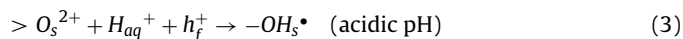


[☆] Answer from Dr. J. Yang: We have read carefully the comments proposed by J.F.Montoya et al., concerning our recently published paper “Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO₂-film electrodes” (J. Photochem. Photobiol. A: Chem. 208 (2009) 66–77).

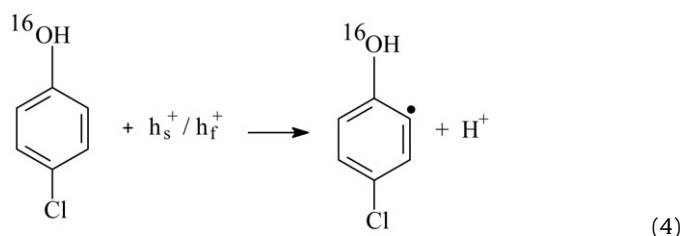
^{☆☆} Based on the related references of the comments, J.F.Montoya et al. explanation of the generation of ¹⁸O oxygenated intermediates (detected by our experiments) is reasonable to a certain extent. J.F.Montoya et al. have emphasised the important role of bridging oxygen atom and bridging oxygen vacancies in the photocatalytic mechanism, which are indeed neglected in our recently published paper.

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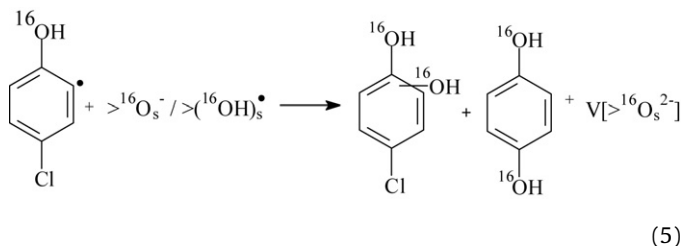
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These reactions in fact represent the initial step of the photoelectrocatalytic oxidation of organic compounds, in general, [3,4] and phenol in particular [5]. In a second step, a surface trapped hole is transferred adiabatically to a dissolved 4-chlorophenol molecule weakly interacting with the TiO₂ surface and a 4-chlorophenoxil radical is generated according to reaction (4) [5]. Simultaneously, 4-chlorophenoxil radicals may be generated via inelastic transfer of VB free holes to specifically adsorbed 4-chlorophenol species, as assumed by Yang et al. (see Eq. (2) of ref. [1]), although this alternative reaction seems to be improbable in aqueous medium [5].

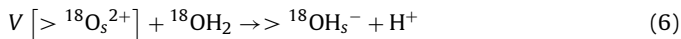


According to reaction (5), hydroquinone and/or chloro-catechol is further produced via trapping of a surface trapped hole (either $-\text{O}_s^\bullet$ or $-\text{OH}_s^\bullet$) by a chlorophenoxil radical.



The bridging oxygen vacancy, $\text{V}[> \text{O}_s^{2+}]$, left behind at the TiO₂ surface during reaction (5) is rapidly filled with a ¹⁸OH⁻ ion, via

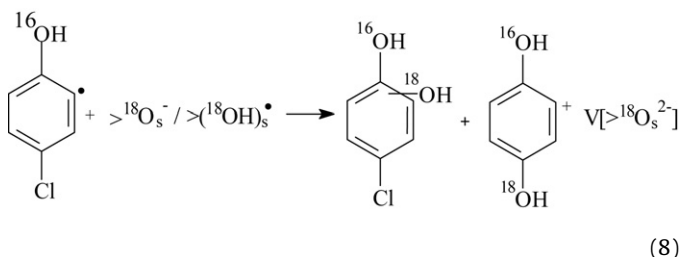
dissociative adsorption of a $^{18}\text{H}_2\text{O}$ molecule from the electrolyte, according to reaction (6). Such a regeneration of bridging oxygen atoms was first demonstrated via high resolution STM experiments by Schaub et al. [6] and further confirmed by Wendt et al. [7].



The $> ^{18}\text{OH}_s^-$ bridging hydroxyl so generated is further oxidized with a valence band free hole and a bridging hydroxyl radical is generated according to reaction (7)



Finally, according to reaction (8), an hydroxylated intermediate is generated via the attack of a 4-chlorophenoxil radical generated in (4) with the bridging hydroxyl radical generated in (7)



From reaction (8), a new oxidative cycle is initiated with reaction (6).

Summing up, the proposed mechanism of 4-chlorophenol photooxidation reasonably explain the generation of ^{18}O oxygenated intermediates, as detected experimentally by Yang et al., [1] without invoking the participation of $^{18}\text{OH}^\bullet$ radicals generated from the

photooxidation of $^{18}\text{OH}_2$ adsorbed molecules with VB free holes. Particularly singular is the role that bridging oxygen atoms and bridging oxygen vacancies play in the proposed mechanism. This has been described with more detail in a recent publication on the photoinduced oxygen exchange reactions taking place at the gas phase-TiO₂ interface [8].

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