Response to the referee's remarks and questions
„Preparation and characterization of nitrogen-doped TiO_2 semiconductors for photocatalytic degradations"

Reviewer:

Dr. Attila Demeter, DSc

First of all, I would like to thank and appreciate the time and effort that reviewer has dedicated to provide the valuable comments, remarks and questions.

Before going to specific questions, I would like to respone the general comment risen by reviewer.

Response to general comment

i) Obviously, the main objective of this work is to study the material and photoactivity of TiO_2 modified by different elements (N and Ag) in the Lab scale. The catalysts were prepared by using simple methods, characterized comprehensively, and applied for photocatalytic experiments also involving investigations to reveal photocatalytic pathways in these systems.

However, I have realized that there were severals drawbacks of the heteregenous photocatalysis as mentioned by the reviewer. I have mentioned some of them in the last two paragraphs of Chapter 3.2 in the literature review. For instance, it can only be used in last step of water purification systems (usually after biological treatment or other simple methods), owing to high concentrations of pollutants in the real wastewater applications. Therefore, in the heterogeneous photocatalysis, the highest values of degradation rate are obtained for the lowest initial concentration of pollutant [1]. *Ayekoe et al.*, applied heterogeneous photocatalysis to support coagulation-flocculation technique for removal of the humic substances in real treated water from Agbô River (Ivory-Coast) as illustrated in Fig. 1. The combined methods were able to degrade all

humic substances and mineralize them to 80% (initial content 7.82 mg L^{-1}) within a 220-min UV irradiation [2].

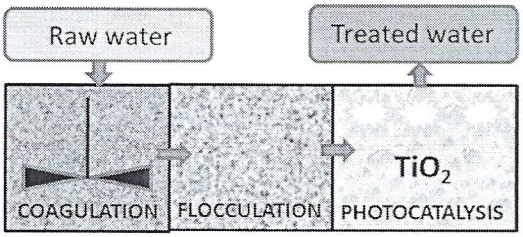

Fig. 1. Schematic illustration of heterogeneous photocatalysis combined with coagulation-flocculation [2].

ii) I have modified Equations 3.8 – 3.12 as below

$$^{\bullet}O_{2\,ads}^{-} + H^{+}_{(aq)} \leftrightarrow {}^{\bullet}OOH_{ads} \quad (3.8)$$

$$2\,{}^{\bullet}OOH_{ads} \rightarrow H_2O_{2(aq)} + O_{2ads} \quad (3.9)$$

$$H_2O_{2(aq)} + {}^{\bullet}O_{2\,ads}^{-} \rightarrow {}^{\bullet}OH_{\,ads} + OH^{-}_{(aq)} + O_{2\,ads} \quad (3.10)$$

$$H_2O_{2\,(aq)} + h\nu \rightarrow 2\,{}^{\bullet}OH_{\,ads} \quad (3.11)$$

$$\text{Pollutant}_{\,ads} + (h_{vb}^{+}, e_{cb}^{-}, {}^{\bullet}OH, {}^{\bullet}O_2^{-})_{\,ads} \rightarrow \text{Mineralization} \quad (3.12)$$

The adsorbability of pollutant on the surface of the catalyst is one of the key factors in the photocatalytic efficiency. *Mattsson and Österlund* [3] compared the adsorption and the photocatalytic degradation efficiency regarding acetone and acetic acid in the presence of anatase TiO_2 catalyst. They concluded that acetate ($k = 0.08$ min^{-1}) showed a lower degradation rate compared to that for acetone ($k = 0.64$ min^{-1}). It can be attributed to the bonding strength and coordination of acetate: strongly bonded μ-acetate species on the TiO_2 hinder the further reaction. However, too weak bonding results in site competition with water, ion formation, and a slower interfacial transfer rate of photoelectrons to the pollutant.

iii) Thank you very much for the advice. Yes, it is true that metal deposition on the catalyst is able to enhance the adsorption of the pollutant by increasing the specific surface area (see S_{BET} result in the dissertation). *Wang et al.*, reported an increase of the specific surface area of TiO_2 catalyst from 60.58 m^2 g^{-1} to 76.93 m^2 g^{-1}, after Ag modification

[4]. On the higher specific surface area, more pollutants were adsorbed by the catalyst and more active sites were available for the photocatalytic degradation process.

In addition, *Sun et al.*, mentioned that the presence of Ag on TiO_2 also could enhance the current density from 0.010 mA cm^{-2} to 0.026 mA cm^{-2}. This phenomenon can be attributed to a faster electron transport and a more efficient separation of the photogenerated holes and electrons [5].

iv) Every literature has different parameters (model compound, lamp, reactor, etc.) for the photocatalytic experiment. I agree, it is difficult to compare them in quantitative ways. In addition, not all of those literatures provide the quantum yield efficiency.

Response to some remarks

2. Yes, the sentence is evidence from literature but I forgot to write the reference. However, it can also be estimated because the 7-OHC product indicates the OH radical reaction with coumarin.

3. The results regarding the optimum dosing order and synthesis temperature originated from series experiments and we could reproduce the optimum conditions of the preparation (second dosing order at 10 ^{o}C).

5. See answer a) below.

8. Yes, it means the coumarin reaction with other species (beside coumarin reaction with OH radical).

Response to specific questions

(a) There are different approches between anaerobic and aerobic atmospheres, regarding the estimation of coumarin reaction with OH radical [6]. Under anaerobic condition, 2 molecules of coumarin and 2 molecules of OH radical produce a hydroxycoumarin (OHC) as shown in Fig. 2.

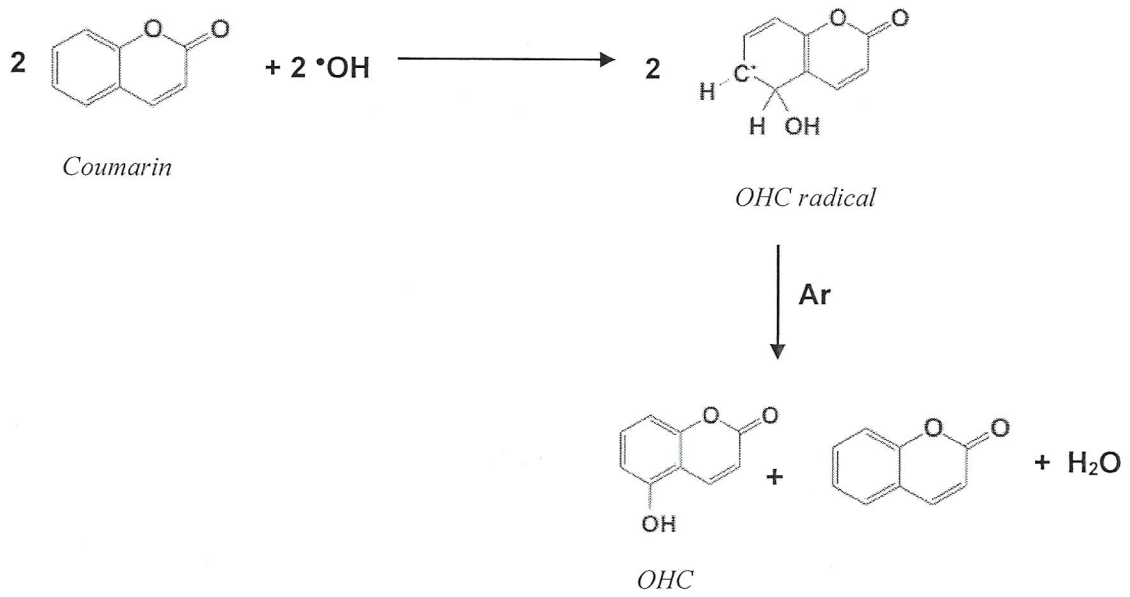

Fig. 2. Proposed reaction of OHC formation under anaerobic atmosphere.

however, in the presence of oxygen, only 1 molecule of coumarin is required to generate OHC product (Fig. 3).

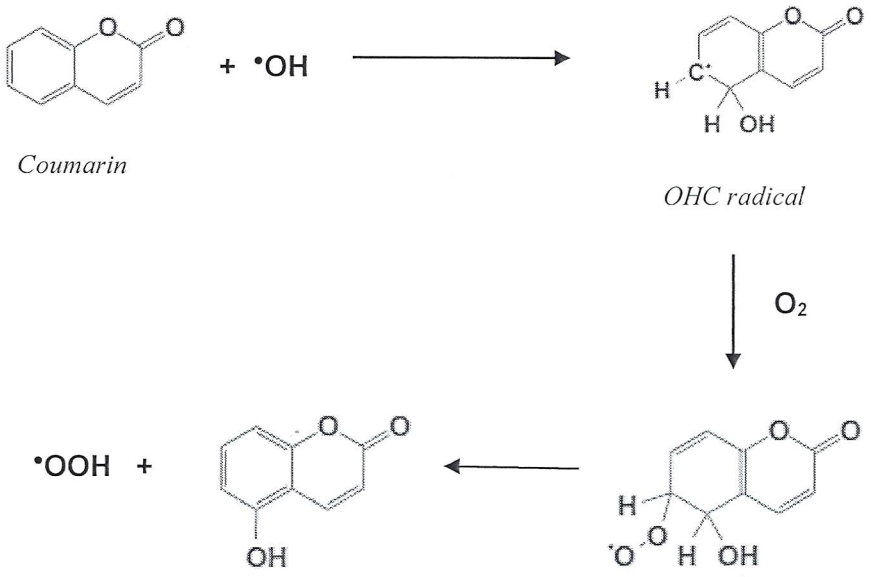

Fig. 3. Proposed reaction of OHC formation under aerobic atmosphere.

Hence, to calculate the coumarin reaction with OH radical in the anaerobic condition, the detected OHC products were multipled by 2 indicating there were 2 molecules of coumarin involved in the formation of 1 OHC molecule. In contrast, the ratio of OHC product and coumarin (1:1) is similar in case of aerobic condition [6].

As a result, the coumarin reaction with OH radicals presented in Fig. 5.15 seems to be similar in both anaerobic and aerobic conditions, although the detected OHC (7-OHC) product was twice as much as in the presence of oxygen.

(b) During the photocatalytic reaction, coumarin was transformed into 7-OHC in the first step of reaction. Simultaneously or after completing the coumarin transformation, the formed 7-OHC along with other OHC products could be degraded in further reactions due to the relative excess of *ROS* ($^{\bullet}OH$, $^{\bullet}O_2^-$) produced [7,8]. As a consequence, the concentration of the 7-OHC product decreased at longer UV irradiation as presented in Fig. 5.13 (aerobic atmosphere) in the dissertation.

(c) The modification of TiO_2 with transition metal nitrides such as TiN is one of the strategies to enhance the visible-light harvesting due to its plasmonic properties. Similarly to the noble metal (Ag) in our work, the presence of TiN possibly transfers hot electrons into TiO_2 during visible irradiation (Fig. 4),leading to the enhancement of the photocatalytic activity [9,10].

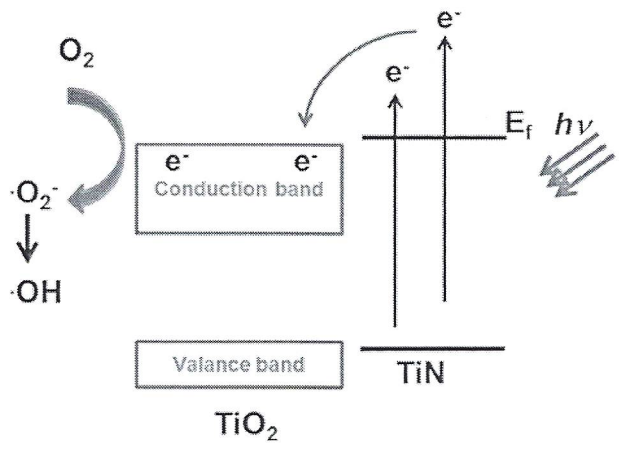

Fig. 4. Plasmonic process of TiN/TiO_2 photocatalyst under visible-light illumination [9].

Several works have devoted to explore the TiN/TiO_2 composite for photocatalytic enhancement, for instance, *Li et al.*, prepared TiN/TiO_2 photocatalyst by using a vapor-

phase hydrothermal method. The optical properties of TiN/TiO_2 showed a red-shift of light absorption into ~680 nm [9]. The result is also in line with another literature reported by *Clatworthy and co-workers* preparing TiN/TiO_2 composite by using ultrasonication. The diffuse-reflectance results showed a red-shift of light absorption into ~690 nm for TiN/TiO_2, which is due to the surface plasmon resonance effect of TiN [10]. These results prove that transition metal nitrides exhibit a role (hot electron transfer) similar to the noble metal used in our work in order to shift the light absorption of TiO_2 into the visible region.

Veszprém, June 7, 2021

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