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

Reviewer:

Emília Tálas, PhD

First of all, I would like to thank and appreciate the time and effort that the reviewer has devoted to provide the valuable comments and remarks. I will response the spesific questions risen by reviewer point by point.

What role does surface plasmon resonance play for Ag/TiO_2 catalysts in general and in the own system?

Surface plasmon resonance (SPR) is defined as a collective oscillation of conduction electrons at the interface between a metal and a semiconductor. Once the metal is irradiated by light, the electron density decreases on one side and increases on the other. This redistribution of charge generates an electron cloud, which is in opposite direction with the electric field (Fig. 1) [1,2].

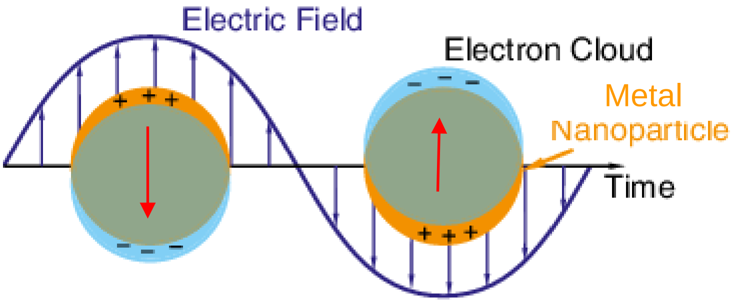

Fig. 1. Schematic of surface plasmon resonance [2].

There are three possible mechanisms of SPR to enhance the photoreaction as shown in Fig. 2:

- *Photon scattering*, when the light illuminates the plasmonic metal, the incident photon is spread out to the semiconductor, leading to a higher rate of charge-carrier formation.
- *Plasmon resonance energy transfer (PRET)*, the photon energy is transferred from the metal to the semiconductor via the existence of an intense oscillation electric field around the metal, promoting the rate of electron-hole formation.

- *Hot electron transfer,* the plasmon energy generates hot electrons with a relatively high energy level, and they can be directly injected into the conduction band of the semiconductor (photocatalyst) [1,3].

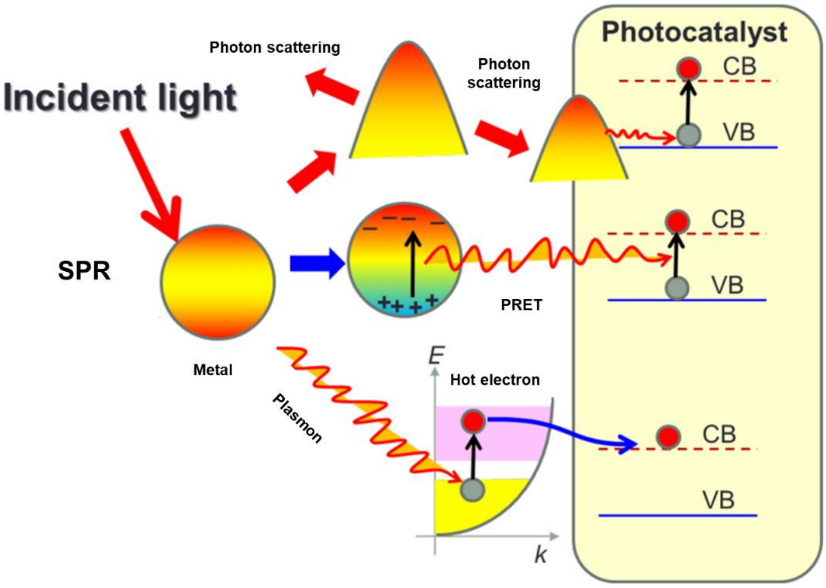

Fig. 2. Mechanisms of SPR to improve photoreaction [3].

In our system, Ag loading on the TiO_2 (NT-U) was able to enhance the visible-light absorption due to the SPR effects, then leading to increase the degradation rates of coumarin and 1,4-hydroquinone. Our results were in accordance with a previous paper authored by *Zhou, et al.*, in which they found that Ag/N-TiO_2 exhibited a stronger absorption of visible light than those provided by N-TiO_2 and TiO_2. Furthermore, the degradation of methylene blue under visible illumination also showed a linear trends, where the apparent rate constants of Ag/N-TiO_2, N-TiO_2, and TiO_2 were 1.02, 0.51, and 0.29 h^{-1}, respectively [4].

What is the probable reason why the highest antibacterial effect can be observed at the lowest Ag load?

It is well-known that the metallic characteristics of such Ag nanoparticles (AgNPs) depend on their sizes and shapes. Thus, it is important to control these parameters to achieve the desired properties. Generally, a smaller AgNPs shows a better antibacterial activity because it allows AgNPs to easily penetrate through the biological membrane and reach the insides of the cell, producing toxicity effect, then bacterial inactivation (Fig. 3). In addition, the shape of AgNPs also affect the degree of particle toxicity [5–7].

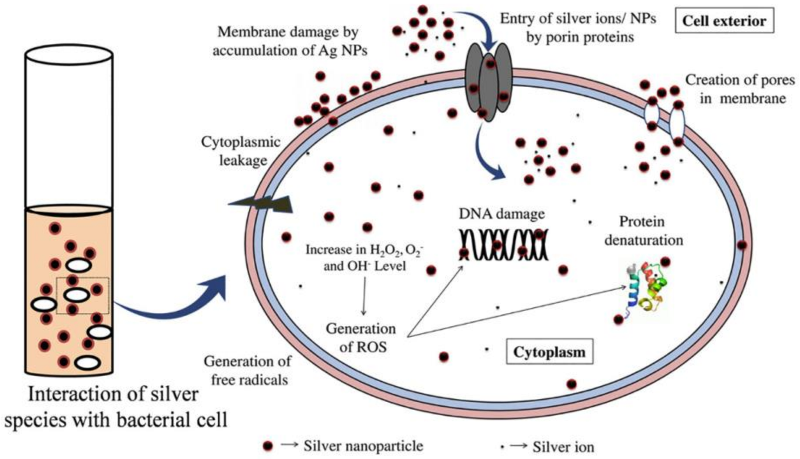

Fig. 3. Proposed mechanisms of bacterial inactivation in contact with AgNPs [5].

Several studies have been conducted to investigate the effect of size and shape of AgNPs toward antibacterial activity. For instance, *Li et al.*, conducted toxicity test of AgNPs with various sizes (25, 35, 45, 60, and 70 nm) against human lung fibroblast. They found that the smaller AgNPs possessed a higher toxicity affect due to generation of higher levels of reactive oxygen species [8]. In addition, *Kumari et al.*, reported the effect of different shapes (spherical, rectangular, penta, and hexagonal) of AgNPs against the multiple drug resistance bacteria. The results showed that the spherical AgNPs possessed more antibacterial effect than other shaped AgNPs. It might be due to the higher specific surface area as well as active sites in the spherical shape. From this point of view, a smaller size and more "spherical" shapes of AgNPs can improve the antibacterial activity [9].

Similarly in our work, at lower amount (10^{-6} mol Ag g^{-1} N-TiO_2), AgNPs were possibly distributed homogeneously with smaller sizes. It generated a higher surface area (active sites) and allowed AgNPs to establish a strong interaction with the cell membrane (*Vibrio fischeri*) for bacterial inactivation. However, AgNPs tended to agglomerate when they were present in larger amount (10^{-4} mol Ag g^{-1} N-TiO_2), which affected their size, shape as well as surface area, leading to a reduction of their antibacterial activity. *Ghilini, et al.*, reported a tendency similar to our work, in which at higher amount of AgNPs started to agglomerate and decreased the antibacterial activity as shown in Fig. 4 [10].

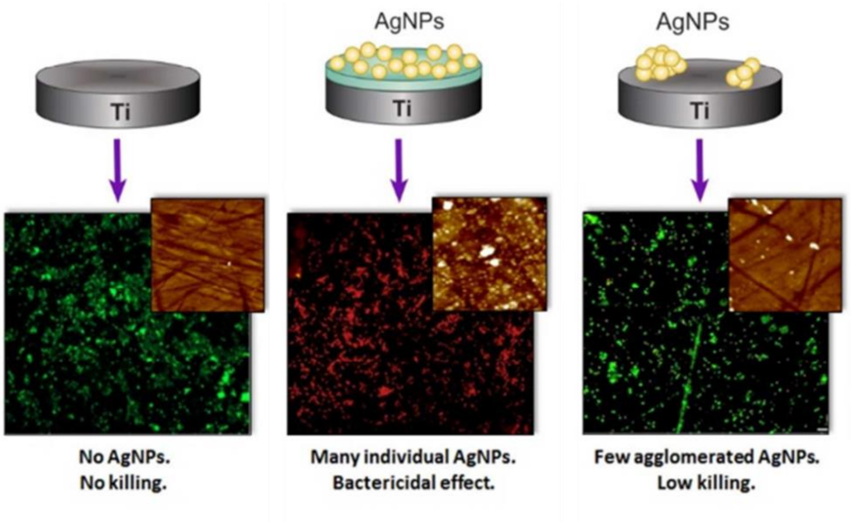

Fig. 4. Effect of AgNPs amount on their size and shape for bacterial inactivation [10].

What does the Candidate think about the recyclability of photocatalysts in general and in the own system?

Unfortunately, we did not investigate the recyclability of the catalysts in the present work and probably it can be realized in a further step of our research in the future.

One of the disadvantages of powdered photocatalysts (non-magnetic) is their reuse because it requires further efforts to re-generate the catalyst (filtration or sedimentation, washing and drying), which is of rather high cost and not very easy in practical application. *Zhou*, *et al.*, investigated the reuse of rod-like Ag/N-TiO_2 (powder) for degradation of methylene blue under UV irradiation. The results exhibited that the catalyst provided high photocatalytic activities; 97% of methylene blue could be degraded for the first time, and it slightly decreased to 91% after 5 cycles of application [4].

In order to tackle the re-generation problem, some researchers have demonstrated the immobilization of photocatalysts on different support materials, such as glass, ceramic, polymer, etc. However, it should be noted that it may reduce their effective surface area, and, accordingly, decreases the photocatalytic performance [11]. Besides, the stability of the support material should also be taken into consideration during the cyclic reactions.

In another work (presented on a conference), we have immobilized Degussa P25 TiO_2 in different support materials such as polymer (polyacrylamide) [C1] and glass [C2]. Our result indicates that under artificial solar irradiation, the adsorption and photodegradation of methylene blue (5 mg dm^{-3} initial concentration) decreased within a 3-cycle experiment in the presence of TiO_2/polymer composite hydrogel. The adsorptions were reduced from 49.5 % in the first cycle to 27.7 % and 23.5% after the second and third cycles, respectively. The degradations of methylene blue were 95.3 %, 74.5 %, and 74.7 % for the first, second, and third cycles, respectively. However, this composite (TiO_2/polymer) was instable in aqueous medium (by increasing the TOC content of the solution phase) due to the dissolution of the polymer compound during the irradiation [C1]. *Kangwansupamonkon and fellow workers* prepared a Degussa P25 TiO_2/poly[acrylamide-co-(acrylic acid)] composite hydrogel. The recyclability of 0.2 g sample composite was studied in the presence of methylene blue (5 mg dm^{-3}) under UV irradiation. The results showed the photocatalytic degradation of methylene blue reduced from 91% in the first cycle to 82, 22 and 17% in the second, third, and fourth cycles, respectively [12].

Furthermore, a better mechanical stability and recyclability was observed for TiO_2 grafted on a glass material. In 5 reaction cycles, coumarin degradations (10^{-4} M initial concentration) were relatively stable around 53.7-54.1 % under UV irradiation, and mass recoveries of TiO_2 were about 99-100 %, indicating that the catalyst was strongly attached to the glass material [C2]. *Bouarioua and Zerdaoui* reported the recyclability of TiO_2 immobilized on glass substrates toward methyl orange degradation. The photocatalytic activity of TiO_2/glass proved to be relatively stable within 5 cycles under UV irradiation, resulting in 98-96 % efficiency of methyl orange degradation [13].

To the Candidate's knowledge, is doped TiO_2 already used in practice (processes, patents, etc.)?

Several companies have used doped TiO_2 in the practical application for various purposes, particularly for self-cleaning surface against viruses, stop mould, and break down bacteria both indoor and outdoor. For instance, "Photocatalyst-coatings (ecotio$_2$)", a company based in New South Wales, Australia (www.photocatalystcoatings.com) has actively marketed its products for different applications. In addition, Kaktus (www.kastus.com), a company based in Dublin, Ireland has patented a surface coating technology with a permanent manufacturing application for glass and ceramic surfaces such as on the mobile screen to protect from virus or bacterial contamination.

However, there is still a great deal of challenges for real application of doped TiO_2 in the wastewater treatment, owing to the large concentration of pollutants and the low quantum efficiency of the catalyst, which are not favorable from economic points of view. Therefore, doped TiO_2 can only be used in the last stage of water purification systems to tackle the resistant pollutants which cannot be degraded by using biological or other traditional methods [14]. *Shaban, et al.* applied a pilot-scale equipment for photocatalytic degradation of polychlorinated biphenyls (PCBs) in seawater by using carbon modified titanium oxide (CM-n-TiO_2) nanoparticles. Clean seawater samples were collected from Red Sea coast, Sharm Obhur, Jeddah, Saudi Arabia, and then contaminated with various concentrations of PCBs. The photocatalytic experiments were carried out by using solar falling film reactor (SFFR) (surface area of 1.5 m^2 and volume of 20 dm^3) irradiated on sunny days between 11:00 a.m. and 3:00 p.m. with an average solar intensity of 1140 W m^{-2} (Fig. 5). The result showed a total decomposition of PCBs (1 mg dm^{-3} initial concentration) after a 75-min irradiation under natural sunlight, indicating that the system (CM-n-TiO_2/SFFR) was an attractive and promising technique for wastewater treatment at pilot-scale application [15].

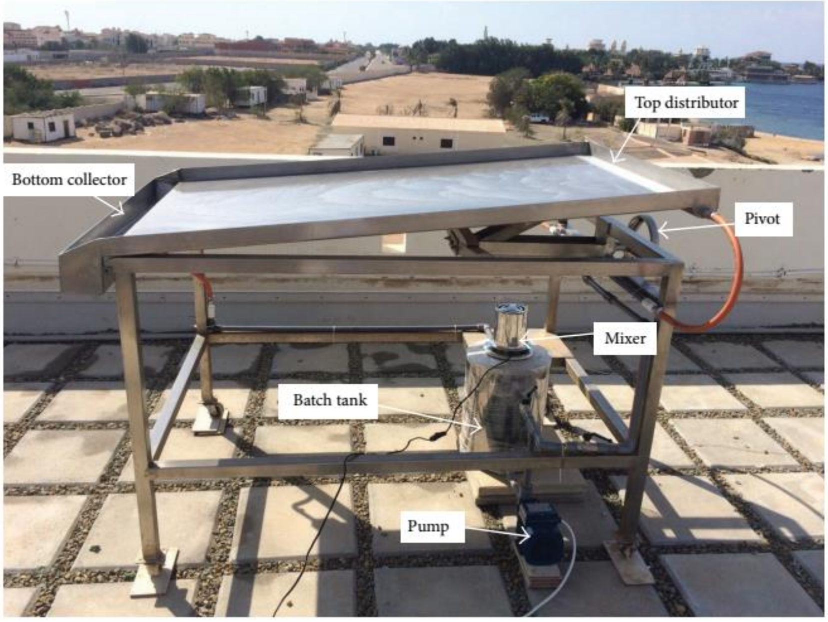

Fig. 5. Photograph of the solar falling film reactor [15].

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Conferences

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