Response Letter and Summary of Changes

We thank the reviewers for their helpful comments and suggestions to improve the manuscript. Changes were made in the revised manuscript (highlighted in yellow for easy identification) according to the reviewers’ comments. The following summarizes our responses to the points raised.

Reviewers Comments:

Reviewer 2:

The issue tackled in this manuscript is interesting per se for the scientific community in the field of photocatalysis. Often, many articles dealing with the pre-treatment TiO2 photocatalysts do not make such a systematic study, but instead assume that a particular pre-treatment is optimum for performance. Therefore, the approach in this work is acknowledged. Having said so, several drawbacks have been found during review, and to my opinion, should be amended. Characterisation of the materials needs to be thoroughly revised, and the supplementary information has to be provided (it is mentioned in the text yet is not available). The specific issues are outlined as follows:

1. The concept of oxygen vacancies is appropriately denoted as a most likely benefit for photocatalytic activity, especially under light of visible wavelengths, but this should then be checked for the materials under study by using UV-free or, even better, monochromatic light; photo-action studies would be the ideal proof for this. The authors should also clearly state whether they feel that it is the extension of band gap which is the cause of activity enhancement, or if
instead, charge carrier separation is the main factor. Finally, the term “O2-vacancy” is not correct, since it is not dioxygen molecules which are absent from TiO2, yet individual O atoms.

- Thanks for the comment. Both of reduction in band gap value and improvement of charge carrier separation have positive effect on the photocatalytic activity of samples. Another piece of information to elucidate the chemical structure of samples is provided by showing the spectrum of UV–vis diffuse reflection of four samples in Fig. 2(a). As is shown in this figure, the light absorption characteristics of P25 is greatly affected in both H-400 and V-400 samples which is due to oxygen vacancy generation. A sharp increase in the absorbance of all samples can be observed ranging from 400 to 200 nm, which is ascribed to anatase phase of TiO2. The H-400 and V-400 samples show a redshift in absorption edge of UV–visible range. Measured by given Eq. 1, the band gap values of three samples are listed in Fig. 2(b) along with the physical appearance of powders. According to the calculated values, they can be arranged from the lowest to highest band gap in the order of H-400<V-400<A-400<P25. The band gap value of H-400 and V-400 samples are smaller than that of P25, resulting in its light-absorption toward redshift. In order to elucidate a better picture of the photocatalyst (P25, V-400 and H-400) properties, prepared in this study, the photoluminescence (PL) spectra were obtained at excitation wavelength of 325 nm and presented in Fig. 7. From this result, two major peaks at ca. 466 and 548 nm can be identified in the PL spectrum of P25. To a great degree, one may decipher the reduction in PL intensity into existence of higher electron–hole segregation (long-lasting photogenerated charge carriers) [56,57]. The PL intensity of H-400 and V-400 was lower than P25 which is indicative of H-400 and V-400 facilitating reduced recombination rate of photogenerated electron-hole pairs [58]. Therefore, the generation of the oxygen
vacancy on the surface of H-400 and V-400, which is behaving as electron scavengers, suppress photoluminescence intensity. This is why H-400 and V-400 showed higher photocatalytic performance than P25 [57].

2. TiO$_2$ (P25) is not a microporous “molecular sieves” material, and mentions to this should be removed.

   - Thanks for the useful comments. The molecular sieve was wrongly used in this manuscript. Commercial P25 (Aeroxide P25 nanopowder (with average particle size of 21 nm)) was utilized as TiO$_2$ source.


   - Thanks for the comments. These references has been added to the manuscript.


   - Thanks for the comments. These references has been added to the manuscript.

5. It is said that black TiO2 is prepared, but the materials presented are not too similar to the original black TiO2 (Science, 2011, 331, 746), the reducing conditions employed in this manuscript are noticeably less severe.

   - Thanks for the comments. The “black TiO$_2$” used in the manuscript was not appropriate.

The colored TiO$_2$ is used in the revised manuscript.
6. The determination of band gaps should be graphically illustrated, since the explanation is not totally clear.

- Thanks for the comments. \( F(R\infty) = \frac{(1 - R\infty)^2}{2R\infty} \). Where, \( R\infty \) is reflectance. The reflectance data were reported as the \( F(R\infty) \) value from Kubelka-Munk theory versus the wavelength. Band gap determinations were made by plotting \( [F(R\infty) * h\nu]^2 \) versus \( h\nu \) (eV).

7. Photocatalytic experiments: was any wavelength filter used?

- Thanks for the comments. Any wavelength filter was not used.

8. Photocatalytic experiments: how was contact of the suspension with atmospheric oxygen (as the oxidising agent) ensured?

- Thanks for the comments. The concentration of MB during the reaction time for the samples without photocatalyst and in dark condition has been added to the Figure 6. As can be seen, the concentration of MB does not change during the reaction without photocatalyst under 1.5G solar light illumination. Under dark condition in presence of photocatalyst, less than 10% of MB was removed due to the adsorption of MB by photocatalyst.
9. Photocatalytic experiments: The procedure for reuse experiments should be thoroughly detailed.

- The recycling of the photocatalyst was implemented as follows: after a first photodegradation cycle, the treated solution of the dye was centrifuged with a rotation of 10,000 rpm for 10 minutes to remove photocatalyst. The liquid phase was filtered by a vacuum system with a Millipore membrane (0.45 μm) and the solid phase containing the photocatalyst was carefully separated for reuse. After allowing it to dry in an oven for 12 h at 50 °C, the separated photocatalyst was added again to the next cycle. The process was repeated 5 times.

10. XPS: The Ti signals are not “satellite” but genuine ones.

- Thanks for the comment. This comment has been amended in the manuscript.
11. XPS: The lack of trend is suspicious; if both H- and V- samples have Ti3+ species, then both should show lowered Ti 2p binding energies, as also suggested by EPR; might this be due to the fact that the binding energies have not been corrected to adventitious carbon (284.6 eV)? Please explain in the experimental a section about energy correction in XPS.

In order to test for Ti3+ and oxygen vacancies, Ti 2p and O1s XPS spectra are measured and the Ti 2p3/2 peak of the vacuum activated sample became unsymmetrical compared with the peak of pure P25 (Fig. 2b), indicating the existence of Ti3+ [1]. Furthermore, the ΔE value between Ti 2p1/2 and Ti 2p3/2 was 6.2 eV for the vacuum activated sample, suggesting the presence of Ti3+ [2, 3].

REFERENCES:


12. PL spectra show a signal at 548 nm which the authors assign to Ti3+; then, why is this signal also seen for P25, which does not have Ti3+?

- Thanks for the comment. The description is carefully corrected.

13. Degradation efficiency (Figs. 8 and 9) should be clearly defined.

- Thanks for the comment. The degradation (photodegradation) efficiency was calculated by Eq.3:

\[
\text{Degradation efficiency} \, (\%) = (\frac{(C_0 - C_t)}{C_0}) \times 100
\]  

(3)
14. Fig. 9: The conduction band of rutile is higher in energy according to Nat. Mater. 12 (2013) 798–801, and thus electrons are expected to flow from rutile to anatase.

- Thanks for the comment. As mentioned the reviewer, the electron flow is from CB of rutile to CB and V_o state of anatase that clearly indicated in the Figure 9. The Electron transfer from CB of anatase to V_o state of rutile is removed from Figure 9.

![Figure 9](image)

**Fig. 9.** The photo-excited electrons-transfer under the simulated sun light irradiation for V-400 and H-400.

15. The sentence in lines 299-300 must be corrected.

- Thanks for the comment. These lines are carefully corrected.

16. Which is the reason for the 10% decline in activity upon reuse (Fig. 10)? Maybe EPR, XPS or other techniques could be applied to the used photocatalysts to find the causes.

- Thanks for the comment. To find the reason for this reduction, EPR analysis of the samples was used. The results are shown in Fig. S4. The EPR signal intensity shows the oxygen vacancy density; as can be seen, the signal intensity of the used samples is slightly reduced.
It can be concluded that the photocatalytic activity of used samples is reduced based on the reduction of oxygen vacancy density in used samples.

**Fig. S4.** EPR spectra recorded at room temperature for fresh and used samples.

17. Refs. 8 and 19 should be completed/corrected.

- Thanks for the comment. These references has been corrected.