Dear Prof. Petrović,

We are sending to you the revised article: “Visible light absorption of surface-modified TiO2 nanoparticles with vitamin B6: a comparative experimental and DFT study”. We have revised this manuscript along the lines that reviewers have suggested. All corrected or added text is marked with yellow color in the manuscript.

Regarding to the concrete suggestions from the reviewers we reply here with the following answers:

**Reviewer A:**

Line 49: It should be written “over such mentioned surface modified”. In the introduction the results (average size and level of crystallinity) of the presented work should not yet be revealed. If those results originate from some reference please list it.

**Answer:** Phrase “surface-modified TiO2” is replaced with “visible-light responsive TiO2” (page 2). Phrase suggested by the Reviewer A can be misleading implying that literature data concerning photocatalytic reactions were performed only over aromatic mono-hydroxy compounds. The average size and level of crystallinity of TiO2 NPs were introduced in the last paragraph of Introduction, at the point where the focus of this study is announced. The synthetic procedure for colloid preparation has been used for decades, and it is properly cited in the Experimental section.

Line 79: You should not mention the size of the NPs if it is not known from the given reference or if it is not yet shown in the paper. When referring to some information given in the reference please provide the original (parental) paper, not just to give one that calls further looking up. Specifically, I mean mentioning reference [9] that goes to the reference [11] from that article it further goes to reference [3] etc. Link to that in the Experimenal part (from the line 93) it is said that TEM analysis was done on the surface modified TiO2 NPs, but it seems that Fig. 1a presents NPs before modification, since that analysis provided the insights of the NPs size and that information was used in order to calculate the vitamin B6 concentrations required to cover TiO2 surface (line 86). Please clarify this and follow the order in presenting results according to the need of the work. If the size of the NPs was known previously it should be clear.

**Answer:** Size of TiO2 NPs (45 Å) given at the beginning of experimental part is erased. Synthetic procedure in reference 27 might be considered as parental since authors (Rajh *et al.*) did not refer to any previous literature. TEM analysis is indeed presented with unmodified TiO2 NPs. Of course, size obtained from TEM measurements is used to calculate, strictly speaking, concentration of surface Ti atoms, not concentration of vitamin B6 required to cover TiO2 surface. To follow order in presenting results, we moved part concerning description of TEM and XRD measurements from section “*Characterization of surface-modified TiO2 NPs by vitamin B6*” after paragraph describing synthesis of TiO2 NPs (page 3). In addition, section “*Synthesis of surface-modified TiO2 NPs by vitamin B6*” is merged with section “*Characterization of surface-modified TiO2 NPs by vitamin B6*”. Section is named “*Synthesis and characterization of surface-modified TiO2 NPs by vitamin B6*” (page 3).

Line 97: The experimental procedure must be re-phrased, do not use ”some different volumes”, specify in which volume ratio of Tisurf and vitamin B6 (0.025 M). In the line 183, you wrote [Tisurf]+[B6] = 0.025 M, but from the line 97 it seems that both the concentrations are 0.025 M.

**Answer:** The part concerning determination of the CTC composition by Job’s method is rewritten (page 4). Job’s method is based on spectrometry of series of solutions with different ratio of complex forming components (metal and ligand), but keeping sum of their concentrations constant. Because of that, [Tisurf]+[B6]=0.025 M for any solution/mixture is equal to the initial concentration of Tisurf or B6 solution (0.025 M).

I think that results of the DFT calculation should be put at the end, meaning after FTIR.

**Answer:** We prefer to keep DFT part where it is. Reason is simple: the DFT calculation of electronic excitation spectrum (Figure 4) follows optical (absorption) characterization of the CTC. Coordination of B6 to Tisurf can’t occur differently than over single Ti‒O‒C linkage. Because of that, it is not necessary to first perform FTIR and then constructed cluster. The constructed cluster mimic quite well the CTC as can be noticed by comparing Figures 2 and 4.

The sentence in the line 142 and 143 “In TiO2 NPs a large fraction of atoms is located at the particle surface, thus significantly changing nanoparticle’s properties compared to the bulk material.” is not properly linked to the next one commenting the absorption properties of the sample. If you refer to the absorption onset of unmodified TiO2 to be blue shifted compared to the bulk TiO2 you should write that and then compare the absorption edge of unmodified and modified samples.

**Answer:** It is well-known that TiO2 has extremely small Bohr radius, and 45 Å TiO2 NPs can’t display size quantization effect, i.e. blue absorption shift in comparison to bulk material. However, some other properties can be changed due to small size of TiO2 NPs, like surface structure that facilitates CTC formation, so we rephrased the sentence (page 5). Absorption spectrum of unmodified TiO2 colloid is presented in Figure 2 (curve a) and its absorption onset correspond to band gap value of anatase (Eg= 3.2 eV as stated in Introduction). To clarify, red-shift of 0.4 eV means absorption onset at 2.8 eV (energy) or 440 nm (wavelength), as can be seen in Figure 2 (curve b).

Line 148: You comment the absorption shift in eV but the graph is in nm. You should add the calculation E = 1240/λ.

**Answer:** Equation E=1240/λ is Plank’s law with suitable chosen units (eV and nm). Plank law belongs to high-school curriculum and we believe that there is no need to include calculations like this in the manuscript.

Line 156: Why 0.09 M TiO2?

**Answer:** Actually it was 18 mM TiO2. Several runs with different initial concentrations of TiO2 colloid were performed in order to determine stability constant of CTC. We chose to present absorbance at 400 nm of CTC *vs* concentration of B6 because most of the A400 values are in optimal spectrophotometric range (0.3-0.9).

Line 163: You shoud use [ ] or C for concentration all along, not combining.

**Answer:** In the revised version of the manuscript concentrations are expressed in brackets.

Line 165: For the case of the readers you should add the equation for calculation of Kb.

**Answer:** The intercept (1/KbAmax) and the slope (1/Amax) of the linearized form of equation used for calculation of Kb are included in the revised version of the manuscript (page 6).

Line 180: Please explain why it was unexpected non-equimolar ratio.

**Answer:** Since the CTC formation takes place by dehydration reaction between two hydroxyl groups originating from oxide’s surface and from vitamin B6, the malar ratio [Tisurf]:[B6]=1:1 is expected, not [Tisurf]:[B6]=1.5:1. But, to avoid any ambiguity, the sentence was rewritten and phase “unexpected non-equimolar ratio” erased (page 7).

Line 205: Please add the labeling for the blue spheres.

**Answer:** Added; blue sphere is nitrogen (page 8).

Line 216: In FTIR spectrum in a) there is a peak at 1220 cm-1 that has not been discussed.

**Answer:** We indeed omitted to mention peak at 1220 cm-1 in the first version of the manuscript. That peak belongs to bending C‒H vibration, and it is does not help in understanding how B6 coordinates to the Tisurf. Because of that, instead to draw readers’ attention to unnecessary details, we changed a little bit Figure 5. In the revised version of the manuscript, the FTIR spectra are given in the wavenumber range 1600‒1240 cm-1.

Line 238: Since you wrote “undercoordinated surface Ti atoms” in conclusion you can add that phrase also in the introduction.

**Answer:** We added the phase “undercoordinated surface Ti atoms” in the first sentence of the second paragraph of Results and Discussion section (page 5).

Generally, you should write concrete results in conclusion, i.e. absorption red shift, value of Kb.

**Answer:** Explicit data concerning absorption red shift and stability constant of the CTC complex are included in the conclusion (page 10).

In my opinion, this manuscript should: be published after minor revision without additional review

**Reviewer B:**

1. Lines 59-60: It is stated: “For the first time, the Ti–O–C linkage between biologically active molecule pyridoxine hydrochloride (vitamin B6) and TiO2 NPs was achieved”. Explain why it is important (biologically active)?

**Answer:** Phrase “biologically active” is just the adjective describing ligand molecule, vitamin B6.

2. Line 87: It is not clear “molar concentration of TiO2 in molecular units”!

**Answer:** In the revised version of the manuscript “in molecular units” is erased.

3. Lines 97-98: It is not clear: “the solutions were prepared by mixing some different volumes of equimolar solutions of Tisurf and vitamin B6 (0.025 M)”. Later, in the title of Fig.3, it was stated: [Tisurf] + [B6] =0.025 M. It is not clear whether the concentration of [Tisurf] and [B6] was 0.025 M, or sum of these concentrations was 0.025 M.

**Answer:** Same question raised the Reviewer A. So, answer is the same. The part concerning determination of the CTC composition by Job’s method is rewritten (page 4). Job’s method is based on spectrometry of series of solutions with different ratio of complex forming components (metal and ligand), but keeping sum of their concentrations constant. Because of that, [Tisurf]+[B6]=0.025 M for any solution/mixture is equal to the initial concentration of Tisurf or B6 solution (0.025 M).

4. Use mol dm-3, not M.

**Answer:** Frankly, we do not see reason. We noticed various ways of expressing concentration in Journal of the Serbian Chemical Society (M, mol dm-3, %, ppm, g L-1, *etc.*).

5. It was said that TEM was performed for the characterization of surface-modified TiO2, but the results were given for bare TiO2.

**Answer:** Presented TEM images are indeed of unmodified TiO2 NPs. Surface-modification does not change the particles size distribution. To avoid any ambiguity we moved part concerning TEM and XRD instrumentation right after paragraph describing synthesis of TiO2 NPs (page 3). In addition, section “*Synthesis of surface-modified TiO2 NPs by vitamin B6*” is merged with section “*Characterization of surface-modified TiO2 NPs by vitamin B6*”. Section is named “*Synthesis and characterization of surface-modified TiO2 NPs by vitamin B6*” (page 3). Similar/same question was raised by the Reviewer A.

6. It is stated “the crystallite size given by the XRD measurement is in agreement with the size of nanoparticles by TEM analysis of TiO2 colloid”. But, according to XRD, average crystallite size is 15 Å, and according to TEM, sizes of particles are about 45 Å. What it means that the results are in agreement?

**Answer:** It is not necessary to obtain identical results by two independent techniques to say that they are in agreement. It is sufficient to either have close values or that they follow the same trends. But, we change the sentence avoiding to use phrase “in agreement” (page 5).

7. The sentence „In TiO2 NPs a large fraction of atoms is located at the particle surface, thus significantly changing nanoparticle’s properties compared to the bulk material.” is at the beginning of the paragraph related to optical properties of the modified TiO2. Why? This sentence is not in connection with the optical properties of the modified TiO2.

**Answer:** The TiO2 NPs have different surface structure compared to bulk (distorted, undercoordinated) as stated in Introduction and supported with literature data. So, it has direct influence on the CTC formation. We rephrased the sentence (page 5) and directed readers to the proper literature (references 9 and 10). Similar question was also raised by the Reviewer A.

8. In the legend of Fig. 2, it is stated that concentration of TiO2 is 0.09 M, but in line 163 – concentration is 18.0 mM. Explain!

It should be clearly stated in experimental procedure that solution for the binding constant (not constants) determination were prepared with the constant TiO2 concentration and the increasing concentration of B6 (there is just the sentence: For the determination of binding constants, the absorption spectra were recorded at room temperature using Thermo Scientific Evolution 600 UV-Vis spectrophotometer.)

**Answer:** We thank to the Reviewer B for noticing our mistake. The experimental conditions concerning Kb determination described in the text are right ([TiO2] = 18.0 mM), while concentration given in figure caption for inset (0.09 M TiO2) is concentration of unmodified and modified TiO2 colloids whose absorption spectra are presented in Figure 2 (curve a and b, respectively). We properly changed figure caption (page 6).

Sentence concerning the binding constant determination is rephrased as suggested by the Reviewer B (page 4).

9. Fig. 2 (inset) and through whole text: Use c or [] for concentration, not both.

**Answer:** The same question was raised by the Reviewer A and the answer is the same. In the revised version of the manuscript concentrations are expressed in brackets.

10. It is not clear from the sentence: “By plotting 1/A vs 1/CB6, the straight line was obtained, and from the ratio of the intercept and the slope, Kb value was found to be 3.0×102 M-1” how the constant was calculated. There are no references. Despite the fact that the method for the constant calculation is given in the literature, it is necessary to give short explanation.

**Answer:** The same question was raised by the Reviewer A and the answer is the same. The intercept (1/KbAmax) and the slope (1/Amax) of the linearized form of equation used for calculation of Kb are included in the revised version of the manuscript (page 6).

11. Line 169-172: It should give short explanation that the Langmuir adsorption constant is an indicator of the bond strength between adsorbent and adsorbate.

**Answer:** Discussion concerning the Langmuir adsorption constant is based on literature data. We think that this discussion should not be extended since we directed readers to original work by J. Araña et al. (reference 42). In addition, these authors did not report the CTC formation. Reason for that lies in different experimental conditions; they applied significantly lower concentrations of ligands (up to 150 ppm) onto Degussa P25, not 45 Å TiO2 NPs.

12. Lines 166-172: Explain (give some assumption) why the stability constant is much lower than for catecholate- and salicylate-type of ligands.

**Answer:** The difference between stability constants of CTCs with vitamin B6 and catechol with TiO2 NPs are roughly one order of magnitude (3.0×102 and 2.5×103 M-1, respectively), so stability constant for B6 is not “much lower” in our opinion. We would prefer not to guess at this point way the stability constants differ.

13. Line180: Explain why non-equimolar ratio was unexpected, i.e., what was expected?

**Answer:** The same question was raised by the Reviewer A and the answer is the same. Since the CTC formation takes place by dehydration reaction between two hydroxyl groups originating from oxide’s surface and from vitamin B6, the malar ratio [Tisurf]:[B6]=1:1 is expected, not [Tisurf]:[B6]=1.5:1. But, to avoid any ambiguity, the sentence was rewritten and phase “unexpected non-equimolar ratio” erased (page 7).

14. Fig. 4. Explain “by convolution with full width at a half maximum of 5000 cm-1.” I think it will be useful for the journal readers.

**Answer**: We think that the additional explanations are unnecessary. Experts in the field know very well that it is a way how the software draws (convolutes) the spectral curve based on the calculated excitations. The default value in Gaussian software is 3000 cm-1, but somewhat more diffuse spectrum is achieved with the convolution at 5000 cm-1, which is a value that is broadly used in many papers. For non-experts these are just meaningless details.

15. I think that it is much better to give the results of FTIR spectroscopy before DFT calculations, because DFT calculation “is based on dehydration reaction between two hydroxyl groups: first, originating from vitamin B6, and the second one, from oxide’s surface (lines 187-189)”, what was proved by FTIR spectroscopy.

**Answer:** We prefer to keep DFT part where it is. Reason is simple: the DFT calculation of electronic excitation spectrum (Figure 4) follows optical (absorption) characterization of the CTC. Coordination of B6 to Tisurf can’t occur differently than over single Ti‒O‒C linkage. Because of that, it is not necessary to first perform FTIR and then constructed cluster. The constructed cluster mimic quite well the CTC as can be noticed by comparing Figures 2 and 4. It should be mentioned that the same question was also raised by the Reviewer A.

16. Lines 210-211: Infrared spectrum of TiO2 has also band at about 1620 cm-1, which is associated with the scissoring vibration of adsorbed water molecules (ref. 43) and the band at about 500 cm-1 for Ti-O and Ti-O-Ti bonds in the TiO2 lattice.

**Answer:** The presence of bands in the FTIR spectrum of unmodified TiO2 at about 1620 and 500 cm-1 is included in the revised version of the manuscript as suggested (page 8 and 9).

17. Fig. 5. Why the band at about 1220 cm-1 was not mentioned?

**Answer:** The same question was raised by the Reviewer A and the answer is the same. We indeed omitted to mention peak at 1220 cm-1 in the first version of the manuscript. That peak belongs to bending C‒H vibration, and it is does not help in understanding how B6 coordinates to the Tisurf. Because of that, instead to draw readers’ attention to unnecessary details, we changed a little bit Figure 4. In the revised version of the manuscript, the FTIR spectra are given in the wavenumber range 1600‒1240 cm-1.

18. Line 229-230: “its intensity decreased in comparison to results obtained for free vitamin B6” → “its intensity decreased in comparison to results obtained for free vitamin B6 much more than intensity of other bands”

**Answer:** We rephrased the sentence as suggested by the Reviewer B (page 9).

19. Do not use in conclusion terms that are not used in the main text (undercoordinated surface Ti atoms (defect sites)).

**Answer:** We are in position to choose between suggestion of the Reviewer A and suggestion of the Reviewer B. So, we rephrased the first sentence in the second paragraph of Results and Discussion by including phrase “undercoordinated surface Ti atoms” (page 5), and kept this phrase in the conclusion of the revised version of the manuscript.

20. The second part of conclusions (starting from “The presented results indicate that…) should be first mentioned in the discussion. In addition, similar conclusions were made in references 19 and 47. It should give the conclusion for B6 as a ligand.

**Answer**: The second part of conclusion “*The presented results indicate that tunable optical property of hybrids is not exclusively consequence of formation of binuclear (bridging) complexes between salicylate- and catecholate-type of ligands and surface Ti atoms, and can be achieved through single Ti–O–C linkage.*” is first mentioned in the Introduction directing readers to the first reports concerning Ti‒O‒C linkage, of course, not by using the same words. The Reviewer A, also, suggested that experimental results for B6 should be explicitly stated in Conclusion. We made suggested changes in Conclusion (page 10), but, also, kept part that gives the perspective for further work.

In my opinion, this manuscript should:

be published after minor revision without additional review

Hoping that we have readjusted our manuscript to the demands of Journal of the Serbian Chemical Society,

Kind regards,

Dr. Jovan Nedeljković