molecules

MDPI

*Supplementary Material*

# $La^{3+}$ Effect on the Surface (101) of Anatase for Methylene Blue Dye Removal, a DFT Study

**Ximena Jaramillo-Fierro *, Sneyder Gaona and Eduardo Valarezo**

Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Técnica Particular de Loja, San Cayetano Alto, Loja 1101608, Ecuador

* Correspondence: xvjaramillo@utpl.edu.ec; Tel.: +593-7-3701444

**Abstract:** Density functional theory (DFT) is a widely used method for studying matter at the quantum level. In this study, the surface (101) of $TiO_2$ (anatase phase) was considered to develop DFT calculations and explain the effect of lanthanum ion ($La^{3+}$) on the electronic properties, adsorption capacity, and photocatalytic activity of this semiconductor. Due to the presence of the $La^{3+}$ ion, the bandgap energy value of $La/TiO_2$ (2.98 eV) was lower than that obtained for $TiO_2$ (3.21 eV). TDOS analysis demonstrated the presence of hybrid levels in $La/TiO_2$ composed mainly of O2*p* and La5*d* orbitals. The chemical nature of the La-O bond was estimated from PDOS analysis, Bader charge analysis, and ELF function, resulting in a polar covalent type, due to the combination of covalent and ionic bonds. In general, the adsorption of the methylene blue (MB) molecule on the surface (101) of $La/TiO_2$ was energetically more favorable than on the surface (101) of $TiO_2$. The thermodynamic stability of doping $TiO_2$ with lanthanum was deduced from the negative heat-segmentation values obtained. The evidence from this theoretical study supports the experimental results reported in the literature and suggests that the semiconductor $La/TiO_2$ is a potential catalyst for applications that require sunlight.

**Keywords:** DFT calculations; anatase; lanthanum; adsorption; methylene blue

**Citation:** Jaramillo-Fierro, X.; Gaona, S.; Valarezo, E. La3+'s Effect on the Surface (101) of Anatase for Methylene Blue Dye Removal, a DFT Study. *Molecules* **2022**, *27*, 6370. https://doi.org/10.3390/molecules27196370

Academic Editors: Pierfrancesco Cerruti and Arash Moeini

Received: 3 September 2022
Accepted: 23 September 2022
Published: 27 September 2022

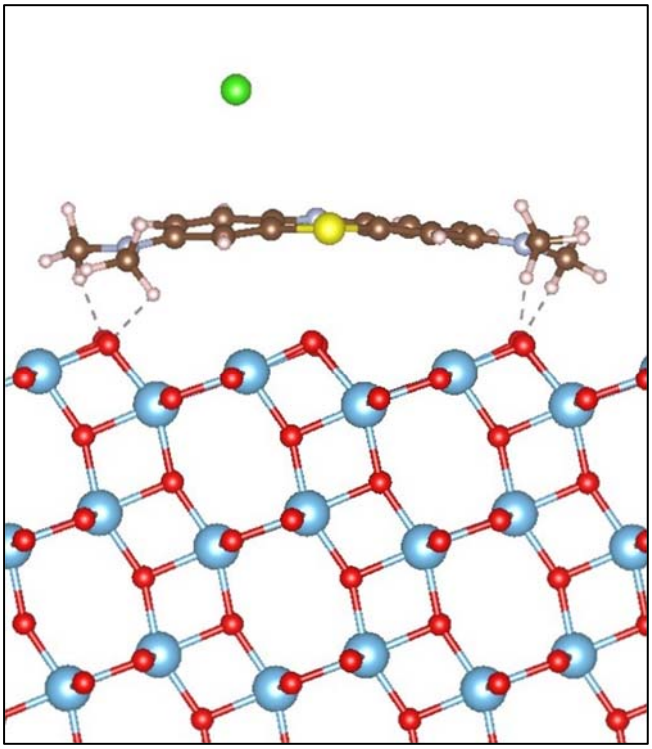

**Figure S1.** Aromatic ring of MB bent slightly on the surface (101) of $TiO_2$.

**Table S1.** Bader`s charge analysis of the optimized MB molecule free and adsorbed on $TiO_2$ and $La/TiO_2$ surfaces.

| No. | Atom | $TiO_2$ surface | | | $La/TiO_2$ surface | | |
|---|---|---|---|---|---|---|---|
| | | MB Charge (-*e*) | MB-$TiO_2$ Charge (-*e*) | Difference Charge (-*e*) | MB Charge (-*e*) | MB-$La/TiO_2$ Charge (-*e*) | Difference Charge (-*e*) |
| **1** | C | −0.072 | −0.016 | 0.056 | −0.979 | 0.013 | 0.992 |
| 2 | C | 1.195 | 1.044 | −0.151 | 1.275 | 1.094 | −0.181 |
| 3 | C | 1.377 | −0.034 | −1.411 | 0.771 | 0.115 | −0.656 |
| 4 | C | −0.214 | −0.097 | 0.117 | −0.026 | −0.149 | −0.123 |
| 5 | C | −1.515 | −0.062 | 1.454 | −1.446 | −0.321 | 1.126 |
| 6 | C | 1.164 | 1.336 | 0.172 | 0.822 | 1.107 | 0.285 |
| 7 | C | −0.301 | −0.294 | 0.007 | −0.251 | −0.201 | 0.050 |
| 8 | C | −0.022 | 0.094 | 0.116 | −0.710 | 0.208 | 0.918 |
| 9 | C | 1.186 | 1.088 | −0.098 | 0.860 | 0.912 | 0.053 |
| 10 | C | −0.063 | −0.202 | −0.140 | −0.931 | −0.055 | 0.876 |
| 11 | C | −0.256 | 0.162 | 0.418 | 0.026 | 0.182 | 0.156 |
| 12 | C | 1.128 | 1.352 | 0.225 | 0.092 | 1.085 | 0.993 |
| 13 | C | 0.175 | 0.689 | 0.515 | 0.053 | 0.738 | 0.685 |
| 14 | C | 0.209 | 0.716 | 0.507 | 0.005 | 0.658 | 0.653 |
| 15 | C | 0.271 | 0.616 | 0.346 | 0.240 | 0.740 | 0.501 |
| 16 | C | 0.382 | 0.778 | 0.396 | 0.260 | 0.789 | 0.529 |
| 17 | S | 0.575 | 0.267 | −0.308 | 0.618 | 0.306 | −0.312 |
| 18 | N | −2.373 | −2.674 | −0.301 | −2.214 | −2.649 | −0.435 |
| 19 | N | −2.301 | −2.417 | −0.116 | −2.025 | −2.452 | −0.427 |
| 20 | N | −2.277 | −2.431 | −0.154 | −2.406 | −2.530 | −0.124 |
| 21 | CL | −0.942 | −0.374 | 0.567 | −0.789 | −0.629 | 0.160 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 22 | H | 0.215 | 0.090 | −0.124 | 1.000 | 0.100 | −0.900 |
| 23 | H | 0.264 | 0.276 | 0.012 | 0.122 | −0.031 | −0.153 |
| 24 | H | 0.283 | 0.041 | −0.243 | 1.000 | 0.185 | −0.815 |
| 25 | H | 0.307 | 0.077 | −0.231 | 1.000 | 0.027 | −0.974 |
| 26 | H | 0.158 | 0.058 | −0.100 | 0.999 | 0.051 | −0.948 |
| 27 | H | 0.155 | 0.190 | 0.035 | 0.994 | −0.096 | −1.090 |
| 28 | H | 0.173 | 0.024 | −0.149 | 0.195 | 0.024 | −0.171 |
| 29 | H | 0.161 | 0.047 | −0.114 | 0.134 | −0.004 | −0.138 |
| 30 | H | 0.213 | 0.032 | −0.181 | 0.166 | 0.058 | −0.108 |
| 31 | H | 0.107 | 0.009 | −0.098 | 0.131 | 0.056 | −0.076 |
| 32 | H | 0.123 | 0.037 | −0.086 | 0.152 | 0.047 | −0.105 |
| 33 | H | 0.071 | 0.060 | −0.011 | 0.158 | 0.033 | −0.125 |
| 34 | H | 0.024 | 0.065 | 0.042 | 0.063 | 0.015 | −0.049 |
| 35 | H | 0.101 | 0.044 | −0.056 | 0.090 | 0.048 | −0.042 |
| 36 | H | 0.048 | 0.080 | 0.032 | 0.098 | 0.033 | −0.065 |
| 37 | H | 0.098 | 0.056 | −0.042 | 0.176 | 0.030 | −0.146 |
| 38 | H | 0.104 | 0.040 | −0.064 | 0.122 | −0.001 | −0.123 |
| 39 | H | 0.069 | −0.030 | −0.099 | 0.155 | 0.029 | −0.126 |