Supporting Information

Investigating polaron formation in anatase and brookite TiO$_2$ by density functional theory with hybrid-functional and DFT+U methods

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Table S1. Unperturbed, and electron- and hole-polaron structures of brookite, average Ti-O bond lengths, and deviations from the average bond lengths due to electron and hole formation calculated using PBE0.\textsuperscript{a}

|        | unperturbed | electron | hole          |
|--------|-------------|----------|---------------|
| Ti\textsubscript{1} - O\textsubscript{a}/Å | 2.03/1.87  | -0.01/+0.02 | -0.03/+0.04   |
| Ti\textsubscript{1} - O\textsubscript{eq}/Å | 1.98/1.93  | -0.04/+0.06 | +0.01/-0.01  |
| Ti\textsubscript{2} - O\textsubscript{a}/Å | 2.03/1.87  | -0.01/+0.02 | -0.01/+0.01  |
| Ti\textsubscript{2} - O\textsubscript{eq}/Å | 1.98/1.93  | -0.01/+0.01 | +0.01/-0.01  |
| Ti\textsubscript{3} - O\textsubscript{a}/Å | 2.03/1.87  | -0.01/+0.03 | -0.04/+0.05  |
| Ti\textsubscript{3} - O\textsubscript{eq}/Å | 1.98/1.93  | -0.05/+0.07 | +0.01/-0.02  |
| Ti\textsubscript{4} - O\textsubscript{a}/Å | 2.03/1.87  | -0.01/+0.01 | 0/0          |
| Ti\textsubscript{4} - O\textsubscript{eq}/Å | 1.98/1.93  | -0.02/+0.02 | +0.01/-0.01  |

\textsuperscript{a}Ti\textsubscript{1} and Ti\textsubscript{2} are calculated at 25\% HF, and Ti\textsubscript{3} and Ti\textsubscript{4} are calculated at 35\% HF. Ti\textsubscript{1} and Ti\textsubscript{3} are at the fully localized polaronic sites, while Ti\textsubscript{2} and Ti\textsubscript{4} are at delocalized electron-polaron sites. Ti\textsubscript{1} - O\textsubscript{a} is the bond length between the Ti ion and the axial oxygen atoms; similarly, Ti\textsubscript{1} - O\textsubscript{eq} is the bond length between the Ti ion and the equatorial oxygen atoms. The plus sign indicates elongation of the bond with respect to the unperturbed structure, while the minus sign indicates shortening of the bond from the unperturbed structure.
Table S2. Unperturbed, and electron- and hole-polaron structures for brookite (upper) and anatase (lower), and average Ti-O bond lengths and deviations from the average bond lengths due to electron- and hole formation using on-site Hubbard U values of 6 eV for brookite and 8 eV for anatase.

|                  | unperturbed | electron | hole   |
|------------------|-------------|----------|--------|
| Ti1-Oa/Å         | 2.03/1.87   | +0.02/+0.16 | -0.02/+0.04 |
| Ti1-Oeq/Å        | 1.98/1.93   | +0.12/+0.13 | +0.03/-0.02 |
| Ti2-Oa/Å         | 2.03/1.87   | -0.03/+0.04 | 0/0    |
| Ti2-Oeq/Å        | 1.98/1.93   | -0.01/+0.02 | +0.01/-0.01 |

|                  | unperturbed | electron | hole   |
|------------------|-------------|----------|--------|
| Ti1-Oa/Å         | 1.97/1.97   | +0.04/+0.08 | -0.01/-0.01 |
| Ti1-Oeq/Å        | 1.93/1.93   | +0.02/+0.02 | +1.00/-0.09 |
| Ti2-Oa/Å         | 1.97/1.97   | +0.03/+0.03 | +0.02/+0.02 |
| Ti2-Oeq/Å        | 1.93/1.93   | -0.01/-0.01 | -0.01/0|

Ti1 is at the localized polaronic site and Ti2 is away from the localized polaron. Ti1-Oa is the bond length between the Ti ion and the axial oxygen atoms; similarly, Ti1-Oeq is the bond length between the Ti ion and the equatorial oxygen atoms. The plus sign indicates elongation of the bond with respect to the unperturbed structure, while the minus sign indicates shortening of the bond from the unperturbed structure.

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Figure S1. Fully delocalized (a) electron- and (b) hole-polaron structures of anatase. Color scheme: blue, titanium; red, oxygen; yellow, polaronic wavefunction at an isosurface value of 0.005 e/Bohr$^3$.

Figure S2. Disordered fully localized (a) electron- and (b) hole-polaron structures of anatase at $U = 10$ eV. (c) Brookite hole-polaron structure at $U = 8$ (and 10) eV. Color scheme: blue, titanium; red, oxygen; yellow, polaronic wavefunction at an isosurface value of 0.003 e/Bohr$^3$. 