Structural Origin for the Enhanced Photocatalysis of Zr-Ti Oxide

Composites from Machine Learning

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Abstract:

Multi-element oxides are notorious for their structural complexity, offering ample room for structure engineering toward applications. Here we demonstrate, via comprehensive machine learning (ML) based techniques to explore millions of likely structures on Zr-Ti oxide global potential energy surface, that the Zr-Ti ratios can cover a full range of composite structure types, including the cation-disordered solid solution, the cation-ordered homogeneous crystals, and heterophase junctions. We show that the three-phase junctions are the global minima at x=0.375 and 0.625 of Zr2Ti7/2O22, constituted by a monoclinic ZrO2 phase, a thin layer of orthorhombic Zr2Ti5O12 phase, and an anatase TiO2 phase. This three-phase junction has a OR of (100)h//([110]h)/([001]h) with low interfacial energy (0.21 J/m² with respect to monoclinic ZrO2 and anatase TiO2), and more importantly, possesses a unique electronic structure of type-II band features, where the valence band maximum (VBM) is mainly located at the interface O lattice sites nearby the monoclinic ZrO2 phase and the conduction band minimum (CBM) is delocalized on the lattice Ti sites of anatase TiO2 phase. This finding clarifies the intriguing experimental findings of the high photocactivity of Zr-added TiO2 at particular Zr:Ti ratios (39 mol% ZrO2). The theoretical framework outlined in this work provides a general tool for searching multi-element photocatalysts with desired band features.

Keywords: Metal Oxides, Photocatalyst, Atomic structure, Machine learning Simulation

1. Introduction

The titania, particularly the commercial Degussa P-25 composed of anatase and rutile phases, is well known to have good photocatalytic activity, widely utilized for many applications in environmental remediation and solar energy conversion. The key for the success of P-25 is attributed to the presence of Type II heterophase junctions (see Figure 1a for Type I and Type II junctions), including anatase-rutile and anatase-TiO2(II) and rutile-

Figure 1. (a) schematic mechanism for Type I junction and Type II junction; Briefly, in Type I junction, both the holes and electrons will accumulate on semiconductor B because the valence band maximum (VBM) and the conduction band minimum (CBM) of the semiconductor B are within the band gap of semiconductor A. By contrast, Type II junction consists of two semiconductors with a staggered band alignment. During a photocatalytic process, the electrons at the CBM will transfer from semiconductor A to the semiconductor B while the holes at the VBM move from semiconductor B to A, which spatially separates the carriers and increases the photo-activity. (b) The band level of several typical semiconductors.
influence significantly the activity (see SI Table S1 for summarized experimental results)12-21. The high photocatalytic performance of the ZrO$_2$-TiO$_2$ composite is puzzling since only a Type I junction is expected according to the band positions of ZrO$_2$ and TiO$_2$ (Figure 1a). It is therefore of significance to clarify the atomic structure and electronic structure of the Zr-Ti oxide composite.

The photocatalytic performance of the Zr-Ti oxide composite is sensitive to both the synthetic conditions and the Zr:Ti ratio. For example, using the solid-state reaction for synthesizing catalyst, Pozan et al. found that 39 mol% ZrO$_2$ exhibits much higher photocatalytic activity than pure TiO$_2$ and P-25 in the degradation of phenol under UV irradiation, i.e. the reaction rate constant increases from 0.54 L·min$^{-1}$ in TiO$_2$ and 0.62 mg L·min$^{-1}$ in P-25 to 0.73 mg L·min$^{-1}$ in 39 mol% ZrO$_2$-TiO$_2$ system. In the degradation of Alizarin cyanine green dye, the 39 mol% ZrO$_2$-TiO$_2$ mixed oxide prepared by combustion synthesis also achieves a comparable activity as P-25.22 On the other hand, Liang et al. showed that by using the atomic layer deposition method (ALD), the optimal Zr concentration can be much lower. The Zr$_x$Ti$_{1-x}$O$_2$ with a small amount of ZrO$_2$ (0.73mol%) deposited on TiO$_2$ has a kinetic constant 10 times larger than that of the pure TiO$_2$ sample for the degradation of methylene blue under UV.15 Similarly, the 12.1mol% ZrO$_2$@TiO$_2$ core-shell prepared using the wet chemical method shows a photocactivity of 3.4 times higher than that of pure TiO$_2$ for the degradation of Alizarin Yellow GG dye.23

The high performance of the ZrO$_2$-TiO$_2$ composite was tentatively explained in literature based on the X-ray diffraction (XRD) and transmission electron microscope (TEM) characterization results, but no consensus is achieved yet. Considering that TiO$_2$ (anatase) is the major photoactive component, the most straightforward explanation is that the presence of ZrO$_2$ modifies the surface properties of anatase so as to increase the stability of small anatase particle,24 hinder the crystal growth,25 higher the surface area and increase the surface acidity.26 However, the sensitivity to Zr:Ti ratio in photocatalysis is still difficult to rationalize using the structural modification role of ZrO$_2$. Alternatively, Pozan et al. suggested that the ZrO$_2$ monoclinic (M$_{2O2}$) surfaces could be more effective for photodegradation since M$_{2O2}$ composition in the best performance sample is found to reach the maximum (83.8%) among samples prepared using the solid-state reaction.21 But, if only Ti Type I band alignment between ZrO$_2$ and TiO$_2$ is possible, the photogenerated holes cannot reach to ZrO$_2$ surfaces. On the other hand, many groups identified new structures (Zr-Ti mixed crystalline phases or the ZrO$_2$-TiO$_2$ junctions) in composites from XRD and TEM, including a ZrTiO$_4$ (orthorhombic phase) when ZrO$_2$ ≥ 50 mol%,14,17,26 a cubic phase with an unknown crystal structure for samples with ZrO$_2$ ratio ≥ 50 mol%21 and the tetragonal/anatase (T/A) junction for sample with ZrO$_2$ ratio below 15 mol%.12,13 Although these structures may be the cause for the high photocatalytic performance, the truly responsible phase and the underlying mechanism remain elusive.

Herein using our recently-developed machine learning-based global potential energy surface (PES) exploration methods, we explore exhaustively the likely bulk and interface structures of Zr$_x$Ti$_{1-x}$O$_2$ at different Ti/Zr ratios. We demonstrate that the bulk phases of Zr-Ti oxides, no matter the cation-ordered crystal phases or the cation-disordered solid-solution phases, are generally less stable than the individual pure ZrO$_2$ and TiO$_2$. However, the two-phase oxides can glue together via a stable interface thin layer that can be assigned to the cation-ordered ZrTi$_x$O$_{2-x}$ bulk crystal phases. This interface has a unique electronic structure for charge separation, which rationalizes the high photocatalytic activity of Zr-Ti oxide composite.

### Table 1. The properties for the identified global minima of 14 compositions from SSW-NN.

<table>
<thead>
<tr>
<th>ZrO$_2$mol%</th>
<th>Phase</th>
<th>Zr$^{4+}$</th>
<th>Ti$^{4+}$</th>
<th>ΔE (meV/O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% (1:19)</td>
<td>Ass</td>
<td>6</td>
<td>6</td>
<td>9.13</td>
</tr>
<tr>
<td>10% (1:9)</td>
<td>Ass</td>
<td>6</td>
<td>6</td>
<td>33.8</td>
</tr>
<tr>
<td>12.5% (1:7)</td>
<td>Zr$<em>{602}$/Ti$</em>{202}$</td>
<td>6</td>
<td>6</td>
<td>12.2</td>
</tr>
<tr>
<td>20% (1:4)</td>
<td>Zr$<em>{602}$/Ti$</em>{202}$</td>
<td>6</td>
<td>6</td>
<td>28.1</td>
</tr>
<tr>
<td>25% (1:3)</td>
<td>M$<em>{2O2}$/Ti$</em>{2O2}$</td>
<td>6</td>
<td>6</td>
<td>34.3</td>
</tr>
<tr>
<td>33.3% (1:2)</td>
<td>O</td>
<td>8</td>
<td>6</td>
<td>22.4</td>
</tr>
<tr>
<td>37.5 (3:5)</td>
<td>M$_{2O2}$/O</td>
<td>7</td>
<td>6</td>
<td>38.5</td>
</tr>
<tr>
<td>50% (1:1)</td>
<td>M1</td>
<td>7</td>
<td>6</td>
<td>20.5</td>
</tr>
<tr>
<td>62.5% (5:3)</td>
<td>M$_{2O2}$/O</td>
<td>7</td>
<td>6</td>
<td>30.7</td>
</tr>
<tr>
<td>66.7% (2:1)</td>
<td>M$<em>{2O2}$/Ti$</em>{2O2}$</td>
<td>7</td>
<td>6</td>
<td>17.2</td>
</tr>
<tr>
<td>75% (3:1)</td>
<td>M2</td>
<td>7</td>
<td>6</td>
<td>15.9</td>
</tr>
<tr>
<td>80% (4:1)</td>
<td>M$<em>{2O2}$/Ti$</em>{2O2}$</td>
<td>7</td>
<td>6</td>
<td>20.2</td>
</tr>
<tr>
<td>87.5% (7:1)</td>
<td>M$<em>{2O2}$/Ti$</em>{2O2}$</td>
<td>7</td>
<td>6</td>
<td>12.6</td>
</tr>
<tr>
<td>95% (19:1)</td>
<td>Mss</td>
<td>7</td>
<td>6</td>
<td>10.1</td>
</tr>
</tbody>
</table>

*a: the notations for various phases appear in the manuscript:
A: Anatase; M: Monoclinic; O: Orthorhombic; ss: solid solution
M$_{2O2}$: Monoclinic ZrO$_2$; T$_{2O2}$: Tetragonal ZrO$_2$; A$_{2O2}$: Anatase ZrO$_2$; R$_{2O2}$: Rutile ZrO$_2$; O$_{2O2}$: Orthorhombic ZrO$_2$; A$_{1O2}$: Anatase TiO$_2$; R$_{1O2}$: Rutile TiO$_2$; M$_{1O2}$: Monoclinic TiO$_2$; O$_{1O2}$: Orthorhombic TiO$_2$; O$_{2T}O_{2}$: Orthorhombic ZrTiO$_4$; O$_{2Z}O_{2}$: Orthorhombic ZrTi$_2$O$_4$; T$_{2Z}T_{2O}$: Tetragonal Zr$_2$Ti$_2$O$_6$.

*b: the coordination number (CN) for cations.

c: relative formation energy per O atom with relative to M$_{2O2}$ and A$_{2O2}$ using the following equation

ΔE = 0.5[($E_{x}+E_{2O_{2}}$)−($xE_{2O_{2}}+(1-x)E_{TiO_{2}}$)]

### 2. Method and calculation details

All simulations for PES exploration were carried out by using our recently-developed LASP code, Large-scale Atomic Simulation with neural network Potential (referred at www.lasphub.com)27, which implements the data-generation using stochastic surface walking (SSW) global optimization28,29, training and evaluation of global neural network (G-NN) potentials30. The Ti-Zr-O ternary G-NN potential was trained by learning the global PES data generated by SSW global optimization, as reported previously31,32. In brief, our Ti-Zr-O global dataset consists of 33154 structures collected from SSW global PES exploration, covering pure Zr, ZrO$_x$, Ti, TiO$_x$, and Ti/Zr ~1:1 to ~19:1 mixed oxides. All data are calculated by plane-wave DFT calculations33 at the same high accuracy setup. The description of the dataset can be found in SI Table S2. The G-NN potential has a five-layer (245-60-30-30-1) feed-forward NN structure, in a total of 59073 fitting parameters. The final root-mean-square (RMS) errors for the energy and the force of the G-NN potential are 5.687 meV/atom and 0.162 eV/Å, respectively.

The G-NN potential training relies on the density functional theory (DFT) computed energy, forces, and stresses of structures.34
To achieve high accuracy and data consistency, our DFT calculations as performed using VASP code utilize the following setups: DFT functional at the level of generalized gradient approximation (GGA-PBE)[16]; the kinetic energy cutoff at 450 eV; the projector augmented wave (PAW) pseudopotential[17] to describe ionic core electrons; the fully automatic Monkhorst–Pack K-mesh with 25 times the reciprocal lattice vectors[18] for the first Brillouin zone k-point sampling. We have also benchmarked the G-NN accuracy against DFT results for important structures, which shows that the energy RMS is 2.514 meV/atom for the low-energy Ti-Zr-O structures (see SI Table S3). This small error suggests that the G-NN PES is a good approximation to DFT PES and can be utilized to expedite the global structure search.

3. Results and Discussion

3.1. Zr-Ti bulk oxide phases

For identifying the likely (Type-II) junctions in Zr-Ti oxide system, the first step is to know all the likely bulk phases. By using SSW-NN global structure search, we first investigated the phase space for bulk Zr\(_x\)Ti\(_{1-x}\)O\(_2\) with 14 different compositions, which have the Zr: Ti ratios at 1:19, 1:9, 1:7, 1:4, 1:3, 1:2, 3:5, 1:1, 5:3, 2:1, 3:1, 4:1, 7:1, and 19:1, corresponding to ZrO\(_2\) concentrations of 5%, 10%, 12.5%, 20%, 25%, 33.3%, 37.5%, 50%, 62.5%, 66.7%, 75%, 80%, 87.5%, and 95%. For each composition, we generally collected more than 20,000 minima by using different supercells ranging from 12 to 120 atoms. The global minimum (GM), the most stable structure from structural search, is thus obtained for each composition. It should be mentioned that the same SSW-NN search is also performed for pure ZrO\(_2\) and TiO\(_2\) and the results are consistent with previous studies[19, 40] (see Figure S2 in SI for the details on the monoclinic, orthorhombic, anatase, rutile lattices of pure ZrO\(_2\) and TiO\(_2\)).

Below we take Zr\(_x\)Ti\(_{1-x}\)O\(_2\) with Zr: Ti=1:2 as the example to illustrate the GM identification using SSW-NN method. This ratio is of particular importance since a homogenous oxide crystal phase Zr\(_{16}\)Ti\(_{6}\)O\(_6\) is identified as the GM. After SSW-NN simulations, in total 13553 distinct structures in the supercells ranging from 18 atoms to 96 atoms are obtained, which can be classified into different structure categories, including crystals, biphasic junctions and amorphous structures. To visualize these structures, we project them on a two-dimensional structure-fingerprint-vs-energy contour plot in Figure 2a. The color scheme, from red to blue, is utilized to indicate the density of structure minima (DOM). DOM = \(N_{str}/N_{total}\).

**Figure 2.** (a) Global PES for Zr\(_{16}\)Ti\(_6\)O\(_6\) with Zr: Ti ratio=1:2 using the OP\(_2\)-E contour plot from the SSW-NN PES data. OP\(_2\): the structure order parameter with \(l=2\). Some representative structures mentioned in text are labelled by symbol. The insert figure is enlarged from dotted square. (b) The atomic structures of several typical structures for Zr: Ti = 1:2, 1:9, 3:5 and 5:3. (c) Simulated X-ray diffraction patterns of the GM structures that are compared with the standard ZrO\(_2\) and TiO\(_2\) phases. The top panel with the composition of 39mol% ZrO\(_2\) is from experiment. *M: Monoclinic; T: tetragonal; A: Anatase; R: Rutile; O: Ortho.*
where \( N_{\text{ip}} \) refers to the number of structure mimina at a certain energy interval and \( N_{\text{total}} \) refers to the total number of minima. The structure fingerprint (x-axis) utilizes the distance-weighted Steinhart order parameter \( \text{OP}_{i,j} \) with the degree \( l=2 \) (\( \text{OP}_l \)), as described in the following equation (also see Ref.42).

\[
\text{OP}_{i,j} = \left( \frac{4\pi}{2L+1} \sum_{m=-L}^{L} \left[ \frac{1}{N_{\text{bonds}}} \sum_{i>j} e^{-\frac{\text{r}_{ij} - r_{ij}}{2T}} \right]^{\frac{1}{2}} \right)^{\frac{1}{2}}
\]

In Eq.1, \( Y_{\text{LM}} \) is the spherical harmonic function, \( i, j \) are atoms in the lattice, \( r_{ij} \) is the vector between the atom \( i \) and \( j \), and \( r_{ij} \) is their distance; \( r_{ij} \) is set as 60% of the typical single bond length for \( i \) and \( j \) atoms (e.g. \( \sim 2.5 \) Å for Zr-O bond, \( \sim 2.1 \) Å for Ti-O bond); \( N_{\text{bonds}} \) is the number of bonds in the first bonding shell. By choosing a suitable degree \( L \), the order parameter can measure the short- and medium-range ordering of atoms in the lattice and thus distinguish important crystal structures, junctions, and amorphous structures.

In Figure 2a, the deep blue area corresponds to the amorphous states with high energy, which have the highest population of distinct structures. We are however more interested in the low-energy crystalline structures, which usually correspond to the structures formed in the experiment.

Six lowest-energy structures are marked in Figure 2a inset using black dots (crystals) and triangles (biphasic junctions). The GM ZrTiO\(_4\) crystal appears at \( \text{OP}_L=0.19 \), which is an orthorhombic crystal phase with the space group number \#60, as highlighted in Figure 2b. The orthorhombic lattice is largely the same as that of TiO\(_2\)(II), a high-pressure phase of TiO\(_2\), but with a longer \( a \) axis (\( a=14.37, b=5.34, c=5.04 \) Å), where the coordinate number of Zr is eight and that of Ti is six. All orthorhombic phases mentioned in this work refer to this lattice, namely O phase (also see SI). The next low energy phases are two energetically degenerate structures marked with \( a \) and \( b \) in Figure 2a, which are the cation-disordered solid solutions with Zr distributed randomly in the TiO\(_2\) lattice. They are 0.043 eV/ZrTiO\(_2\) (per ZrTiO\(_2\) formula) above the GM, where both Zr and Ti have the same coordination number of six.

Apart from the single crystal phases, we also identify many biphasic junctions between ZrO\(_2\) crystal phases, including monoclinic (M\(_{ZrO\_2}\)), anatase (A\(_{ZrO\_2}\)), O\(_{2}\), and TiO\(_2\) crystal phases, including anatase (A\(_{TiO\_2}\)) and O\(_{TiO\_2}\). Among them, the lowest energy heterophase structure is an A\(_{ZrO\_2}\)/A\(_{TiO\_2}\) structure (marked by Arabic number 1) located at \( \text{OP}_L=0.51 \) in Figure 2a with an energy of 0.057 eV/ZrTiO\(_2\) above the GM. In this structure, both Zr and Ti have the same coordination number of six. The second lowest energy heterophase structure O\(_{ZrO\_2}\)/O\(_{TiO\_2}\) appears at \( \text{OP}_L=0.31 \) (marked by Arabic number 2 in Figure 2a) with the energy of 0.091 eV/ZrTiO\(_2\) above the GM. The third lowest energy junction M\(_{ZrO\_2}\)/A\(_{TiO\_2}\) appears at \( \text{OP}_L=0.32 \) (marked by Arabic number 3), which is 0.12 eV/ZrTiO\(_2\) above the GM. For the latter two junctions, the coordinate number of Zr is seven and that of Ti is six.

For all the other Zr:Ti ratios, the GM can be cation-disordered solid solution oxide phases with the anatase or monoclinic lattice (Zr: Ti=1:19:1, and 19:1), the cation-ordered monoclinic phase (Zr: Ti=1:1 and 3:1), or the mixed phase junction (Zr: Ti=1:7, 1:4, 1:3, 3:5, 2:1, 5:3, 4:1 and 7:1) depending on the Zr: Ti ratio. The information on the structural and energetic properties of the GMs is listed in Table 1. It should be emphasized that the energetics of all ZrO\(_2\)/TiO\(_2\) structures are all less stable than the pure M\(_{ZrO\_2}\) and A\(_{TiO\_2}\), suggesting the Zr-Ti oxides tend to be composite by forming stable solid-solid interfaces in between pure ZrO\(_2\), TiO\(_2\) and ZrTiO\(_2\) phases.

At the low ZrO\(_2\) concentrations, e.g. Zr: Ti=1:19 and 1:9, the GM adopts the anatase solid solution (ASS) structure, where Zr is randomly distributed in TiO\(_2\) anatase lattice, as shown in Figure 2b for Zr: Ti=1:9. The coordination number of Zr is the same as Ti, being 6-coordination. Similarly, at the Zr-rich condition, e.g. Zr: Ti=19:1, the GM adopts the monoclinic solid solutions (Mss), where Ti is randomly distributed in the ZrO\(_2\) monoclinic lattice. The coordination number of Zr is seven, while that of Ti is six. In these solid solution phases, the volume increases if Ti is replaced by Zr, and vice versa. For example, the volume increases by 2.4% in Zr: Ti=1:9 ASS structure due to the introduction of Zr, where Zr-O distance 2.09 Å in Ass, longer than the Ti-O distance 1.99 Å in anatase.

We note that at the Zr: Ti=3:5 and 5:3 ratios, the GMs are the three-phase junction, named as the M/O/A junction. In this structure, the thin-layer intermediate phase is characterized as the O phase, which glues the M\(_{ZrO\_2}\) and A\(_{TiO\_2}\) phases, as shown in Figure 2b. In the O phase, the coordination number of Zr and Ti are seven and six, respectively, and the bonding pattern of oxygen atom follows the orthorhombic crystal phase. The orientation relationship (OR) between the three phases is M(100)/O(100)/A(112). The formation energy of the junction structures are 38.5 meV/O and 30.7 meV/O for the 3:5 ratio (37.5%) and 5:3 ratio (62.5%), respectively, with respect to M\(_{ZrO\_2}\) and A\(_{TiO\_2}\) (see Table 1). The junction has the low interfacial energy (0.21 J/m\(^2\)) with respect to M\(_{ZrO\_2}\) and A\(_{TiO\_2}\).

Figure 2c plots the simulated X-ray diffraction (XRD) patterns for the GM structures. We found that at the low Zr contents, e.g. the 10% (Zr: Ti=1:9) and 20% (Zr: Ti=1:4), the main peak appears at 25° (20), corresponding to the (101) peak of anatase, reflecting the presence of a single anatase crystal phase. At the 33.3% content, Zr: Ti=1:2, a new main peak appears at 30.7°, a characteristic feature of the orthorhombic crystal phase, which is accompanied by the disappearance of the 25.1°. Further increasing to 37.5%, an obvious peak appears at 27.8°, corresponding to the (111) peak of the monoclinic phase, indicating the emergence of the monoclinic phase. At these intermediate concentrations, the 25.1° peak of anatase together with the 30.7° peak of the orthorhombic phase are still present, indicating the M, A, and O phase form the three-phase junctions. Importantly, the XRD pattern also suggests that the 62.5% GM is similar to that of 37.5%, both being M/A/O three-phase junctions. When the Zr concentration increases to 80%, the 30.7° peak of the orthorhombic phase finally diminishes, and there are two main peaks at 27.4° and 31.8°, corresponding to the (111) and (111) of the monoclinic phase. The weak intensity of the 24.4° peak is due to a small amount of TiO\(_2\) anatase phase implying the presence of an M/A junction. Above 90%, the peak of anatase disappears and there are only two main peaks of the monoclinic phase at 20=27.8° and 31.4°.

It should be mentioned that apart from ZrTiO\(_4\), the homogeneous crystalline phase ZrTiO\(_4\) (Orthorhombic, #60, O\(_{ZrTiO\_4}\)) and Zr\(_2\)TiO\(_4\) (Tetragonal, #121, T\(_{ZrTiO\_4}\)) were also observed in experiments. 44,45 These phases, although identified from our SSW-NN structure search, they are less stable compared to the GM. For ZrTiO\(_4\), the GM is a cation-ordered monoclinic phase (M1 phase in Table 1) with the lattice being equivalent to the double of the lattice of M\(_{ZrO\_2}\) in the \( b \) axis, which is 0.042 eV/O (per O atom) more stable than the orthorhombic crystal phase of ZrTiO\(_4\) (O\(_{ZrTiO\_4}\)). For Zr\(_2\)TiO\(_4\), the GM is also a cation-ordered monoclinic phase (M2 phase in Table 1) and the lattice doubles that of M\(_{ZrO\_2}\) in both the \( a \) and \( c \) axis, which is 0.042 eV/O more stable than the tetragonal phase of Zr\(_2\)TiO\(_4\) (T\(_{ZrTiO\_4}\)). Indeed, O\(_{ZrTiO\_4}\) and T\(_{ZrTiO\_4}\) phases observed in experiments are found stable at high temperatures and
the cooling rate from high to low temperatures can be critical for obtaining these phases at ambient conditions. Specifically, $O_{ZrTiO_4}$ is stable only above 800 °C. The $T_{ZrTiO_4}$ phase is synthesized above 1000 °C and can be obtained at ambient conditions by the slow cooling rate such as 1°C/min, which inhibits the T-M phase transition. The faster cooling rates, such as ~140°C/s, cause the T-M phase transition, leading only to the monoclinic phase.  

In summary, the structure evolution of ZrO$_2$-TiO$_2$ structures can be divided into three stages from low to high concentrations of ZrO$_2$. At the low ZrO$_2$ contents, the concentration $\leq$ 20%, the composite exhibits a single anatase lattice, including anatase solid solutions $A_2O_2$ and $A_1O_2$. The two types of structures are generally degenerate in energy (the difference within 2 meV/O). At the high ZrO$_2$ end, the concentration above 90%, the GM adopts the monoclinic lattice, following the GM of pure ZrO$_2$. In the intermediate concentrations (between 20% and 90%), the GM structure is complex, adopting multiple forms, such as the mixed phase of M and A, three-phase junctions, and the homogeneous crystal structure. Importantly, our results confirm that the heterophase structure of ZrO$_2$-TiO$_2$ can form at a wide Zr:Ti ratio from 10% to 90%. This might explain the experimental observation that the heterophase junctions are formed even at low ZrO$_2$ concentrations, e.g. below 15 mol %, as detected by TEM and XRD for the composite materials synthesized under different methods such as ALD, sol-gel and template method \(^{14, 15, 18}\) (also see SI Table S1 for experimental data).

3.2 Heterophase Junctions

With the knowledge of bulk structures, we then proceeded to explore the likely interface structures between different crystal phases (including the ZrTi$_2$O$_6$ orthorhombic phase identified above) using the ML-interface method. In fact, the presence of heterogeneous junction in the Zr-Ti system is already confirmed in the bulk structure search above, where the heterogeneous junction structures are prevalent for ZrO$_2$ concentration between 10-90%.

The purpose of this section is to complete the interface search by gluing different bulk phases, even if the interface might not be the global minimum. The ML-interface is a machine-learning-assisted solid-solid interface search method, as illustrated in Figure 3a, which contains three steps: (i) the OR screening based on the phenomenological theory of Martensitic phase transition, (ii) the interface atomic structure generation, and (iii) the global optimization using SSW-NN. More information on the ML-interface method can be found in our previous work.\(^{47}\) The interfacial energy ($\gamma_{int}$) in Eq. 2 is utilized to evaluate the stability of the heterophase structures,

$$\gamma_{int} = E(\text{HJ}) - \sum_i n_i E_{Zr/TiO_2}/2A \quad (2)$$

where HJ is the acronym for hetero-junction; $E(\text{HJ})$ is the total energy of the heterophase junction, $E_{Zr/TiO_2}$ is the energy of the pure phase, $n_i$ is the number of TiO$_2$ units, and ZrO$_2$ units of different phases components in the heterojunctions and $A$ is the surface area of the interface. Obviously, the lower $\gamma_{int}$ is, the more stable the interface will be.

Our ML-interface simulations consider four ZrO$_2$ forms (M, T, A, R (rutile)), four TiO$_2$ forms (A, R, M, O$_{TiO_2}$), and the homogeneous ZrTi$_2$O$_6$ crystal oxide ($O_{ZrTiO_4}$) as the starting bulk material. For each possible interface with low strain (<5%), more than 10$^3$ minima are searched using the SSW-NN. Ten interfaces with distinct OR and low interfacial energy (less than 1.0 J/m$^2$) are finally obtained, which are shown in Figure 3b. The interfaces in these structures are coherent without defects. The key properties of
In the M phase, the coordination number ranging from 6 to 8. For example, 7
87.5%.

Figure 4. Partial charge densities at CBM or VBM of M$_2$O$_5$/A$_{102}$ in (a) and O$_{ZrTi2O6}/A$_{102}$ in (c); and the color map of the corresponding local DOS along the direction normal to the interface (x-axis) for M$_2$O$_5$/A$_{102}$ in (b) and O$_{ZrTi2O6}/A$_{102}$ in (d). The energy is referred to the Fermi level.

These ten heterophase junctions can be classified into two types, the one composed by ZrO$_2$ and TiO$_2$ phases (HJ-1) and the one containing the O$_{ZrTi2O6}$ crystal (HJ-2). Among them, the HJ-1 formed by the same crystal lattice, e.g. M$_2$O$_5$/M$_{102}$, R$_{102}$/M$_{102}$, A$_{202}$/A$_{102}$, as shown in Figure 4b, have the lowest interfacial energy (< 0.25 J/m$^2$) due to the excellent structure match. The A$_{202}$/A$_{102}$ junction is the GM for 12.5 % and 20 % ratios from the bulk SSW-NN search (Table 1). The M$_{202}$/A$_{102}$ interface of the HJ-1 type with the OR (100)/[112]; [001]/[111] has the second lowest interfacial energy with 0.26 J/m$^2$ due to a low strain at the interface (1.4% lattice strain along [010]$_{A_{102}}$ direction). Indeed, the M$_{202}$/A$_{102}$ junction is the GMs for the ZrO$_2$-TiO$_2$ composite at a wide concentration ZrO$_2$ concentration at 20%, 66.7%, 80% and 87.5%. By contrast, the T$_{202}$/A$_{102}$ junction has the highest interfacial energy up to 0.83 J/m$^2$, which is caused by the large strain (2.7% lattice strain along [001]$_{A_{102}}$) and a large magnitude of atomic mismatch in T$_{202}$/A$_{102}$ heterostructures.

In the HJ-1 type, the coordination environment of cations at the interface can be quite different. In particular, Zr exhibits a variable coordination number ranging from 6 to 8. For example, 7-
coordinated Zr exists at the interface of M$_2$O$_5$/TiO$_2$, 8-coordinated Zr appears in the T$_{202}$/O$_{102}$ junction, and 6-coordinated Zr is adopted in the A$_{202}$/TiO$_2$ junction. The variation of Zr’s coordination number is apparently related to the TiO$_2$ bulk crystal phase in the junction that have different Zr coordination (e.g. 7-Zr in the M phase, 8-Zr in the T phase, 6-Zr in the anatase phase).

Among HJ-2 type heterophase junctions, the O$_{ZrTi2O6}/M$_{202}$ also found in the bulk SSW-NN search, has a lower interfacial energy (0.33 J/m$^2$) and a low strain (2.1% lattice strain along [010]$_{A_{102}}$). The O$_{ZrTi2O6}/A$_{102}$ interface is less stable (0.41 J/m$^2$) with a relatively larger strain (3.6% lattice strain along [110]$_{A_{102}}$). For both interfaces, Zr locating at the interface is 7-coordination, and that in the bulk is 8-coordination, and the Ti cations are always 6-
coordinated.

3.3 Band Structure and Charge Separation

With 14 GM structures and 10 heterophase structures, we are now at the position to analyze the electronic structure of ZrO$_2$-TiO$_2$ composite. The band structures of 10 heterophase structures were first computed using DFT PBE functional to search for the likely presence of Type II junction. The bandgaps are shown in Table S4. We found that the M$_{102}$/M$_{202}$ heterostructure has the largest bandgap, which is 0.9 eV higher than that of pure A$_{102}$. In contrast, the O$_{ZrTi2O6}/A$_{102}$ heterostructure has the smallest bandgap. The band gap values of other heterostructures are generally in between those of pure M$_{202}$ and pure A$_{102}$. Importantly, by further plotting the wave functions as shown in Figure S4, we found that the M$_{102}$/O$_{102}$ and M$_{202}$/O$_{ZrTi2O6}$ heterophase structures exhibit the Type II junction characteristics, where the VBM (valence band maximum) and CBM (conduction band minimum) locate at different phases. Specifically, VBM is mainly located at the M$_{202}$ near the interface around the oxygen lattice site, while the CBM is mainly distributed at the O phase side. The other interfaces do not have the feature, where both the VBM and CBM distribute in the TiO$_2$ crystalline phase. These results are summarized in SI (Fig S5 and Table S4).

The same phenomena are also observed for the band structures of the GMs with heterophase junctions, as represented by M$_{202}$/O /A$_{102}$ at 37.5 mol % and M$_{202}$/O /A$_{102}$ at 62.5 mol% and M$_{202}$/A$_{102}$ at 80 mol% ZrO$_2$. Our DFT PBE calculations show that the M$_{202}$/O /A$_{102}$ has a small bandgap, close to that of pure A$_{102}$ and exhibits the Type II junction feature with spatially separated VBM and CBM (SI Figure S5). On the other hand, M$_{202}$/A$_{102}$ has the largest bandgap, 0.8 eV larger than the pure A$_{102}$ and its VBM and CBM appear only in the TiO$_2$ phase.

Since PBE gap is systematically underestimated, the more accurate DFT hybrid functional HSE06 calculations are then performed to further confirm the above findings on the four representative heterostructures using a fixed HF: GGA mixing ratio of 25:75 and a screen parameter of 0.2 Å$^{-1}$, including M$_{202}$/A$_{102}$, O$_{ZrTi2O6}/A$_{102}$, O$_{ZrTi2O6}/M$_{202}$ and a three-phase junction M$_{202}$/O/A$_{102}$ (Zr: Ti=3:5) (The HSE06 band gap is known to be more consistent with the experimental values, e.g. A$_{102}$ 3.36 eV from HSE06 and 3.20 eV from experiment$^{48}$, M$_{202}$ 5.30 eV from HSE06 and 5.83 eV from experiment$^{49}$, see SI Figure S6 for PBE and HSE06 gap comparison). We found that the O$_{ZrTi2O6}/A$_{102}$ has the lowest band gap (3.35 eV), similar to the pure A$_{102}$ (3.36 eV); the O$_{ZrTi2O6}/M$_{202}$ has a higher band gap of 3.73 eV, close to that of M$_{202}$/A$_{102}$ (3.87 eV), slightly higher (by 0.27 eV) than A$_{102}$ but significantly lower (by 1.60 eV) than pure M$_{202}$. This is because O$_{ZrTi2O6}$ is closer to A$_{102}$ in the band structure. The three-phase junction M$_{202}$/O/A$_{102}$ has a band gap of 3.51 eV, in between those of O$_{ZrTi2O6}/A$_{102}$ and O$_{ZrTi2O6}/M$_{202}$.

Figure 4a and 4c shows the VBM and CBM wavefunctions of M$_{202}$/A$_{102}$ and O$_{ZrTi2O6}/A$_{102}$ from HSE06 calculations. In both cases, both CBM and VBM mainly locates on the same side of the A$_{102}$, which is consistent with PBE results (SI Figure S4). On the other hand, for the O$_{ZrTi2O6}/M$_{202}$ and M$_{202}$/O/A$_{102}$ (one Zr-O-Ti layer of O phase, results with more O phase layers are similar and
can be found in SI) as plotted in Figure 5a, the VBM mainly locates at the oxygen lattice site of MZO2 nearby the interface, while the CBM is mainly at the other side, namely the OZTi2O6 phase in OZTi2O6/MZO2 or A12O3 side in MZO2/OA12O3. Obviously, the spatial separation of the carriers is more obvious in the MZO2/OA12O3 due to the presence of the thin O-phase layer (Figure 5d).

To better understand the electronic structure, we also computed the density of states (DOS) projected onto the selected atoms (layers), as shown in the right panel of Figure 4 and Figure 5. For MZO2/A12O3 and OZTi2O6/A12O3 junction, Figure 4b and 4d show clearly that VBM is mainly contributed by the O atom in A12O3 in both junctions, and CBM is on the Ti atom in A12O3 (the atom-projected local DOS could also be seen in Figure S7). Figure 5b-c shows that the VBM of MZO2/OZTi2O6 junction mainly originates from the O1 layer near the interface, and the CBM is at the Ti atom in OZTi2O6 phase. Similarly, the VBM of MZO2/OA12O3 junction as shown in Figure 5e-f originates from the O1 layer near the interface, while the CBM is at the Ti atoms (Ti2,3,4 layer) in the bulk TiO2 phase.

Since the OZTi2O6 phase in Figure 5 (MZO2/OA12O3 junction) is only one layer thick, we also constructed the same junction with more OZTi2O6 layers and calculated the electronic structure. The VBM and CBM wavefunctions are shown in Figure 6a and the local DOS layer by layer is shown in Figure 6b and 6c. For VBM in a three-phase junction, the oxygen atoms in the O1 layer at the interface (pink line) have the highest energy level, followed by the oxygen atoms of bulk TiO2 phase (blue line), and the oxygen atom in the ZrO2 and OZTi2O6 phase (purple and green lines). Therefore, the energy level order of VBM follows interface > TiO2 > ZrO2/OZTi2O6. Similarly, for CBM, the energy level of Ti atoms in bulk TiO2 (red line) has the lowest energy level, and followed by the energy level of Ti atoms in the Ti1,0 layer (brown and cyan line) in OZTi2O6 phase, and then the energy level of Zr atoms in bulk ZrO2 (black line). Accordingly, Figure 6c summarizes the corresponding energy level of the composite material, which suggests that the presence of a thin OZTi2O6 layer as the interface between MZO2 and A12O3 can effectively separate photogenerated carriers, where the holes move to the ZrO2-side interface, and the electrons are left on TiO2 side.

4. Discussions

Based on the above findings, we now can attribute the enhanced photo-activity of Zr-Ti oxide composites to the formation of MZO2/OA12O3 heterophase junction, which has a staggered Type II band structure at the interface, as illustrated in Figure 6d. In the composite, TiO2 with a narrower bandgap is responsible for the photon adsorption under ultraviolet (UV) light. The generated electron-hole pairs are then spatially separated: the electrons stay in TiO2 and eventually, migrate to the TiO2 surface for photoreduction.
reaction; the holes transfer to the interface nearby ZrO2 and finally migrate to the exposed junction in between ZrO2 and TiO2 along the direction parallel to the interface plane M(100)/O(100)/A(112). The photooxidation thus occurs at the periphery in between ZrO2 and TiO2 phases. The presence of the Type II band structure prevents effectively the recombination of electron-hole pairs and boost the photocatalytic activity.

Our results provide a new explain for the 30.5° XRD peak in the catalysts with 39-60 mol % ZrO2, and correlate the peak with the Zr:Ti ratio sensitivity of the photoactivity. Experiments show that the photocatalytic activity significantly improves at 39 mol% and 60 mol% ZrO2 content where the degradation efficiency of phenol reaches 100% in 90 minutes, but declines either when the ZrO2 content rises to 72 mol% (as the degradation efficiency drops to 89%) or when ZrO2 content decreases to 21 mol% (the efficiency decreases by 40%, lower than the 85% of TiO2-P-25 catalyst). The 30.5° XRD peak was previously assigned to several likely phases, including the tetragonal or the cubic ZrO2 phase, and the O2ZT2O6 phase. From our results, this particular peak should, however, be associated with the O2ZT2O6 phase, not only because it helps to create the M/O/A three-phase junction for promoting photocarrier separation, but also because it is energetically more stable than other proposed phases and appear in the GM structure of ZrO2-TiO2 composites with a wide ZrO2 content window (see Figure 2). In addition, since the presence of a thin layer O-phase as the interface would be enough to create the type II band structure, our results suggest the increase of the M2O2 phase content (45.7% to 83.8%) in the 39 mol% ZrO2 content catalysts can further enhance the activity due to a shorter path for the migration of holes, as indeed observed in the experiment.

5. Conclusions

To summarize, this work constructs the first Zr-Ti-O ternary global NN potential and performs extensive SSW-NN global optimization to explore likely structures of Zr-Ti-O and Zr-Ti-O G-NN potential is obtained by training 33154 first principles global PES dataset and achieves the accuracy of 5.687 and 0.162 for RMS energy and force, respectively. In total 14 different Zr-Ti ratio ZrTi1.1xO2 with Zr: Ti ratio from 1:19 (5 mol % ZrO2) to 19:1 (5 mol % ZrO2) are investigated. The GM structures are identified, which indicate that the Zr-Ti oxides tend to be composite by forming stable solid-solid interfaces between pure ZrO2, TiO2 and ZrTi2O6 phases. Apart from the most stable heterogeneous junctions obtained from bulk structure search, the other stable biphase solid-solid junctions are also mapped out using recently-developed ML-interface method, which yields 10 distinct heterogeneous junction structures. Our major findings are highlighted as follows:

(i) at the low ZrO2 contents (≤ 20 mol%), the GMs of ZrTi1.1xO2 prefer the cation-disordered anatase solid solution, although the A2O2/A1O2 junction is very close in energy (within 2 meV/O). At the high ZrO2 contents (> 90 mol%), the GMs of ZrTi1.1xO2 adopt the cation-disordered monoclinic phase.

(ii) At 33.3 mol % ZrO2 content, the GM is a cation-ordered orthorhombic phase O2ZT2O6, where Zr is 8-coordination and Ti is 6-coordination.

(iii) The GM structures of ZrTi1.1xO2 at x=0.375 and 0.625 (Zr: Ti=3:5 and 5:3) belong to the M/O/A three-phase junction, which has a unique electronic structure of Type II band features. The VBM is mainly located at the interface O lattice sites nearby the ZrO2 phase and the CBM is delocalized on the lattice Ti sites of A1O2 phase.

(iv) The M2O2/A1O2, O2ZT2O6 (100)/A1O2 (100) and O2ZT2O6 (100)/M2O2 (100) biphase junctions are among the most stable biphase junctions, which have the low interfacial energy of 0.26, 0.41 and 0.33 J/m², respectively. This rationalizes the preferable formation of three-phase junction M/O/A at a wide Zr composition for Zr-Ti oxides.

ASSOCIATED CONTENT

Supporting Information

Supporting information available: Summary of Experimental results of photocatalysis on Zr-Ti oxides; Global dataset description; Construction of Y-Zr-O ternary G-NN potential; Definition of distance-weighted Steinhart order parameter; Benchmark of G-NN potential against DFT calculations; PES and structure for pure ZrO2 and TiO2; other junctions; VBM and CBM for ten low interfacial energy junctions; Properties for low interfacial energy junctions; local DOS of M2O2/ A1O2 and O2ZT2O6/A1O2 junctions; the XYZ coordination of junctions.
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Notes
The authors declare no competing financial interests.

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References:


TOC Graphic: