We are grateful to all reviewers for their constructive and insightful criticism of the work. We have considered each point below and modified the manuscript to address the concerns. We feel that the work is now improved, and hope that the reviewers agree it is now suitable for publication.

Reviewer(s)' Comments to Author:  
Referee: 1  
  
Comments to the Author  
This study uses density functional theory calculations to investigate elementary steps within the nitrogen photo/electrochemical reduction process on metal-doped rutile titania surfaces.  The main conclusion is that no dopants provide great acceleration, though some dopants are recommended to provide small improvements in activity.  The hypothetical model surfaces are rather narrowly constructed with debatable representation of reality, however, the results are reasonably presented and should provide some interest in readers interested in this topic.  However, I have considerable comments that should be considered in revision before consideration for publication.  
1)  The use of d-band center of the extended metals is a strange and awkward descriptor for single metal atom dopants in TiO2.  The authors use the d-band center that would occur if the dopant metal atoms were in bulk form as a descriptor that is meant to tell something about the stability of single atoms in TiO2, despite such atoms not having a d-band.  Similarly, a bulk cohesive energy is awkwardly used as a descriptor for how a metal atom would bind to N-containing compounds.  These descriptors provide some statistically validity in predicting the specific values they are tested for, but the physical basis for such correlation is rather awkwardly discussed given the irrelevance of an extended metal d-band to the actual electronic structure of isolated metal atoms.  For stability, prior work of Charlie Campbell has suggested a combination of a metal atoms cohesive energy and oxidation enthalpy as a descriptor of bonding to an oxide surface, and this would have more physical relevance.  I expect some measure of oxygen affinity, HOMO and LUMO orbital positions, dimer formation, oxygen affinity, or even just position in the periodic table (a combination of row and mass number) would likely work as well as d-band center and all have as much or more physical relevance to the stability.  I suggest removing any isolated use of a bulk metal property in trying to explain the chemistry of isolated metal atoms, or discussing this as a purely empirical measure that happens to work due to its simple correlation with position in the periodic table, and remove the discussions of why d-band center would be

physically relevant to single atom properties.

We thank the reviewer for their insightful criticism. We agree that the d-band center, a property of the extended metal, is a slightly surprising descriptor. However, we note that the d-band center of the corresponding transition metals acts as a proxy for the average energy of d-electrons and can potentially provide insight into the behavior of the metal nuclei regardless of if the material has a true continuous band structure. As noted in the paper, this is a similar concept to electron affinity, which has been previously proposed as a corelate, but we found that the d-band center provided better predictions. As the reviewer notes, and as noted in the paper, this trend roughly equates to a trend across the periodic table. However, the trend across the periodic table does not shed any light on the underlying electronic structure, and does not account for differences in row, leading to stronger correlation with the d-band center. The use of bulk properties as elemental descriptors is common, and in fact the reviewer provides a suggestion that the cohesive energy, which is also a bulk property, has been used as a descriptor in prior work on SMSI. Indeed, we also find correlations with the cohesive energy in our work. Additional properties such as oxide formation energy may also be good descriptors, but are complicated in our case by the fact that metals form oxides of different stoichiometries and crystal structures, so selecting the appropriate oxide formation energy presents its own challenge.

Nevertheless, for both the d-band and cohesive energy correlations we recognize that our language implied stronger causal conclusions than could be drawn from our analysis. In response we have weakened the claims in this section and removed the detailed description of the d-band model to avoid confusion. We have also added a sentence clarifying that the d-band center is used as a descriptor only and does not imply the use of band models. We believe that our findings warrant reporting and discussion by the community.

Several sentences have been removed at the top of page 3 and the following text has been added to address this comment:

“The correlation between the d-band center, a bulk metal property, and the stability of isolated metal atoms is somewhat surprising. However, the stability of the bulk metal also plays a role in determining the stability of the isolated site, which may explain some correlation, although the d-band center was found to be a better descriptor than the cohesive energy. The observed trends are also consistent with the observation that the interaction between metal surfaces and oxygen weakens from left to right on the periodic table, as predicted by the d-band model [56].”

2) I can’t find the formula used to calculate the formation energies in Figure 2 in the main paper or supplementary info.  This formula should be given.  It is unclear how the difference in oxidation state is considered, as well as how the change in number of Ti upon doping is handled.  I expect these would only alter raw numbers rather than trends.  However, it is quite surprising that, with bulk metals as the reference state, even most early transition metal atoms (Ta, V, Nb, W) seem to have positive formation energies, suggesting they would preferentially cluster into a metal particle rather than forming an oxide.  This suggests the model surfaces used are incredibly unstable, and it is unclear what is gained studying chemistry.  I note some metals have formation energies of positive 5 to 10 eV, suggesting the driving force for the metal atom to be removed from the doped state is larger than the metal’s cohesive energy – ie, it would prefer to move from the TiO2 to a single isolated metal atom state than be in the unstable doped state that is modeled.  This should be clarified, as I question the relevance of any subsequent studies of catalysis on models suggested as being so highly unstable by the reported formation energies.

The oxidation state of the site was chosen based upon the formal oxidation state of the sites assuming the Ti centers remain in the 4+ oxidation state. We have modified the text to clarify that the assigned oxidation states are not necessarily the true oxidation states of the metals in the system.

The formula used to calculate formation energies in now included in the methods section. However, we have changed the phrase “formation energy” to “metal substitution energy” to avoid any confusion on the part of the reader.

While we recognize that many of the sites have exceedingly large metal substitution energies, we also note that unstable structures can exist in kinetically trapped states, meaning they are unable to decompose due to large barriers. Additionally, some of these sites have been studied previously in the literature [3], thus we think that at least reporting the stability is an important point. We also note that many studied sites in the literature also have exceedingly large formation energies, which we see as a serious problem and was the reason for performing this analysis. However, we neglected to state explicitly that many of these sites are too unstable to realistically be formed, which we showed implicitly. We regret this oversight and have added a sentence stating this explicitly. However, despite the high formation energies of many of the sites, this analysis has been performed on all sites to establish trends, as these should hold even outside the range of experimentally observable materials and strengthen the overall conclusions on the chemically relevant sites.

To address this comment we have replaced mentions of “formation energy” with “metal substitution energy” (highlighted throughout the manuscript) and added the following text on page 9 in the methods section:

“Site metal substitution energies were calculated based on the energy of displacing the metal dopant atom from it’s bulk metallic form into the position of a titanium atom, and placing the titanium atom into a bulk metallic titanium form. The following formula was used:

∆Es = ET in−1OyM + ET i(m) − EM(m) − ET inOy (3)

where ∆Es is the metal substitution energy of the dopant metal site, ET in−1OyM is the energy of the doped surface, ET i(m) is the per atom energy of bulk Ti, EM(m) is the per atom energy of the dopant metal, and ET inOy is the energy of the undoped surface”

additionally we have added references to this equation where we discuss this analysis on pages 3 (left column) and in the figure 2 caption on page 4.

3) I was surprised to see no mention of the use of DFT+U methods in correcting self-interaction errors on Ti atoms (which may reduce to 3+ states in some of these, for example were V to take on a 5+ oxidation state when doped into TiO2).  Given the established literature on the need to use U corrections on Ti d states to capture redox properties of TiO2, why are they not used here?  As the SIE would be hard to calibrate, and no direct comparison is made to model experimental systems to establish reliability of the methods used, the authors should at least report how dependent their results are on calculation choices like U correction, or GGA versus hybrid functionals.

It has been noted in the literature the +U corrections are needed to accurately capture d-electron correlation effects. However, the choice of +U corrections adds complexity in the choice of U value, which can be different for different properties and raises issues of which properties are best to choose, and how accurate the method is for each case. This complexity is compounded by the fact that the +U is applied per metal center, so there may be interaction between the appropriate +U value for Ti and the metal dopants. Additionally, it has been suggested in the literature that the selection of U value does not affect the trends in adsorption energies [2,3], which is our primary concern in this work. Rather than carefully benchmark the +U correction for each metal studied we have chosen to neglect this correction, as it unlikely to affect the results. However, a systematic study of how to select the appropriate +U values for these systems would be interesting future work.

To address this comment we have added the following text and corresponding references to the methods section on page 9:

“Previous literature suggests that Hubbard +U corrections are needed to properly capture the behavior of d-electrons within DFT[84]. However, we have chosen not to include these corrections in this work. This was done to avoid issues created by selecting +U values for all metals, for which there is no accepted universal method. [57, 85] Additionally, the primary concern of this work is capturing trends in the surface adsorption properties, which have been shown to be relatively robust to the addition of +U corrections [57].”

4) The correlations of N-containing species binding with cohesive energy look quite rough, as to the scaling relationships used later in developing the volcano relationship.  Some statistical certainty beyond simply R values should be reported, and its implication on the qualitative conclusions reached as to the usefulness of various dopants should be discussed.

While the scaling relations obtained do not appear as clean as seen in other work, we note that the overall error (RMSE~0.2eV) in the energies is similar to previous work in on scaling relations. This is additionally in line with the error expected from GGA DFT. The reason for the rough-looking correlation is simply that the energies of these species do not vary much as the dopant changes. The RMSE is already reported in the paper, and the uncertainty should propagate through the volcano plot analyses to translate to ~0.2 eV error in the predicted overpotentials. We also note that the points in Fig. 6b are colored according to their actual over-potential, allowing the reader to identify the points where the error due to scaling is largest. We have highlighted this fact in the main text to clarify.

Text has been added to address this on page 7 (right column):

“We note that the points on this plot are filled in with their calculated limiting potentinal from DFT, but placed based on their predicted limiting potential from the scaling relations, enabling direct assessment of the error due to scaling relations.”

As well as in the caption of figure 6 on page 8:

“Points are colored in with the limiting potential calculated from DFT.”

5) Doped oxides can have significant restructuring occur, as dopants adopting different oxidation states may prefer different local O coordinations, and the redox flexibility of TiO2 may enable such structural reorganization.  Often this requires manually breaking symmetries, or reorganizing local oxygen coordinations to move the system to a global minimum energy structure.  The authors should discuss how they assured that each doped state was converged to global minimum energy structures.  It is also quite common to have many possible spin states in these systems, and as the energy/spin relationship is not continuous, simply allowing the spin to optimize cannot assure a calculation reaches the lowest energy spin state. The authors might discuss how they sampled various spin states for the doped atom, or if other local spins appeared (ie, on Ti atoms), how the various spin alignments among the localized spins were explored.

For the chosen systems, symmetries were broken for the slab systems to allow the metal oxide to find relaxed geometries. We restricted our study to the two surface structures outlined in the paper to attempt to limit the complexity the reviewer outlines with oxygen coordination. To obtain spin states, the spins of each system were perturbed close to 0 and allowed to relax within the self-consistent electronic structure calculations. For magnetic elements (Fe, Cr, Ni, Co) calculations were performed at both perturbed magnetic states near zero and magnetisms set to the normal magnetism of each element in the bulk phase and the lowest energy magnetic state was selected. Text has been added to the methods section to clarify this.

Text has been added to the methods section on page 9 to detail this:

“For all calculations the magnetic moments have been perturbed. Most elements the magnetic moments were perturbed near zero. However, for elements known to show complex magnetic states (Ni, Fe, Co, Cr) the magnetic moments have been initialized to the natural magnetic moment of these elements in the bulk metal form.”  
  
Referee: 2  
  
Comments to the Author  
Dear editor and authors  
  
The submitted manuscript is well written and presented and the quality of the computational work and research is at a high level. The results shows that TiO2 can be significantly improved for phtotoelectrocatalytic N2 reduction to ammonia at ambient condition by doping with other metal ions. A range of metal ions are taken into account. A few new interesting candidates are proposed with lower limiting potentials than TiO2 and some of them should be stable and abundant. This will therefore presumable spark interests among experimentalists to test these candidates. I have only a few minor comments provided below which may improve the overall presentation of the work, and this manuscript can be accepted after they have been considered.

We thank the reviewer for their comments  
  
1. Figure 1 could be improved and made more clear and nicer. Perhaps showing repeating supercells would be better in order to show these two different substitutions. Other softwares may also be used to get nicer looking atomistic models.

We have improved this figure by repeating the unit cell to show the precise surface being studied. The simplistic atomic models were chosen for easy viewing when printed in black and white. However, these have been replaced with more detailed representations. (see figure 1)

2. In the 1D volcano in Figure 5a it looks like Rh has much lower limiting potential than Ru whereas this is the other way around in the 2D volcano in Figure 5b. Is this a typo? Otherwise this needs to be explained? If this is a typo then all data should be rechecked to avoid other mistakes before published.

We apologize for the unclear diagrams, the positions on the 2D plot represent their predicted overpotential, and the points are filled in with the calculated potential. Thus, the 2D plot was intended to show that Ru is predicted to have a favorable overpotential from the scaling relations, whereas the overpotential expected from DFT is significantly higher. We have added a sentence to the text to clarify this.

Text has been added to address this on page 7 (right column):

“We note that the points on this plot are filled in with their calculated limiting potentinal from DFT, but placed based on their predicted limiting potential from the scaling relations, enabling direct assessment of the error due to scaling relations.”

As well as in the caption of figure 6 on page 8:

“Points are colored in with the limiting potential calculated from DFT.”

3. There is not much discussion about Figure 6 in the text. For some reason these three candidates have been chosen and they all have the same pathways and limiting steps. Free energy diagrams are provided it SI for all candidates and with three mechanisms: associative alternative and distal pathway as well as dissociative pathway. Here the alternative pathway is preferred in all three cases. But why not showing free energy diagrams from candidates on e.g. opposite side of the volcano from Figure 5a? What is the purpose of this figure here and not before the volcanos? There is no discussion about the preferred pathways here for this class of materials. However, for most materials the distal pathway has been predicted and therefore perhaps worthwhile pointing this out.  
  
We have presented Figure 6 to show examples of the most promising candidates. This figure was included to provide some examples of free energy pathways in the main text. However, as the reviewer notes, this is somewhat superfluous. We have removed this figure from the text. We additionally note that the only steps that are limiting for the materials studied are the first and last steps, thus the associative pathway displayed is arbitrary (although the one with lowest overall barriers was selected).  
  
Referee: 3  
  
Comments to the Author  
This manuscript reports a computational and modeling evaulation of the potential for  
transition metal ion substitutional doping to improve the performance of TiO2 for photo or  
electrocatalytic N2 redution to NH3. The work is clearly reported and methods are  
consistent with those that are widely used today.  Following are several comments that  
should be considered in preparing a revised manuscript.  
  
1. The Introduction is considerably longer that I would have expected for this  
  contribution, and spends a considerable amount of space discussing the potential merits  
  of photocatalytic NH3 production without expressing for the non-expert what  
  photocatalytic NH3 synthesis is.  I am sure the merits have been discussed at great  
  length elsewhere, so I would encourage the authors to invest more space in descriptions  
  that will help the reader better understand the motivations and methods and catalytic  
  challenges addressed in this specific work.  The Introduction contains some discussion  
  of prior experiment, but here too general observations are presented without an  
  appropriate description of what those experiments are, what is measured, ....  More  
  critical presentation here and less broad motivations and generalities relative to H-B  
  would make the Introduction more useful.

We thank the reviewer for their suggestions, we have removed several paragraphs from the introduction to shorten it. We have also added text with additional details on the photocatalytic experiments and the nature of the metal addition for several of the experimental studies to provide additional context.

On page 2 the following text was added:

“In these studies the dopant metals were co-preciptated with the TiO2 samples, thus having significant concentrations in the bulk. These studies were also performed without the use of isotopic labeling, and careful controls are not always included, making interpretation difficult. More recently, Hirakawa et al. used a modern photochemical

setup along with isotopic labeling and found that depositing noble metals (Ru, Pt, Pd) onto an already prepared rutile (110) surface led to a decrease in reaction rates [22].”

2. Page 2, "strategies for enhancing the rate of ....viable route...."  Is this really  
  true?  Is it appropriate for this Introduction?

Using doped TiO2 has been proposed as a potentially viable route for photocatalytic ammonia synthesis, but whether or not it is true is certainly an open question. However, this paragraph has now been removed according to the reviewer’s suggestion.

3. Page 2, line 50, micromol scale for rates?  What does this mean?

We thank the reviewer for highlighting this unclear use of terminology. A more precise phrase would be “on the scale of mircomol/hour”. However, this statement has also been removed.

4. Page 2, line 43 "under only under" is a typo

Thanks for catching this error. However, this paragraph has been removed.

5. TiO2 is to my understanding a semi-conductor that in a conventional DFT calculation  
  will have a gap of perhaps a volt or so.  What is the electronic structure then of  
  these doped models?  Authors discuss in terms of a d band.  Is this accurate?  I might  
  expect discrete d states for the dopant, perhaps smeared out due to the details of the  
  calculation.  If truly a band, then are the models actually appropriate to describing  
  an "isolated" substitutional ion?  Has the robustness of the electronic structure been  
  checked against the size of the supercells (which appears to be rather modest)?  
  Against the dopants/cell?  For instance, if the cells of Figure 1 are doubled in 1  
  direction with the identical overall structure, are electronics the same?  One might  
  imagine an ion that can take more than one oxidation state to converge to a ground  
  state in which one ion is in the higher and the other in a lower state, something  
  impossible to accommodate in the supercells as constructed here.  Overall, the work  
  would benefit greatly from a more careful treatment and description and interrogation  
  of the model itself, and explanation/justification of the d band descriptor.

We agree with the reviewer that the band models are not appropriate for a semi-conductor. The d-band center of the corresponding transition metal was chosen as a descriptor, as it captures the average energy of electrons in a given metal atom, and thus was not intended to imply the use of band models. While we have not closely examined the effects of unit cell size in this paper, we additionally note that a similar model surface has been used in prior literature [3], and should therefore be sufficiently accurate for a trends study. This fact is now highlighted in the main text. The distance between dopant atoms is > 3.5 Angstrom, so we feel that direct metal-metal interactions are unlikely, though we agree that the concentration of dopant atoms is far higher than would be expected for realistic systems. However, we expect that the effects of dopants should be greater at higher concentrations, so the present study provides a good limiting case.

As for the specific question about the electronic structure of the dopant atoms, we did run some additional calculations to check this. We found that the dopant atoms do generally have a band structure, and there are states at the Fermi level suggesting they may act as low-lying defects. However, we note that detailed analysis of the band structure may be inaccurate without +U corrections (though trends in adsorption should hold [2,3]) and we therefore leave these questions for future work.  
  
The following text and references have been added to address this comment:

“We also note that these models are similar to those studied previously in the literature [39, 53].”

6. Figure 2 reports formation energies with respect to what references?  Most of these  
  numbers are very positive. What does this say with regards the plausibility of the  
  models?

We have changed all instances of “formation energy” to “metal substitution energy” and included the equation in the methods section. We agree with the reviewer that many of these energies are exceedingly high, and thus these materials are unlikely to be synthesized. This analysis was performed to demonstrate that some structures are likely unrealistic despite being proposed in prior experimental and theoretical work. However, regretfully we neglected to state this explicitly in the text. Text has been added to state this. We note that many authors neglect stability in describing proposed active sites, and this has motivated its inclusion.

“Site metal substitution energies were calculated based on the energy of displacing the metal dopant atom from it’s bulk metallic form into the position of a titanium atom, and placing the titanium atom into a bulk metallic titanium form. The following formula was used:

∆Es = ET in−1OyM + ET i(m) − EM(m) − ET inOy (3)

where ∆Es is the metal substitution energy of the dopant metal site, ET in−1OyM is the energy of the doped surface, ET i(m) is the per atom energy of bulk Ti, EM(m) is the per atom energy of the dopant metal, and ET inOy is the energy of the undoped surface”

additionally we have added references to this equation where we discuss this analysis on pages 3 (left column) and in the figure 2 caption on page 4.

7. The value of the subsequent NH3 surface chemistry hinges I think on answering the  
  questions above about the model construct. The presentation focuses on energies (Fig 3,  
  Fig 4, the very extensive SI) while leaving the reader to guess what exactly the  
  relevant structures are. Always assumed to be the same?  Tested somehow?  Some  
  adsorbates span multiple sites?

We apologize for the lack of clarity on the exact structures. A section has been added to the methods describing our process for obtaining converged geometries. In short, we optimized geometries for the Fe defects, and assumed that the geometries stay roughly constant by using the most stable Fe geometries as an initial guess. While this may not always be true, it is a reasonable route to decoupling the effects of electronic structure from adsorbate configuration. Moreover, the adsorbates studied are relatively small, suggesting that there are relatively few possible adsorption configurations.

The following text has been added to address this comment:

“Adsorption Structure Optimization: To obtain reasonable initial guesses for structural optimization, all calculations were first performed using using Fe as the dopant metal. In these initial runs multiple adsorbate geometries were used as initial guesses. These converged structures were then used as initial guesses for all other dopant metals by replacing Fe with the corresponding metal. These structures were then allowed to relax to obtain the new lowest energy structure. All structures may be obtained from the provided SI.”

8. In any case in which binding is stronger on Ti than a dopant, does that imply that the  
  NH3 chemistry for the doped system will be identical to Ti, as that is where adsorbates  
  will segregate?

In cases where binding to Ti is stronger than the dopant metal it is possible that Ti competively binds these intermediates. However, the there is a kinetic barrier to the movement of these species, implying that you may also see the activity of the dopant sites. Thus an ensemble of outcomes would exist in reality, and the activity of the material might lie somewhere between the activity predicted for the doped surface and pure Ti. However, the details of such predictions are beyond the scope of this study, which is primarily focused on identifying elements that may be promising for improving performance of TiO2.

9. The discussion at the bottom of p 8 regarding thermochemical steps is very important  
  and one that in my opinion deserves to be surfaced earlier in the presentation. This  
  gets back to the issue of describing early on the overall picture of the catalytic  
  chemistry of interest.

We concur with the reviewer that this absolutely critical to predicting the activity of a catalyst and that this section in particular is important. We additionally note that few many authors do not perform this analysis, which was the impetus for including it. Thus, we have shifted this discussion further up in this section of the paper.

The text that has been moved begins on page 6 in the left column “A primary consideration…” and ends on page 7 “reduction if kinetic barriers are low”  
  
  
Overall this is good and interesting work.  It has the potential to be more valuable in my opinion if considerations like those raised above are given more thorough attention.

We thank the reviewer for their constructive criticism

[1] M. T. Curnan and J. R. Kitchin, “Effects of concentration, crystal structure, magnetism, and electronic structure method on first-principles oxygen vacancy formation energy trends in perovskites,” J. Phys. Chem. C 118, 28776–28790 (2014).

[2] Z. Xu, J. Rossmeisl, and J. R. Kitchin, “A linear response, DFT+U study of trends in the oxygen evolution activity of transition metal rutile dioxides,” J. Phys. Chem. C (published online).

[3] García-Mota, M., Vojvodic, A., Abild-Pedersen, F., & Nørskov, J. K. (2012). Electronic Origin of the Surface Reactivity of Transition-Metal-Doped TiO2(110). The Journal of Physical Chemistry C, 117(1), 460–465. doi:10.1021/jp310667r