Computational Screening and Adsorption Analysis of Potential CO_2 Reduction Photocatalysts

Ricardo Buarque, Oxana Andriuc, Martin Siron, Kristin Persson

Abstract: A screening procedure using density functional theory (DFT) was devised to select promising materials for the CO_2 reduction reaction (CO_2RR) from the Materials Project (MP) database. Criteria such as aqueous and thermodynamic stability, computational cost, and photochemical suitability were considered. The selected materials are further investigated using a high-throughput workflow for generating adsorption data for semiconductor surfaces. By considering species relevant to the CO_2RR as adsorbates, the descriptors computed by the workflow offer additional insight into the photocatalytic performance of the researched materials, making this approach a powerful materials discovery tool.

We use publicly available data and computer simulations to accelerate the discovery of materials that can use sunlight to turn carbon dioxide into fuels.

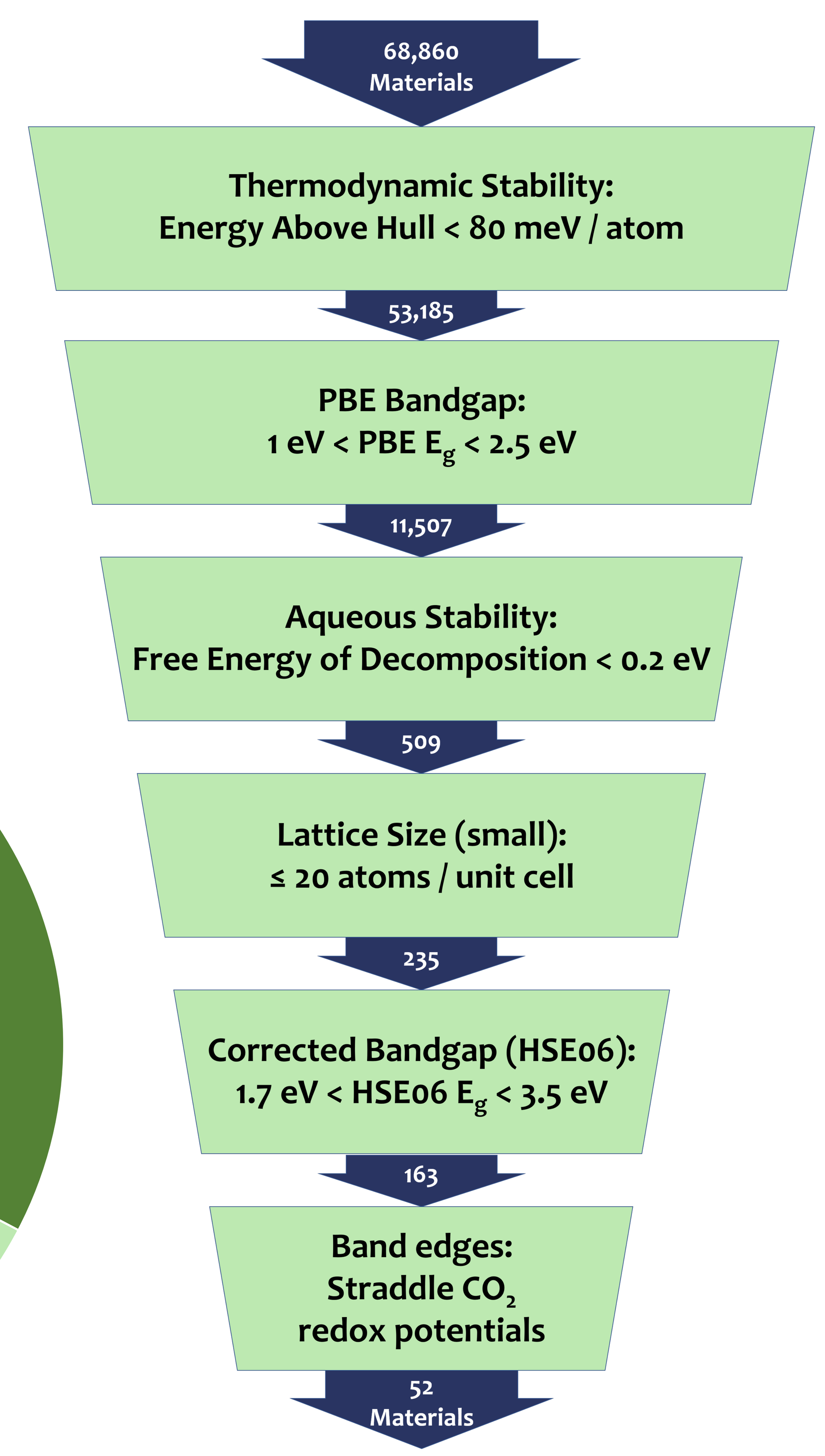
Introduction

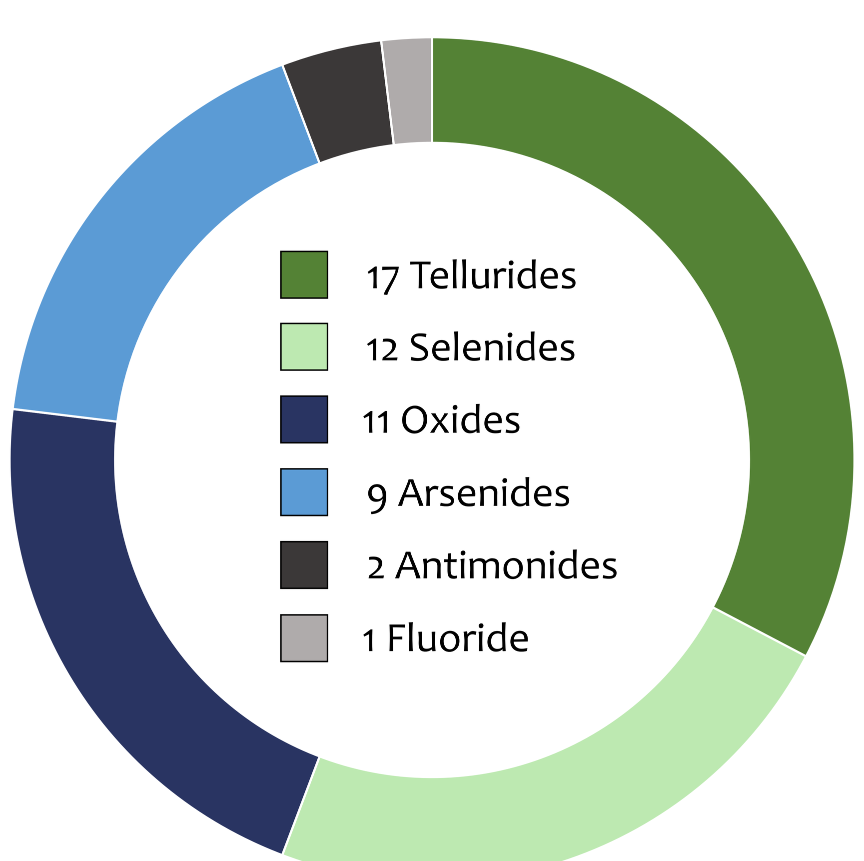
Photocatalysts are materials that are capable of absorbing solar energy to enable or accelerate an oxidation or reduction reaction. One such reaction is the reduction of CO_2 to hydrocarbons, which both enables the development of sustainable fuels, and facilitates managing greenhouse gas emissions.[1] Desirable properties for a successful photocatalyst include a visible range bandgap, suitable band alignment, stability,[2] and an appropriate binding energy to the adsorbate undergoing the reaction.

We propose a high-throughput computational approach to finding CO_2RR photocatalysts, which enables the screening of thousands of materials from the MP database[3] within a reduced time frame. As existing adsorption workflows focus on metallic systems,[4] we have developed a semiconductor-specific methodology to assess the adsorption capabilities of the selected materials. Combined, these two methods can significantly accelerate the discovery of novel photocatalytic systems for CO_2 reduction, an essential step in developing renewable energy technologies.

Pre-screening

This screening procedure led to a final pool of 52 materials, 15 of which are layered. Furthermore, 43 of these materials have been previously synthesized and 9 have already been tested for CO_2 reduction[2].





Adsorption workflow

BULK
DFT geometry optimization

Generate all surfaces

SLAB
1. DFT geometry optimization
2. Density of states and band structure calculations

Find all adsorption sites

SLAB + ADSORBATE
1. Input surface – adsorbate distance optimization
2. DFT geometry optimization
3. Density of states and band structure calculations

Collect all data

ANALYSIS
Save all descriptors to a personal user database for easy querying

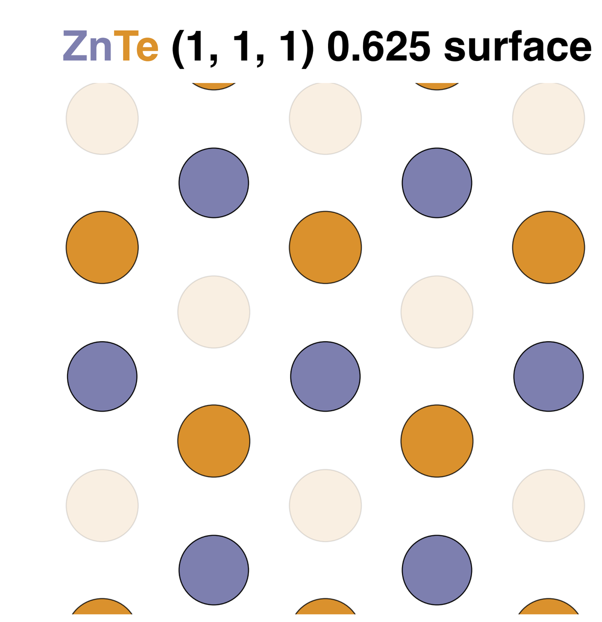
Results

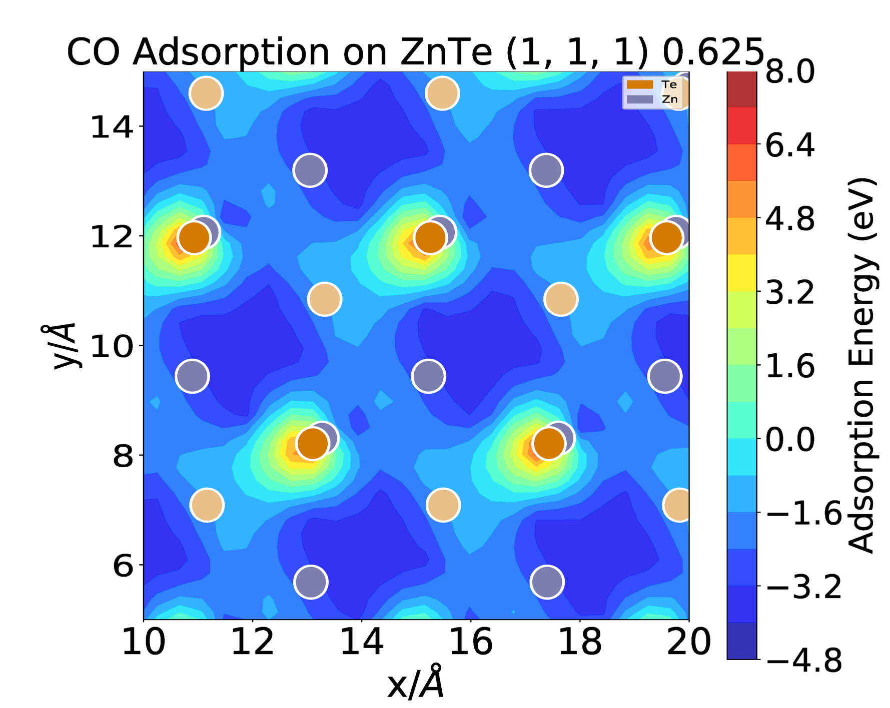
The data generated by the workflow includes adsorption energies, coordination numbers, adsorption site type, translation vectors, charge transfer and work function analysis, p-band center, orbital and elemental compositions of band edges, among others.

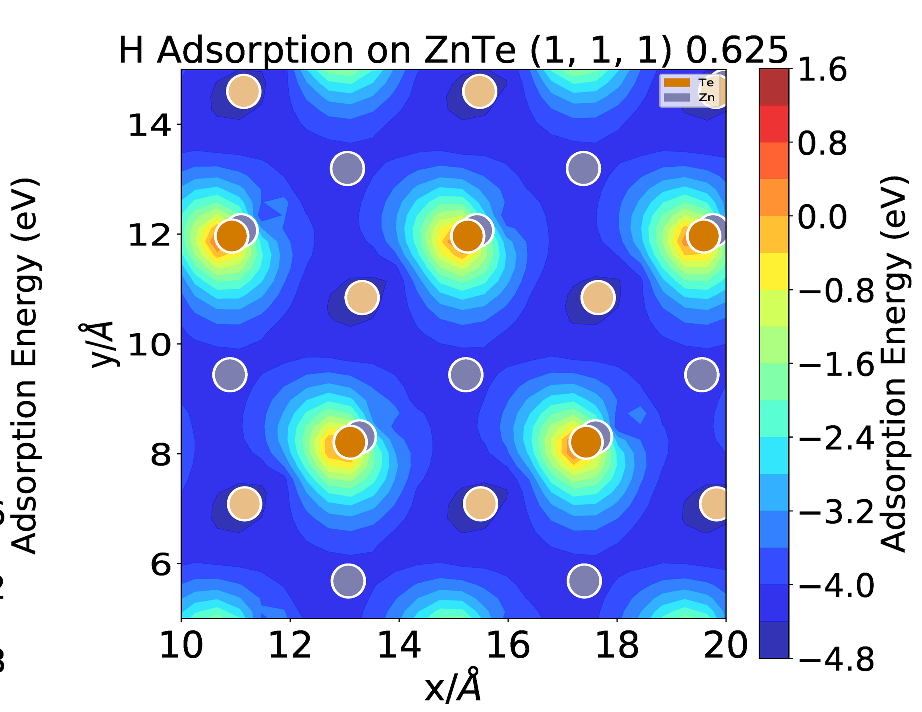
Case study: zinc telluride

Zinc telluride is one of the 52 materials selected by the screening strategy. It has been previously used in CO_2RR photocatalytic devices.[5]

The considered adsorbates are CO and H as they are relevant species for the CO_2RR and competing hydrogen evolution reaction (HER).







Adsorption energy maps of CO (left) and H (right) on the ZnTe (1, 1, 1) 0.625 surface (top right) reveal:

- CO is strongly favored on Zn and hollow sites and strongly disfavored on Te sites
- H adsorption follows a similar trend and is generally more strongly binding than CO on this surface

Outlook

Our pre-screening filtered an initial pool of over 60,000 materials to 52 potential candidates for photocatalytic CO_2 reduction. The application of the adsorption workflow to the selected materials is expected to offer insights into the selectivity and suitability of these potential photocatalysts. This will enable us to perform more advanced studies on the most promising candidates, as well as propose them for experimental testing.

References:

1. P. Usubharatana, D. Mcmartin, A. Veawab and P. Tontiwachwuthikul, *Industrial & Engineering Chemistry Research*, 2006, **45**, 2558–2568.
2. A. K. Singh, J. H. Montoya, J. M. Gregoire and K. A. Persson, *Nature Communications*, 2019, **10**.
3. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Materials*, 2013, **1**, 011002.
4. J. H. Montoya and K. A. Persson, *npj Computational Materials*, 2017, **3**.
5. J.-W. Jang, S. Cho, G. Magesh, Y. J. Jang, J. Y. Kim, W. Y. Kim, J. K. Seo, S. Kim, K.-H. Lee and J. S. Lee, *Angewandte Chemie*, 2014, **126**, 5962–5967.

Acknowledgements: This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE SC0004993. This work used data and software infrastructure from the Materials Project, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract DE-AC02-05-CH11231: Materials Project program KC23MP.