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Excitonic effects in absorption spectra of carbon dioxide reduction photocatalysts

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The formation and disassociation of excitons play a crucial role in any photovoltaic or photocatalytic application. However, excitonic effects are seldom considered in materials discovery studies due to the monumental computational cost associated with the examination of these properties. Here, we study the excitonic properties of nearly 50 photocatalysts using state-of-the-art Bethe–Salpeter formalism. These ~50 materials were recently recognized as promising photocatalysts for CO₂ reduction through a data-driven screening of 68,860 materials. Here, we propose three screening criteria based on the optical properties of these materials, taking excitonic effects into account, to further down select six materials. Furthermore, we study the correlation between the exciton binding energies obtained from the Bethe–Salpeter formalism and those obtained from the computationally much less-expensive Wannier–Mott model for these chemically diverse ~50 materials. This work presents a paradigm towards the inclusion of excitonic effects in future materials discovery for solar-energy harvesting applications.

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INTRODUCTION

Excitons, which are quasiparticles, form when light is absorbed by semiconductors or insulators. They consist of a photoexcited electron and a hole bound by Coulomb interaction. In photocatalytic and photovoltaic processes these excitons must dissociate into free carriers and eventually reach the reacting species (in a photocatalytic process) or get converted into photocurrent (in a photovoltaic device) before any recombination processes can occur. Spontaneous generation of electron–hole (e–h) pairs from the dissociation of excitons is only possible when exciton binding energy (EBE) is lower than $T\Delta S_{\text{diss}}$ where T is the environmental temperature and ΔS_{diss} is the entropy increase upon dissociation¹. In a system where the number of photogenerated excitons (n_x) and the number of dissociated free e–h pairs ($n_c = n_e = n_h$) attains quasi-equilibrium, they are related as²,

$$n_c^2 = n_x T^{3/2} \exp(-E_b/2k_B T) \quad (1)$$

where T is the temperature, E_b is the EBE, and k_B is the Boltzmann constant. Therefore, if everything remains the same, by increasing the EBE by 50 meV the number of available free carriers (n_c) will be reduced by a factor of ~2.6 at 298 K. This reduction in n_c directly affects the reaction rate of a photoreduction process. Once free e–h pairs are available, a low carrier recombination rate is desirable as it ensures most of these e–h pairs can be utilized in photocatalytic/photovoltaic applications. Both radiative, which are predominant in direct gap semiconductors, as well as non-radiative recombination processes have adverse effects on the quantum efficiency of a photocatalytic/photovoltaic device. However, with the help of innovative solutions such as use of multi-junction photocatalysts or solar cells^{3,4} one can go beyond the limit set by radiative recombination processes. In the context of solar cells, this limit is given by the Shockley–Queisser limit⁵ and a lower limit is expected for photocatalysts⁶. Non-radiative recombinations that fall in the category of Shockley–Read–Hall⁷ or trap-assisted recombinations can also be controlled by improving device quality and using defect-free semiconductors⁸. The other kind of non-radiative recombination, known as Auger

recombination^{9,10} is quite hard to eliminate¹¹. High EBE is detrimental for a photovoltaic/photocatalytic device as it can facilitate these Auger recombination processes^{10,12}. Although, qualitatively it is obvious that a higher EBE will increase the Auger recombination rate (R_{Auger}), we could not find any study that explicitly calculates this functional dependence in case of 3-dimensional semiconductors. However, in 1-dimensional systems it has been shown¹³ that the Auger recombination rate $R_{\text{Auger}} \propto \text{EBE}^3$. Therefore, it is important to consider excitonic effects while looking for promising photovoltaics and photocatalysts.

Excitonic effects have been seldom considered in material discovery studies conducted in the past for identifying promising photovoltaic or photocatalytic materials^{14–18}. For instance, recently, Singh et al.¹⁸ performed the largest CO₂ photocathode search to date, where they shortlisted 52 materials starting from a list of 68,860 candidate materials. Their first-principles computation-based screening strategy was based on evaluating the thermodynamic stability, the electrochemical stability¹⁹, and the electronic structure compatibility with the CO₂ reduction reaction¹⁸. Their screening criteria were highly selective of robust photocatalysts when applied to the scores of known photocatalysts. It is noteworthy that the 52 materials shortlisted by Singh et al. were selected based on their (photo)electrochemical stability in the harsh reducing conditions needed for CO₂ reduction reactions^{18,19}. However, despite its success, the screening did not incorporate any excitonic effects. In recent years, Bethe–Salpeter formalism (BSE) has gained remarkable success in probing excitonic effects in bulk^{20–22} as well as 2-dimensional materials^{23–25}, where these effects are more pronounced. The BSE formalism has a high computing resource requirement, both in terms of CPU time and memory. But, it has been found to have excellent agreement with experimental measurements across various materials classes^{20–25}.

Most of the CO₂ reduction photocatalysts available today such as TiO₂ (probably the most studied material in this context) are wide bandgap semiconductors that are most efficient under

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UV radiation and can utilize only a negligible fraction of solar radiation (5%)²⁶. To enhance the visible light (53% of solar radiation at the sea level) response of candidate photocatalytic materials, and thus utilize the major fraction of the solar energy, the search for promising materials for CO₂ reduction photocatalysts should assess the optical response of these materials. Our study's central goal is to assess the feasibility of absorbing visible-light through the computation of the entire frequency dependent absorption spectra of materials as opposed to looking at only the bandgap of materials as done in several other similar high-throughput studies done in the past^{27,28}.

In this study, we design a materials screening strategy which is based on the optical properties and considers excitonic effects to identify the most efficient photocatalysts for CO₂ reduction among the 52 materials shortlisted by Singh et al. We employ many-body perturbation theory within GW approximation together with^{29–31} BSE to explore quasiparticle and optical properties. Our screening strategy involves three distinct properties—EBE of the materials, the capability to absorb incident (visible or UV) radiation, and the degree of anisotropy in absorbing light of different polarizations. For each of these properties, we propose the limiting value for the criteria by looking at some of the well-known photocatalysts used for CO₂ reduction. Using these criteria we identify a shortlist of six suitable materials from Singh et al.'s study that display optical properties which are at par or better than known photocatalysts. This screening approach is broadly applicable to the discovery of materials for other solar-energy applications. The limiting value corresponding to each of the properties in such a screening strategy will, however, change based on the specific application.

As the BSE is computationally resource intensive and time-consuming, we also assess the prospect of using the computationally much less demanding Wannier–Mott model to compute the EBE of materials. We compare the EBE obtained from the BSE method and the Wannier–Mott (WM) model for 48 materials from Singh et al.'s study. These materials are chemically diverse—comprising of oxides, sulfides, tellurides, and arsenides. We find that the WM model is effective in classifying low and high EBE materials. Thus, we surmise that the WM model can be used in place of the BSE method to identify materials with low EBE in a computational cheaper, hence potentially a high-throughput manner, to enable computational data-driven materials discovery for applications involving solar-absorption such as photovoltaics and photocatalysis.

RESULTS AND DISCUSSION

Comparison between GW-BSE and HSE results

Singh et al.¹⁸ had employed density-functional theory (DFT) with a hybrid exchange-correlation functional to compute the bandgaps and band edges of potential photocatalysts and identified materials that can utilize the visible-light spectrum which accounts for 44% of the solar radiation and simultaneously facilitate the reduction reaction of CO₂. DFT which is designed to explore ground state properties suffers from bandgap underestimation problem as the bandgap is an excited state property of materials. Hybrid functionals such as HSE and HSE06, overcome this issue by adding a fraction (α) of Hartree–Fock exchange to the traditional exchange-correlation potential (LDA or GGA) and is quite successful in predicting correct bandgaps of a wide variety of materials. While hybrid functionals typically exhibit improved treatment of semiconductor bandgaps, they are heavily reliant on the fraction of the exact exchange (α) included in the functional and are thus limited in their predictive capacity³². Once the accurate bandstructure is procured, although TDHSE can capture excitonic effects like BSE, solving the Cassida's Equation is equally expensive³³. Moreover, earlier studies which employed TDHSE in probing excitonic effects seem to always underestimate EBE (often by an order of magnitude)³⁴. Our TDHSE calculations (available in the Supplementary Table 7 and Supplementary Fig. 2) for AlSb, TiO₂, and MoSe₂ also draw similar conclusions.

Many-body perturbation theory within GW approximation is often an order of magnitude more expensive than standard DFT with hybrid functionals but does not require any empirical parameters and is found to be remarkably successful in case of various materials classes. The GW formalism combined with BSE has been proven to be the state-of-the-art method to study the electronic structure and optical properties of a wide variety of semiconductor and insulator materials in recent years with an excellent predictive capacity^{35–37}. Moreover, the GW-BSE computed absorption spectra have very good agreement with experimentally measured spectra. Thus, we reevaluate the bandgaps of 48 photocatalysts from Singh et al.'s study using the GW method. We have restricted our study to the non-magnetic 48 of the 52 materials identified by Singh et al. We exclude the ZrVF₆ and the two phases of VOF as they have a magnetic ground state and the CdHgAsBr since it was found to be metallic according to our GW calculations.

Figure 1 shows the difference between the HSE06 bandgaps, E_g^{HSE} , reported in Singh et al.'s work and the quasiparticle (QP) gaps obtained from G_0W_0 , $E_g^{G_0W_0}$, as well as the optical gaps obtained from G_0W_0 -BSE, $E_g^{G_0W_0\text{-BSE}}$ calculations. The difference between the quasiparticle gap of a material and its optical gap is

Fig. 1 Differences between E_g^{HSE} and $E_g^{G_0W_0}$ (orange) as well as $E_g^{G_0W_0\text{-BSE}}$ (green). The chemical formula and Materials Project id's (mp-id) for each material are shown on the bottom and top x-axis ticks respectively. The layered materials have been labeled in blue.

Table 1. Comparison between the computed (Theo) and experimental (Expt) lattice constants (a , b , c in Å, and α , β , γ in °), the Materials Project material ids (mp-id) and spacegroup (SG) of all the layered materials considered in this study.

mp-id	Formula	SG	a^{Theo}	b^{Theo}	c^{Theo}	α^{Theo}	β^{Theo}	γ^{Theo}	a^{Expt}	b^{Expt}	c^{Expt}	α^{Expt}	β^{Expt}	γ^{Expt}
mp-1863	SiAs	C2/m	16.15	3.72	9.64	90.00	105.76	90.00	15.98	3.67	9.53	90.00	106.00	90.00
mp-1943	GaSe	P6 ₃ /mmc	3.80	3.80	15.73	90.00	90.00	120.00	3.75	3.75	15.99	90.00	90.00	120.00
mp-11342	GaSe	R3m	3.80	3.80	24.14	90.00	90.00	120.00	3.75	3.75	23.91	90.00	90.00	120.00
mp-542812	GaTe	C2/m	17.61	4.14	10.62	90.00	104.60	90.00	17.40	4.08	10.46	90.00	104.50	90.00
mp-1634	MoSe ₂	P6 ₃ /mmc	3.33	3.33	13.17	90.00	90.00	120.00	3.29	3.29	12.93	90.00	90.00	120.00
mp-1018807	MoSe ₂	P6 ₃ /mmc	3.32	3.32	13.06	90.00	90.00	120.00	3.28	3.28	12.92	90.00	90.00	120.00
mp-7581	MoSe ₂	R3m	3.33	3.33	19.78	90.00	90.00	120.00	3.29	3.29	19.39	90.00	90.00	120.00
mp-1821	WSe ₂	P6 ₃ /mmc	3.31	3.31	13.04	90.00	90.00	120.00	3.28	3.28	12.96	90.00	90.00	120.00
mp-27449	GaTeCl	Pnnm	5.90	14.59	4.13	90.00	90.00	90.00	5.85	14.47	4.08	90.00	90.00	90.00
mp-29236	InTeBr	P2 ₁ /c	7.46	7.70	8.32	90.00	115.45	90.00	7.35	7.58	8.34	90.00	117.61	90.00
mp-569454	CdHgAsBr	Pmma	5.17	8.93	9.80	90.00	90.00	90.00	4.70	8.79	9.78	90.00	90.00	90.00
mp-574620	CsYZnSe ₃	Cmcm	4.14	15.82	10.93	90.00	90.00	90.00	4.14	15.81	10.93	90.00	90.00	90.00
mp-567386	Cs ₂ Cd ₃ Te ₄	Ibam	6.74	13.16	15.56	90.00	90.00	90.00	6.67	13.01	15.39	90.00	90.00	90.00
mp-12491	CsLaCdTe ₃	Cmcm	4.66	17.32	12.17	90.00	90.00	105.60	4.64	16.70	12.17	90.00	90.00	90.00

The experimental lattice constants are derived from the ICSD⁴¹ as reported in the Materials Project database.

precisely its EBE. One should note that, G_0W_0 refers to non-self-consistent GW approximation. Here, the single-particle Green's function, G_0 , and the screened Coulomb interaction, W_0 , are calculated using Kohn–Sham eigenvalues and eigenfunctions³⁸.

We have calculated the root mean square difference (RMSD), defined as $\sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta E_{g,i})^2}$, for the gaps obtained from G_0W_0 and G_0W_0 -BSE with the E_g^{HSE} values for all the 48 materials. Where $E_{g,i}$ is the bandgap of the i^{th} of the $N = 48$ materials considered in this study. Note that a positive $\Delta E_{g,i}$ signifies underestimated E_g^{HSE} . From Fig. 1 it is evident that except the layered materials, the E_g^{HSE} is almost always significantly underestimated compared to the QP gap obtained from G_0W_0 calculations. We find an RMSD value of 0.16 eV for optical gaps and 0.31 eV for QP gaps for the non-layered materials considered in this study, which highlights the importance of studying photocatalytic materials with the GW-BSE methodology. In the case of layered materials, the difference between previously reported E_g^{HSE} and $E_g^{G_0W_0\text{-BSE}}$ resulting from our calculation, has a different origin, which we will discuss in the following section.

Layered materials and Van der Waals correction

We observe a large difference in the previously reported E_g^{HSE} values and our $E_g^{G_0W_0}$ as well as $E_g^{G_0W_0\text{-BSE}}$ values for the layered materials. This difference originates primarily from the change in the lattice parameters due to the Van der Waals (vdW) corrections included in our work. Singh et al. used the lattice parameters computed by the Materials Project for their computational screening of more than 68,000 potential candidates¹⁸. The Materials Project structural relaxation simulations do not account for any vdW corrections. In contrast, in this work we have included vdW corrections using the non-local vdW density functional (vdW-DF) proposed by Dion et al.³⁹ with optimized exchange functionals (optB88)⁴⁰. Once we obtain an accurate lattice structure we have used the traditional PBE functional to obtain Kohn–Sham wavefunction and eigenvalues for the mean-field starting point for subsequent GW calculation.

In Table 1 we compare the lattice parameters obtained by using vdW corrections for the structural optimization in case of the layered

materials with the experimental lattice parameters and we find a very good agreement. The experimental lattice constants are obtained from the ICSD⁴¹ lattice constants available through the Materials Project database. We also find that for these layered materials the Materials Project computed lattice parameters, and hence those used in Singh et al.'s work, are typically underestimated in the direction of the vdW bonding. This gives rise to larger E_g^{HSE} bandgaps in Singh et al.'s work and the significantly smaller $E_g^{G_0W_0}$ and $E_g^{G_0W_0\text{-BSE}}$ gaps in this work. A RMSD of 0.54 eV for optical gaps and 0.47 eV for QP gaps is observed for the layered materials considered in this study, underscoring the importance of vdW corrections. See Supplementary Table 1 for the lattice parameters of all the 48 materials obtained from the vdW corrected functional.

In the case of the direct bandgap layered materials, GaSe and GaTe, the optical gap is found to be smaller than 1.7 eV, the lower end of the desirable 1.7–3.5 eV bandgap window of a visible-light photoabsorber¹⁸. For the dichalcogenides MoSe₂ (all three phases) and WSe₂ the direct absorption edge is just above 1.5 eV, however, at finite temperature the phonon assisted indirect absorption edge will be at an energy lower than 1.5 eV. These observations suggest that these materials may not be ideal for visible-light photocatalysis due to their low optical gap.

Accuracy of GW_0 in comparison to G_0W_0

We also computed the bandgaps using the partially self-consistent qp GW_0 and qp GW_0 -BSE calculations. For brevity we use GW_0 and GW_0 -BSE instead of qp GW_0 and qp GW_0 -BSE, respectively, in the rest of the article. In GW_0 , the eigenfunctions from ground-state calculations (i.e. DFT) are maintained, and G_0W_0 calculations are performed to compute QP energies, which is then updated in the calculation of the Green's function, G^3 . These calculations show a significant increase in the QP gap for most of the oxides as well as several other materials such as CsYZnSe₃ and RbTeAu (see Supplementary Table 2). As a result, the RMSD value for the QP gap obtained from the GW_0 calculation shoots up to 0.8 eV. A relatively low RMSD value of 0.32 eV is obtained for the optical gap, as the EBE's are high (~0.5 eV) for these materials.

Table 2 presents a comparison of the $E_g^{G_0W_0\text{-BSE}}$ and $E_g^{GW_0\text{-BSE}}$ with experimentally measured optical gaps. Experimental measurements of the optical gaps were available in the literature for 10 of

Table 2. Comparison between optical gaps obtained from G_0W_0 -BSE, $E_g^{G_0W_0-BSE}$, GW_0 -BSE calculation, $E_g^{GW_0-BSE}$, and the experimental values previously reported in the literature.

Material	$E_g^{G_0W_0-BSE}$	$E_g^{GW_0-BSE}$	Experimental
TiO ₂ (rutile)	3.07	3.91	3.03 ⁸⁵
TiO ₂ (anatase)	3.31	4.19	3.42 ⁸⁶
SrTiO ₃	3.24	4.21	3.30 ⁸⁷
CeO ₂	3.68	6.04	3.78 ⁸⁸
MoSe ₂	1.08	1.14	1.09 ⁸⁹
WSe ₂	1.18	1.25	1.20 ⁸⁹
ZnSe	2.30	2.65	2.82 ⁹⁰
ZnTe	2.22	2.49	2.39 ⁹⁰
AlAs	2.04	2.26	2.15 ⁹¹
AlSb	1.71	1.89	1.62 ⁹¹

All values are in eV. The $E_g^{G_0W_0-BSE}$ is in better agreement with the experimentally measured values in comparison to the $E_g^{GW_0-BSE}$.

the materials that we considered in this work—four oxides, three selenides, one arsenide, and an antimonide. The $E_g^{G_0W_0-BSE}$ has a better agreement (RMSD = 0.19 eV) with the experimentally obtained optical gaps than the $E_g^{GW_0-BSE}$ (RMSD = 0.86 eV). This might be due to the fact that the four oxides are wide bandgap materials and self-consistency tends to overestimate the bandgap in such materials⁴². The only materials for which the GW_0 -BSE provides better agreement with experiments is ZnSe and ZnTe. In case of MoSe₂ and WSe₂ self-consistency does not change the QP gap significantly and both G_0W_0 -BSE and GW_0 -BSE provide excellent agreement with experiments. Therefore, in all the subsequent calculations reported in this study we have restricted ourselves with G_0W_0 level of calculation to find the QP energies.

Design of the screening criteria

We designed three screening criteria to identify the photocatalysts with the most suitable optical properties among the 48 materials considered in this study. Below we describe these criteria in detail.

As we have already discussed, high EBE is not desirable for photocatalytic or photovoltaic applications. Therefore, we consider materials that have an EBE of less than 200 meV as suitable candidates for photocatalysis. The motivation behind choosing 200 meV as the EBE criteria limit came from looking at the experimental EBE of materials that are currently accepted as a viable choice for photocatalytic applications, such as the anatase phase of TiO₂ (EBE = 180 meV)⁴³ and MoS₂ (EBE = 240 meV)⁴⁴. The cut off of 200 meV was chosen because we wanted to look for materials that are as good as (if not better than) the most promising photocatalysts known in the literature (e.g. TiO₂). We find that 26 of the 48 materials considered in this study have an EBE of less than 200 meV. We examine these materials in detail in the Outcome of Screening for Optical Properties section.

While it is necessary for a photoabsorber or photocatalytic material to have an optical gap in the visible-light region to absorb a significant amount of sunlight, it is not sufficient. It is also necessary that the material is able to absorb visible light of all possible polarizations. The amount of incident radiation of a certain frequency and polarization that will be absorbed by a material is determined by its absorption coefficient at that particular frequency and polarization.

Considering this, we propose to use an additional screening criteria to search for good photoabsorber/photocatalytic materials, one that is based on their integrated absorption coefficient, α_{int}

for light polarization along the x ($\parallel \hat{a}$), y ($\parallel \hat{b}$) and z ($\parallel \hat{c}$) crystal axes, namely α_{int}^x , α_{int}^y , and α_{int}^z .

α_{int} is computed by integrating the frequency dependent absorption coefficient ($\alpha(\omega)$) in the 1.7–3.5 eV range¹⁸ for polarization of light along x ($\parallel \hat{a}$), y ($\parallel \hat{b}$), and z ($\parallel \hat{c}$) axes. To compute $\alpha(\omega)$ one needs both the real ($\epsilon_1(\omega)$) and the imaginary ($\epsilon_2(\omega)$) part of the dielectric function. In case of light polarization along x ,

$$\alpha_{\text{int}}^x = \int_{\omega_{\text{min}}}^{\omega_{\text{max}}} \alpha^x(\omega) d\omega \text{ where } \alpha^x(\omega) = \frac{2\pi \left(\sqrt{(\epsilon_1^x(\omega))^2 + (\epsilon_2^x(\omega))^2} - \epsilon_1^x(\omega) \right)^{1/2}}{\lambda} \quad (2)$$

where ω and λ are the frequency and wavelength of incident radiation. Here, we obtain $\epsilon_2(\omega)$ directly by solving BSE and use the Kramers-Kronig relation to calculate $\epsilon_1(\omega)$.

Through this integration of the $\alpha(\omega)$ in the energy range of visible photons and averaging for different light polarization, one can eliminate all the materials that have excitons in the desired energy range but are optically inactive or ‘dark’. Optically ‘dark’ excitons exist as a solution to the BSE but have zero oscillator strength, hence, do not contribute to optical absorption^{45,46}.

To find a suitable cutoff value of $\alpha_{\text{int}}^{\text{avg}}$ (defined as $\frac{\alpha_{\text{int}}^x + \alpha_{\text{int}}^y + \alpha_{\text{int}}^z}{3}$) for identifying promising photocatalysts we again look at the most widely studied material for this application, the anatase phase of TiO₂. However, the anatase TiO₂ is not used as a visible-light photocatalyst. The optimum performance for this material can only be achieved under exposure to UV radiation. Therefore, we have computed the $\alpha_{\text{int}}^{\text{avg}}$ in the range of 3.5–4.2 eV for TiO₂ and used that as the cutoff. We find the value of $\alpha_{\text{int}}^{\text{avg}}$ for TiO₂ (in the UV range) is $3.6 \times 10^4 \text{ cm}^{-1} \text{ eV}$ which is almost three times smaller than the $\alpha_{\text{int}}^{\text{avg}}$ for silicon ($10.5 \times 10^4 \text{ cm}^{-1} \text{ eV}$ in the visible range), the most widely used photoabsorber of this time. The $\alpha_{\text{int}}^{\text{avg}}$ for silicon was computed using experimental data for $\alpha(\omega)$ ⁴⁷ in the 1.7–3.5 eV range.

Anisotropic absorption of light is undesirable as it would make certain surfaces of a poly-crystalline sample less capable of absorbing incident unpolarized solar radiation, and hence, reducing the efficiency of the solar-to-chemical energy conversion process. Thus, we consider an additional screening criteria, $\alpha_{\text{int}}^{\text{aniso}}$, that assess the anisotropy in the integrated absorption coefficients along x , y , and z polarization axis. Here, $\alpha_{\text{int}}^{\text{aniso}} = \frac{\text{minimum}(\alpha_{\text{int}}^x, \alpha_{\text{int}}^y, \alpha_{\text{int}}^z)}{\text{maximum}(\alpha_{\text{int}}^x, \alpha_{\text{int}}^y, \alpha_{\text{int}}^z)}$.

By computing $\alpha_{\text{int}}^{\text{aniso}}$ one can eliminate materials that absorb lights with preferential polarization. We chose an $\alpha_{\text{int}}^{\text{aniso}}$ of > 0.8 as the criteria of selection for this study.

In summary, the three criteria that we propose for screening photocatalysts with suitable optical properties are,

- (1) EBE < 200 meV
- (2) $\alpha_{\text{int}}^{\text{avg}} > 3.6 \times 10^4 \text{ cm}^{-1} \text{ eV}$
- (3) $\alpha_{\text{int}}^{\text{aniso}} > 0.8$

Outcome of screening for optical properties

In Fig. 2 we present the calculated optical gaps, $E_g^{G_0W_0-BSE}$, and the EBE of all the 48 materials. The bar heights denote the $E_g^{G_0W_0-BSE}$ and their colors denote the EBE. Most of the oxides considered here have high EBE’s, making them unappealing for photovoltaic and photocatalytic applications. We, however, find 26 materials with very low EBE’s of <200 meV. The EBEs of all the 48 materials computed from both G_0W_0 -BSE as well as GW_0 -BSE are listed in the Supplementary Table 2.

With the exception of NaCaAs, all the materials considered in this study that have a F43m spacegroup (AlSb, AlAs, ZnTe, ZnSe, and LiMgAs) have EBE < 200 meV. All of these materials have a Zinc-blend crystal structure except LiMgAs, which has an additional Mg atom at the center of the unit cell. AlAs and ZnTe

Fig. 2 The bar heights denote the optical gap, $E_g^{W_0-BSE}$ in eV, and their colors denote the exciton binding energy (EBE) as obtained from G_0W_0 -BSE calculations for the 48 materials. We find that 26 of the 48 materials have EBE less than 0.2 eV. The radial heights corresponding to 1.5, 2.5, and 3.5 eV optical gaps are labeled in the figure. The indirect absorption edges are shown as white bars for each material. For direct gap materials, they are equal to the optical gap.

with Wurtzite crystal structure (spacegroup $P6_3mc$) also have quite low EBE's, 145 and 169 meV respectively. Among the materials with low EBE (<150 meV) we find two group-II-IV-V₂ ternary compounds with body centered tetragonal chalcopyrite structure (spacegroup $I\bar{4}2d$) namely, $MgSiAs_2$ and $BeSiAs_2$. These two materials are known to be promising materials for spintronics, electronic and optoelectronic applications such as infrared-nonlinear optical material, solar energy converters, infrared detectors, visible and invisible light-emitting diodes^{48,49}.

A group of telluride materials ($Zn(GaTe)_2$, $Cd(GaTe)_2$, and $Sr(InTe_2)_2$), which are generally synthesized by preparing solid solutions of A_2Te_3 ($A = Ga, In$) with other $A''B^{IV}$ tellurides⁵⁰, also exhibit low EBE's (140–180 meV). The layered chalcogenides ($GaTe$, $GaSe$, $MoSe_2$, and WSe_2) have EBE < 200 meV as well. Interestingly, the different phases of these chalcogenides do not have significantly different EBE. Most of the layered dichalcogenides ($MoSe_2$, WSe_2) with hexagonal crystal unit cell (spacegroup $P6_3/mmc$) have EBE in the range of (130–150 meV). $MoSe_2$ in a hypothetical phase with rhombohedral unit cell (spacegroup $R3m$) has a slightly larger EBE of 208 meV.

In three-dimensional (3D) systems such as bulk semiconductors, the Coulomb interaction between an electron and a hole is effectively screened ($\epsilon \sim 10$) by other electrons and therefore results in a weakly bound exciton (EBE ~ 0.1 eV). However, in low-dimensional materials or 2D materials the electronic screening is less effective as the e-h pair can interact partially through vacuum. Consequently, 2D materials show more pronounced excitonic effects and EBEs order of magnitude larger than their bulk counterpart^{51,52}. State-of-the-earth first principles GW-BSE calculations have been employed successfully in exploring excitonic effects in 2D materials such as hexagonal BN sheet⁵¹, graphene⁵³, monolayered MoS_2 ²⁵, and semi metallic graphene⁵⁴. In our study, we have examined the bulk layered form of the 2D

materials. But one can expect a much higher EBE for the 2D forms of these materials.

Figure 3 shows the α_{int} computed for the case of light polarization along x (red bars), y (blue bars), and z (green bars) axis for all 48 materials under consideration. We find that among materials with low EBE (<200 meV) 14 materials have α_{int}^{avg} values larger than the cutoff of $3.6 \times 10^4 \text{ cm}^{-1} \text{ eV}$.

In Fig. 4 we show the absorption spectra of four representative materials, $BeSiAs_2$ (mp-1009087), $GaSe$ (mp-11342), $BiTeBr$ (mp-33723) and $AlSb$ (mp-2634). The excitation energies for each of these materials are shown as vertical lines in the yellow panels underneath their spectra.

First, let us examine the case of $BeSiAs_2$ (Fig. 4a). For this material, we can see the lowest energy exciton is at 1.54 eV, its optical gap, and there are quite a few excitons in the 2–2.5 eV energy range. However, most of these excitons are 'dark', i.e. they do not yield an appreciable α_{int} . Most of the 'bright' excitons for $BeSiAs_2$ lie above ~ 3 eV and thus this material has a low α_{int} value in the visible-light region. Hence it does not meet the cutoff for criteria 2.

In the case of $GaSe$, which has a 1.67 eV optical gap, there are very few bright excitons below 2 eV and some bright excitons above 2.7 eV, see Fig. 4b. The low number of excitons in the visible frequency range results in a poor α_{int} value. Thus, this material also does not meet the criteria 2 cutoff.

Transition metal dichalcogenides $MoSe_2$ and WSe_2 and other layered material such as $BiTeBr$ (Fig. 4c) absorb significantly poorly if the light polarization is along the z-axis ($\sim 30\%$ compared to light polarization along x or y). This results in a low α_{int}^{aniso} for many of the layered materials. For example, $GaTeCl$ and $CsYZnSe_3$ which are also layered materials show significantly lower absorption if the light polarization is along the axis with the vdW bonding. In the case of $GaTeCl$ ($CsYZnSe_3$) we see 66 (79) % and 92 (38) %

Fig. 3 Integrated absorption coefficient (α_{int}) in case of light polarization along x (red bars), y (blue bars), and z (green bars) axis for all the materials under consideration. We have integrated the absorption coefficient over the 1.7–3.5 eV energy range to show the degree of anisotropy in absorption for the visible region of the solar spectrum. Horizontal dashed lines denote the α_{int} values for silicon (magenta) and TiO_2 (black).

Fig. 4 The imaginary part of the dielectric function, $\epsilon_2(\omega)$, for light polarization along x (red), y (blue), and z (green) axis obtained from G_0W_0 -BSE calculation for four selected materials. **a** BeSiAs (mp-1009087), **b** GaSe (mp-11342), **c** BiTeBr (mp-33723), and **d** AlSb (mp-2624). The yellow panel on the bottom of each figure shows the excitation energies with vertical lines.

decrease in total visible-light absorption if the light polarization is along the y and z-axis respectively compared to if the polarization is along the x-axis. Ga_2Se_3 , RbInTe_2 , $\text{Sr}(\text{InTe}_2)_2$, ZnTe , Ta_2SnO_6 are some of the other materials which have a preference in absorbing visible lights of certain polarization than the others.

The absorption spectra of one of the gifted materials AlSb (mp-2634), which satisfies both the criteria 2 and 3 has been shown in Fig. 4d. It has an EBE of 110 meV, α_{int}^{avg} of $7 \times 10^4 \text{ cm}^{-1} \text{ eV}$, and α_{int}^{aniso} of 1 (cubic system).

The absorption spectra of all the 48 materials can be found in the Supplementary Fig. 3. The Supplementary Table 3 lists the α_{int}^{aniso} , α_{int}^{avg} , α_{int}^x , α_{int}^y , and α_{int}^z in the visible-light (1.7–3.5 eV) range of all the 48 materials.

In Fig. 5 we show a color-coded map to indicate which of the screening criteria are satisfied by each of these 48 materials.

Materials that satisfy the EBE criteria are shaded in blue. Materials that satisfy both criteria 2 and 3 of meeting the cutoff of α_{int}^{avg} and α_{int}^{aniso} in the visible-light region (1.7–3.5 eV) are shaded in orange. Materials that satisfy criteria 2 and 3 in the UV region (3.5–4.2 eV) are shaded in green. In this color-coded map, we can see that only six materials meet the three criteria for visible-light photocatalysis. These six materials are AlSb, GaTe, $\text{Zn}(\text{GaTe}_2)_2$, $\text{Cd}(\text{GaTe}_2)_2$, and LiInTe_2 . All of these materials have been previously synthesized¹⁸. SiAs and GaTe are layered materials. These layered materials can be extracted in two-dimensional forms, which are known to offer high specific surface area, tunability, and potential for heterostructuring^{55–57}. In a recent computational study, Torrisi et al. have shown the two-dimensional SiAs is selective for CO production and has good absorption in the visible-light region⁵⁵. On the other hand, two-dimensional GaTe has been shown to

TiO ₂ mp-2657	TiO ₂ mp-34688	TiO ₂ mp-390	SrTiO ₃ mp-5229	NaTaO ₃ mp-4170	Ta ₂ SnO ₆ mp-556489	CeO ₂ mp-20194	CeThO ₄ mp-36734
Ca ₄ As ₂ O mp-8789	AlAs mp-2172	AlAs mp-8881	SiAs mp-1863	Cd ₂ AsCl ₂ mp-27776	BeSiAs ₂ mp-1009087	MgSiAs ₂ mp-1016197	LiMgAs mp-12558
NaCaAs mp-961685	AlSb mp-2624	Rb ₃ Sb ₂ Au ₃ mp-9274	MoSe ₂ mp-1634	MoSe ₂ mp-1018807	MoSe ₂ mp-7581	WSe ₂ mp-1821	ZnSe mp-1190
Zn(GaSe ₂) ₂ mp-15776	CsYZnSe ₃ mp-574620	CsGaSe ₃ mp-510283	GaSe mp-1943	GaSe mp-11342	Ga ₂ Se ₃ mp-1340	Ga ₂ TeSe ₂ mp-28423	Cs ₂ Cd ₃ Te ₄ mp-567386
CsLaCdTe ₃ mp-12491	LiInTe ₂ mp-20782	RbInTe ₂ mp-22255	Sr(InTe ₂) ₂ mp-35663	RbTeAu mp-9008	ZnTe mp-571195	ZnTe mp-8884	ZnTe mp-2176
Zn(GaTe ₂) ₂ mp-15777	Cd(GaTe ₂) ₂ mp-13949	GaTe mp-542812	YbTe mp-1779	GaTeCl mp-27449	InTeBr mp-29236	BiTeBr mp-33723	Hg ₃ (TeBr) ₂ mp-27853

Fig. 5 The figure shows a color-coded map that indicates which of the screening criteria are satisfied by the 48 materials. The materials that satisfy the EBE criteria 1 are shaded in blue. The materials that satisfy both criteria 2 and 3 of meeting the cutoff of $\alpha_{\text{int}}^{\text{avg}}$ and $\alpha_{\text{int}}^{\text{aniso}}$ in the visible-light region (1.7–3.5 eV) are shaded in orange. The materials that satisfy criteria 2 and 3 in the UV region (3.5–4.2 eV) are shaded in green.

exhibit a sharp decrease in photoluminescence during the transition from the many to few-layer limit⁵⁵.

The materials that satisfy all the criteria in the UV region are markedly more, total 18. In Fig. 5 these materials are shaded in blue and green colors. We observe that most of the oxides do not make the list but several arsenides, tellurides, and selenides emerge as suitable candidates. Supplementary Table 4 lists the $\alpha_{\text{int}}^{\text{aniso}}$, $\alpha_{\text{int}}^{\text{avg}}$, $\alpha_{\text{int}}^{\text{x}}$, $\alpha_{\text{int}}^{\text{y}}$, and $\alpha_{\text{int}}^{\text{z}}$ in the UV-light range (3.5–4.2 eV) of all the 48 materials.

Approximating EBE using Wannier–Mott Model

In case of most inorganic semiconductors, excitons can be approximated as an electron in the conduction band that is bound with a hole in the valence band through some form of screened Coulomb interaction and can be described using the WM model⁵⁸. This model uses effective mass approximation which describes electrons and holes as free particles that have a parabolic dispersion and are characterized by effective masses that depend on the crystal structure.

Within this approximation, the wavefunction of relative e–h motion or exciton can be found from the Schrodinger equation very similar to the one describing the electron state in a hydrogen atom where we replace the electron mass, m_0 , with reduced effective mass, $\mu = \frac{m_e m_h}{m_e + m_h}$, and replace the unscreened Coulomb interaction, $\frac{e^2}{r}$, between the e–h pair with the screened one, $\frac{e^2}{\epsilon r}$. Where m_e (m_h) is the electron (hole) effective masses and ϵ is the dielectric constant of the material. By solving the hydrogen atom like Schrodinger's equation we find the binding energy of the ground excited state (EBE_{WM}),

$$\text{EBE}_{\text{WM}} = \frac{\mu e^4}{2\hbar^2 \epsilon^2} \quad (3)$$

Computationally it is much less expensive to obtain EBE using the WM model than solving the BSE. The input parameters in WM model are the dielectric constant and the effective masses, which can be obtained with reasonable accuracy using less expensive DFT calculations⁵⁹. Here, we test the applicability of WM model for the materials under consideration and the possibility of using WM instead of the expensive BSE calculations for future solar-materials discovery.

The WM approximation and the validity of Eq. 3 depends on the assumption that the interaction potential is slowly varying over the dimension of an unit cell or in other words the dimension of lowest energy exciton is much larger than the lattice dimension⁵⁸. If we assume the validity of the WM model and use $\mu \sim m_e$ and

$\epsilon \sim 10$ in Eq. 3, we get $\text{EBE} \sim 0.1$ eV, which is of the same order of magnitude as the computed EBE of the materials we have considered in this study (0.11–0.59 eV), which motivates us to test the validity of the WM model for these materials.

To find the degree of correlation between the EBE computed using BSE (EBE_{BSE}) and WM model (EBE_{WM}) we calculate the Pearson's correlation coefficient (PCC) and the Spearman's correlation coefficient (SCC)⁶⁰. PCC indicates the strength of linear relationship between two variables whereas, SCC does not assume any particular functional dependence to quantify the strength of the correlation. We find a PCC value of 0.85 and SCC value of 0.76 between the EBE_{BSE} and the EBE_{WM} , which suggests a strong correlation between the two. The high PCC value also suggests that we can scale the EBE obtained from WM model by a scaling factor (3.04) (see Supplementary Table 5) to get a reasonable prediction for the values obtained by solving the BSE. We find that such a scaling of the EBE_{WM} to obtain the EBE_{BSE} results in a mean squared error of 0.11 eV and root mean squared deviation of 0.12 eV, which is similar to the accuracy of standard GW-BSE calculation. Moreover, we have computed the confusion matrix between the EBE_{BSE} and predicted (scaled) EBE from the WM model. To compute the confusion matrix we use 200 meV as the cutoff to classify the materials as low (high) EBE materials. In the Supplementary Fig. 1 we have shown the (a) confusion matrix and, (b) the parity plot between the EBE_{BSE} and predicted (scaled) EBE from the WM model. Based on the confusion matrix, we find that for 37 out of 48 materials (~77%) the WM model with the scaling predicts the correct classification. Therefore, it would be quite reasonable to use WM model for a computational data-driven discovery of materials that have low EBE instead of using the computationally much more expensive BSE calculations.

In case of the other two screening criteria based on the absorption coefficients used in this study, $\alpha_{\text{int}}^{\text{avg}}$ and $\alpha_{\text{int}}^{\text{aniso}}$, one requires the entire frequency dependent absorption spectra ($\epsilon(\omega)$). Unfortunately, most of the less expensive methods such as RPA don't take e–h interaction into account and therefore provide grossly inaccurate spectra and thus we can not develop a simple surrogate model for these quantities and have to solve the massively expensive BSE.

In summary, we have explored excitonic effects in the optical properties of 48 promising CO₂ reduction photocatalysts. We have designed a screening strategy considering the optical properties of materials that are crucial for such photocatalysts, i.e, the exciton binding energies, the capability to absorb visible light, and the degree of anisotropy in the absorption of light with different polarizations.

Using this screening strategy we have identified six materials that are suitable for visible-light photocatalysis. Interestingly, to our knowledge, none of these materials have been extensively studied to be used as photocatalysts for CO₂ reduction. Three of these materials have been studied before, using various theoretical and experimental methodology, i.e. SiAs^{61,62}, AlSb^{63,64}, and GaTe⁶⁵. However, the other three materials LiInTe₂, Zn(GaTe₂)₂, and Cd(GaTe₂)₂ have remained largely unexplored. It is noteworthy that all of these materials have been previously experimentally synthesized^{64,66–70}. Our screening strategy also identifies 18 materials that are suitable for UV-light photocatalysis.

GW-BSE calculations have been extremely successful in predicting excitonic and optical properties of materials with *s* or *p* electrons, however, a similar success has not been reproduced when applied to *d*-electron systems⁷¹. Nevertheless, the BSE has been proven to be reasonably successful in exploring strong excitonic effects observed in Cu₂O⁷², GaN³⁴, YMnO₃⁷³, rutile and anatase TiO₂⁷⁴. In case of TMOs, when compared to experimental absorption spectra calculated using GW-BSE, the position of excitonic peaks are found to be accurate within ~0.2 eV. To make GW-BSE calculation more accurate when applied to TMOs, several methods have been proposed such as using more appropriate mean-field starting points such as DFT + U or HSE, self-consistent GW calculation, going beyond GW approximation and using vertex correction. However, none of these solutions have been shown to be a universal method appropriate for all TMOs⁷¹. One should also note that, there exists significant technical difficulties that hamper a precise measurement of optical spectra for TMOs due to chemical defects (e.g. oxygen vacancies or presence of TM impurities)⁷⁵. Therefore, our reported data using the state-of-the-art GW-BSE framework represents a first comprehensive map of the optical and excitonic properties of these materials and should serve as a reference for future calculations and experiments.

Using the relatively large amount of the high-quality EBE data from BSE calculations generated in this work, we show that the WM model can be used for estimating exciton binding energies in a computationally cheaper manner for large-scale computational material discovery of photoabsorber materials without the need of performing the extraordinarily expensive BSE calculations.

Overall, our work presents a paradigm towards the inclusion of optical properties for data-driven discovery of materials for solar energy conversion applications.

METHODS

Ground-state calculations using DFT

All the first-principles calculations reported in this study were performed using Vienna Ab initio Simulation Package^{33,38,76}. The Kohn–Sham wavefunctions and eigenvalues were obtained using a plane wave basis with an energy cutoff of 520 eV. We employ the non-local vdW-DF-optB88 exchange–correlation functional^{39,40} as it provides an excellent description of the vdWs interactions in layered materials. The Brillouin zone was sampled using a *k*-grid with 100 kpoints per Å^{−3} of the reciprocal cell. The crystal structures were obtained by relaxing the atomic positions and the lattice parameters by a energy convergence cutoff of 0.0005 eV × number of atoms in the cell, which has been found to produce well-converged structures in most instances⁷⁷.

The macroscopic dielectric constants reported here were calculated using density functional perturbation theory following the formalism originally introduced by Baroni et al.⁷⁸ and later implemented for projector-augmented wave methodology by Gajdoš et al.⁵⁹. The electron and hole effective masses were computed using parabolic line fitting at the direct band edges. We used the SUMO code⁷⁹ to perform the effective mass calculations. In case there are degenerate bands at the conduction or the valence band edge, the SUMO code computes effective masses by performing parabolic fitting on all these bands. We use the lightest effective masses to estimate the minimum EBE.

Excited state calculations using GW-BSE

The quasiparticle energies were obtained by using many-body perturbations theory within both G₀W₀ and GW₀ approximation for the self-energy operator^{29,31,38}. The basis set size for the response functions and *W* was chosen to include all plane waves up to an energy cutoff of 340 eV. The number of unoccupied bands included in the GW calculation was selected such that the QP gap is converged to within 0.1 eV. The excitonic effects were studied by solving Bethe–Salpeter equation within Tamm–Dancoff approximation^{33,80}. We included all the occupied/unoccupied bands which were within 1.5 eV from band edges in the BSE calculation to ensure convergence of the absorption spectra. However, the convergence of the BSE absorption spectra with the number of *k*-points (*N*_{*k*}^{BSE}) is often quite challenging and computationally expensive³³. Nonetheless, in this study we selected the *N*_{*k*}^{BSE} such that the EBE converged to within 0.1 eV. See Supplementary Table 6 for a list of all the converged parameters for each of the 48 materials.

High-throughput workflow

We have developed a Python code for performing automated first-principles calculations within GW-BSE framework and used it carry out all the calculations reported in this article. Our code is built upon open-source Python packages developed by the Materials Project, such as pymatgen⁸¹, fireWorks⁸², and atomate⁸³ to achieve complete automation of the entire multi-step GW-BSE computational framework that requires several convergence parameters. GW-BSE calculation is extremely sensitive to multiple interdependent convergence parameters such as number of bands (*N*_{bands}) included in the GW self-energy calculation, number of *k*-points (*N*_{*k*}^{BSE}) used to sample the Brillouin zone in the BSE calculation etc. Our workflow is capable of performing automated convergence test of all these parameters and using those values to carry out fully converged GW-BSE calculations. However, due to limitation of the computational resources available, we have restricted ourselves with converging *N*_{bands} and *N*_{*k*}^{BSE}, two most sensitive parameters in the GW-BSE calculation. For several other convergence parameters such as, number of (imaginary) frequency grid points in GW calculation, energy cutoff for response function we have chosen a value large enough to produce quasiparticle energies within 0.1 eV. To reduce the computational cost associated with performing convergence tests we have judiciously used COHSEX and DFT level calculations which are significantly cheaper than full GW-BSE calculation. Details about these choices to perform efficient convergence calculations for GW-BSE calculations will be included in a forthcoming manuscript. In this workflow, we have also employed Wannier90⁸⁴, a program for calculating maximally-localized Wannier functions to perform the interpolation required to obtain quasiparticle bandstructure.

DATA AVAILABILITY

All data supporting the findings of this work are available in the article and its Supplementary Information. Extra data and machine readable data are available upon reasonable request to the authors.

CODE AVAILABILITY

The high-throughput GW-BSE workflow code used in this study are available from the authors upon reasonable request.

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AUTHOR CONTRIBUTIONS

T.B. performed the simulations and calculations. Both the authors contributed to designing the research methods, interpreting the data, and writing the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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