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C_2N/WS_2 van der Waals type-II heterostructure as a promising water splitting photocatalyst

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ABSTRACT

Photocatalytic water splitting has long been considered as a source of pollution-free clean energy and finding an efficient photocatalyst for this reaction has remained a major challenge. Here, we study C_2N/WS_2 van der Waals heterostructure as a possible photocatalyst for water splitting. Using first principles calculations, we find that band edges of the heterostructure are found to satisfy both water oxidation and reduction energy levels, ensuring the occurrence of these two reactions. Additionally, it is found to be a type-II heterostructure, that enables the separation of electrons and holes in two different layers upon light irradiation and thereby facilitates water oxidation on WS_2 layer and water reduction on C_2N layer. The charge transfer occurs from WS_2 to C_2N monolayer, which serves dual purpose of separating photoinduced charge carriers and extending their lifetimes. The heterostructure also shows high charge carrier mobilities, indicating their efficient utilization in reduction and oxidation reactions before recombination. Most importantly, light absorption in visible range for the heterostructure is significantly enhanced compared to the constituent monolayers, rendering it to be a suitable photocatalyst for water splitting. Thermodynamic analysis for redox reactions suggest facile hydrogen generation on the heterostructure. Our study explains the underlying mechanism of the enhanced photocatalytic activity of C_2N/WS_2 heterostructure, which could further lead to designing of wider range of 2D heterostructured photocatalysts.

1. Introduction

Photocatalytic water splitting is a promising technology capable of providing inexpensive and clean energy using sunlight. The first breakthrough in this area came from Fujishima and Honda, who achieved the overall photocatalytic water splitting using a titanium dioxide (TiO_2) electrode [1]. Since then, a number of studies of water splitting have been reported on various semiconductor materials [2,3]. Traditionally, water-splitting photocatalysts were based on transition metal oxides[4]. However, as a result of oxygen being highly electronegative, these materials have large band gaps. Hence, they are less efficient for photocatalytic applications. Substitution of oxygen with nitrogen, sulphur and selenium leads to reduction in band gap due to their higher-lying 2*p* orbital levels compared to that of oxygen [5–7]. Sometimes this approach leads to very small band gap in bulk phase [8]. However, this can be overcome to some extent by making their nanomaterials, which may increase the band gap due to quantum confinement. Among nanomaterials, the use of 2D materials have garnered very particular interest in the field of photocatalysis. They help in minimizing the distance that photogenerated electrons and holes have to migrate before reaching the surface, thereby reducing the possibility of charge carrier recombination.

Recently, transition metal dichalcogenides (TMDs) have been widely investigated for their photocatalytic activities among two dimensional materials [9,10]. Charge separation and transport are greatly enhanced in these materials [10]. However, the active sites for hydrogen evolution reaction (HER) on TMDs are edge sites (unsaturated sulphur atoms), therefore yield of the water splitting reaction is limited on these materials [9]. Another class of materials that have gained a lot of attention in recent times are the graphitic carbon nitrides like C_3N_4, C_3N_3 and C_2N [11–13]. The advantage of these materials over TMDs is the availability of more active sites per area, are synthesized from only earth-abundant elements and are stable in reaction conditions. However, there is no inherent tendency for charge carrier separation in these materials [14].

Since none of the 2D materials have sufficient photocatalytic activity for practical applications, it is advantageous to make heterojunctions of 2D structures [15,16]. These are known as van der Waals (vdW) heterojunctions, and they utilize the

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characteristics of constituent 2D materials leaving their electronic properties unaffected to a large extent [17]. Depending on the relative positions of band edges of the two constituent 2D layers, different types of heterojunctions can be formed [4]. If the conduction band minima (CBM) (or valence band maxima (VBM)) of one layer is lower (or higher) than that of the other layer, then it is called a type-I heterojunction. In type-II heterojunction, both CBM and VBM of one layer are lower than the respective band edges of the other layer. Therefore, VBM and CBM of the heterostructure will be at different layers. While in type-III heterostructures, both the VBM and CBM of one layer are lower than VBM of the other layer. Since electrons (or holes) tend to move downward (or upward) to lower energies [4], therefore in type-I heterostructures electrons and holes end up accumulating in the layer with smaller band gap. As a result, the chances of recombination increases and no improvement in photocatalytic activity is observed. The photogenerated electrons and holes in type-III heterostructures are not able to transport across the interface due to their band alignment and hence provide no advantage over using the isolated layers.

The type-II heterojunctions inherently separate electrons and holes [18], which lead to the two redox reactions of water:

$$H_2O + 2h^+ \rightarrow 2H^+ + \left(\frac{1}{2}\right)O_2 \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

at two different layers. This can avoid the unwanted surface back reactions to a large extent [19]. Various such type-II heterojunctions like CdS/TiO_2 [20], CdS/ZnO [21], C_3N_3/C_3N_4 [22] and C_3N_4/C_2N [23] have been reported to show charge separation by following similar mechanism. However, often they suffer from drawbacks such as lack in enhanced harvesting of visible light or not having sufficient charge carrier mobilities to have high photocatalytic activity.

Using first principles calculations, we show here that by combining a TMD (WS_2) and a graphitic carbon nitride (C_2N), these two hurdles can be overcome, simultaneously. C_2N was found to have charge carrier mobilities comparable to graphene and our results also showed it to have better optical properties than g-C_3N_4 on account of lower exciton binding energies [24,25]. WS_2 was chosen as it has similar band gap to that of C_2N, and its charge carrier mobilities were also found to be high among TMDs, next only to PtS_2 and $PtSe_2$ [26]. The C_2N/WS_2 heterostructure forms a type-II heterostructure, which leads to separation of charge carriers to two monolayers and hence would prevent their recombination. A charge transfer was found to take place from WS_2 to C_2N layer, which would further diminish any chances of charge carrier recombination. Based on the band alignments of the heterostructure, we found that C_2N layer facilitates hydrogen evolution reaction (HER), which has very high catalytic sites compared to other photocatalysts. The other constituent monolayer WS_2, facilitates oxygen evolution reaction (OER). Our theoretical analysis also provides fundamental insights into the underlying mechanism for efficient photocatalysis at type-II heterostructures.

2. Methodology

The first principles calculations were performed using density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [27]. Electron-ion interactions were described using all electron projector augmented wave (PAW) pseudopotentials [28] and electronic exchange and correlation were approximated by Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [29]. The periodic images were separated by a 15 Å vacuum along z-direction to prevent spurious interaction between periodic images. For relaxation of structures, the Brillouin zone was sampled by a $9 \times 9 \times 1$ Monkhorst-Pack grid for both monolayers and the heterostructure. All the structures were fully relaxed using a conjugate gradient scheme until the energies and forces converged to 10^{-5} eV and 0.005 eV Å^{-1}, respectively. Since PBE functional underestimates the band-gap due to the presence of artificial self-interaction [30], we used the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional, with 25% Hartree-Fock exchange energy contribution [31], to accurately determine the band-edge positions. We have used a $6 \times 6 \times 1$ Monkhorst-Pack grid to sample the Brillouin Zone of the monolayers and the heterostructure for performing calculations using the HSE06 functional. Also, since the standard PBE functional cannot describe weak interactions accurately, empirical atom-pairwise corrections proposed by Grimme in terms of the DFT-D2 scheme was utilized for describing the long-range van der Waals interactions [32].

To obtain the optical absorption spectra of the structures, we have calculated the frequency dependent dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part of the dielectric function which arises due to the interband transition is calculated using the following equation [33]:

$$\epsilon_2(\hbar\omega) = \frac{2e^2\pi}{\Omega\epsilon_0}\sum_{\vec{k},v,c} |<\Psi^c_{\vec{k}}|\vec{u}\cdot\vec{r}|\Psi^v_{\vec{k}}>|^2 \delta(E^c_{\vec{k}} - E^v_{\vec{k}} - E) \quad (3)$$

where $\Omega, \omega, \vec{u}, v$ and c denote the volume of unit-cell, photon frequency, polarization vector of the incident electric field, the valence band and the conduction band respectively. The real part of the dielectric function, $\epsilon_1(\omega)$, was then calculated by Kramer-Kronig transformation.

The free energy calculations were also performed to check catalytic activity of the heterostructure. The free energies of adsorption of atomic hydrogen (ΔG_H) were calculated, using [34]:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \quad (4)$$

ΔE_H describes the energy needed to increase the coverage by one hydrogen atom, $\Delta E_H = E^*_{nH} - E^*_{(n-1)H} - 1/2E_{H_2}$, where E^*_{nH} and $E^*_{(n-1)H}$ denote total energy of the catalyst system with n and (n − 1) hydrogen atoms adsorbed, while E_{H_2} denotes the total energy of a gas phase H_2 molecule. ΔE_{ZPE} is calculated by $\Delta E_{ZPE} = E^{nH}_{ZPE} - E^{(n-1)H}_{ZPE} - 1/2E^{H_2}_{ZPE}$, where E^{nH}_{ZPE} denotes the zero-point energy of n adsorbed hydrogens on the catalyst neglecting the contribution of catalyst, and $E^{H_2}_{ZPE}$ denotes the zero-point energy of gas phase H_2 molecule. ΔS_H is approximated as $\Delta S_H \simeq -1/2S^*_{H_2}$, where $S^*_{H_2}$ is the entropy of H_2 in the gas phase at standard condition, and the gas phase value is taken as $S^*_{H_2} \approx 130$ J K^{-1} mol^{-1} [35]. For estimating OER activity, the reaction free energies (ΔG) were computed using [36,37]:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (5)$$

where ΔE is the intermediate adsorption energy (OH*, O* or OOH*) calculated from DFT, ΔZPE is the difference in zero point energy, ΔS is the change in entropy and $\Delta G_U = -eU$, where U is the electrode potential. ΔG_{pH} denotes the correction in free energy due to the H^+ concentration in solution and is given by $\Delta G_{pH} = 2.303k_BT \times pH$, where k_B is the Boltzmann constant and T is temperature of the medium which is taken to be 300 K. The zero point energies in both cases were evaluated by calculating the vibrational frequencies of intermediates (H* for HER and OH*, O* or OOH* for OER) using density functional perturbation theory (DFPT), with the catalyst surface fixed [38].