Ultrasonically-assisted synthesis of CeO$_2$ within WS$_2$ interlayers forming type II heterojunction for a VOC photocatalytic oxidation

Esmail Doustkhah$^a$, Ramin Hassandoost$^b$, Negar Yousef Tizhoosh$^b$, Mohamed Esmat$^c$, Olga Guselnikova$^e$, M. Hussein N. Assadi$^f$, Alireza Khataee$^{b,g}$

$^a$ Koç University Toprak Energy Center (KUTEM), Department of Chemistry, Koç University, 34450 Istanbul, Turkey
$^b$ Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran
$^c$ International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
$^d$ Materials Science and Nanotechnology Department, Faculty of Postgraduate Studies for Advanced Sciences (PSAS), Beni-Suef University (BSU), Beni-Suef 62511, Egypt
$^e$ Research School of Chemistry & Applied Biomedical Sciences, National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk 634050, Russia
$^f$ RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
$^g$ Department of Environmental Engineering, Gebze Technical University, 41400 Gebze, Turkey

**ARTICLE INFO**

**Keywords:**
CeO$_2$
Formic acid oxidation
Heterostructure
Layered WS$_2$
Ultrasonically intercalated CeO$_2$
Photocatalytic oxidation

**ABSTRACT**

Here, we investigate the band structure, density of states, photocatalytic activity, and heterojunction mechanism of WS$_2$ with CeO$_2$ (CeO$_2$@WS$_2$) as a photoactive heterostructure. In this heterostructure, CeO$_2$’s growth within WS$_2$ layers is achieved through ultrasonication of WS$_2$ and intercalating CeO$_2$’s precursor within the WS$_2$ interlayers, followed by hydrothermal treatment. Through a set of density functional calculations, we demonstrate that CeO$_2$ and WS$_2$ form an interface through a covalent bonding that can be highly stable. The electrochemical impedance spectroscopy (EIS) found that the CeO$_2$@WS$_2$ heterostructure exhibits a remarkably higher conductivity (22.23 mS cm$^{-1}$) compared to either WS$_2$ and CeO$_2$, assignable to the interface in CeO$_2$@WS$_2$. Furthermore, in a physically mixed CeO$_2$-WS$_2$ where the interaction between particles is noncovalent, the resistance was significantly higher (0.67 mS cm$^{-1}$), confirming that the heterostructure in the interface is covalently bonded. In addition, Mott-Schottky and the bandgap measurements through Tauc plots demonstrate that the heterojunction in CeO$_2$ and WS$_2$ is type II. Eventually, the CeO$_2$@WS$_2$ heterostructure indicated 446.7 μmol g$^{-1}$ CO$_2$ generation from photocatalytic oxidation of a volatile organic compound (VOC), formic acid, compared to WS$_2$ and CeO$_2$ alone.

**1. Introduction**

Solar-driven light in catalysis, i.e. photocatalysis, has a universal appeal for use as a free energy source, which can be incorporated into many applications such as fine chemicals production, energy carriers generation, and pollutants removal [1–4]. Although many semiconductors have suitable energy band gaps that fall in the UV–vis range for photocatalysis, their photocactivity is often less efficient due to the improper band edge (valence band or conduction band) alignment against the potential redox energy level of the target reaction [5,6]. Although there are several pathways for improving the photocatalytic performance in such semiconductors [7,8], among them, a promising solution is a heterojunction within a suitable heterostructure to align the bandgap. Furthermore, the lifetimes of photogenerated electron-hole in most catalysts are short and suffer from fast recombination, which heterojunctions can further improve [9]. However, a heterostructure is only efficient if each of its semiconductor’s band edges is suitably aligned so it can eventually transfer the photogenerated electrons/holes pairs to the reacting species. Another point in a successful heterostructure is the crystalline structure at the interface of the junction [10]. The electron transfer in the boundary will be less efficient if there is no suitable junction due to mismatching, cracked or loose interface. So far, the 2D dichalcogenide WS$_2$ forms promising heterostructures with other photoactive oxides and semiconductors such as TiO$_2$ [11], MoS$_2$ [12], SnS$_2$ [13], and CuO [14]. However, the heterostructure of CeO$_2$ with WS$_2$ in photocatalysis is rarely investigated [15]. Likewise, cerium oxide has

---

*Corresponding authors.
E-mail addresses: edoustkhahheragh@ku.edu.tr (E. Doustkhah), a_khataee@tabrizu.ac.ir (A. Khataee).

https://doi.org/10.1016/j.ultsonch.2022.106245
Received 20 October 2022; Received in revised form 21 November 2022; Accepted 25 November 2022
Available online 28 November 2022
1350-4177/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
attractive crystal and photocatalytic properties and has been found suitable for the heterostructure through materials nanoarchitecture [16–18].

Intercalation of (organo)metallic precursors in 2D layered materials’ interlayers is one of the pivotal approaches to synthesising heterostructures with oriented and uniform growth [19,20]. For such cases, the exfoliation of bulk structures into few/multilayer structures is crucial to intercalate the heterostructure’s precursor. Among the several methods, ultrasound waves as a powerful tool for synthesis of nanomaterials [21], can be also utilised for exfoliating bulk layers are a popular and efficient pathway [22–25]. Likewise, WS₂ is a 2D material that may act as a hard template while it can generate a heterojunction with the grown heterostructure [26]. However, in an efficient heterojunction, along with its well-synthesised architecture, the band edges and the energy bandgaps of the composing compounds must match one another to generate an enhanced photocatalytic activity [27,28]. Therefore, investigating such parameters in parallel with the synthesis method is vital to reach an optimal photocatalysis result.

Here, we have found that the heterojunction of CeO₂ with the WS₂ nanosheets leads to a type II heterojunction which generates a remarkable enhancement in the photocatalytic activity of formic acid decomposition with respect to pure WS₂ and CeO₂. We also demonstrated that the heterostructure in the interface creates a chemical bonding that makes the heterostructure more efficient, stable, and uniform. The Raman spectroscopy and X-ray diffraction results showed the formation of Ce-S bonding in the CeO₂@WS₂. This heterostructure exhibits better photocatalytic activity, 1.8 times of WS₂ and 2.2 times of CeO₂. It also reveals sustainability in the UV range toward photooxidation of volatile organic compound (VOC)—formic acid.

2. Materials and methods

2.1. Synthesis of samples

The detailed synthesis procedure of the CeO₂@WS₂ catalyst is reported in our previous work [15]. In brief, the WS₂ nanoflakes were obtained by ultrasound-assisted exfoliation (Sonica ultrasound bath, 300 W, Italy) of bulk WS₂ (Sigma-Aldrich, 99 %) in DMF (Merck, >99 %) for 2 h. After centrifuging the sample, the supernatant was removed, washed with EtOH, and dried at room temperature overnight. For synthesising CeO₂@WS₂, 0.1 g of the synthesised WS₂ nanoflakes were added to 60 mL 0.1 mol/L Ce(NO₃)₂.6H₂O (Merck, >99.9 %) in aqueous solution and sonicated for 3 h. After that, the mixture was heated to a Na₂P₂O₇⋅12H₂O (Merck, >99.99 %) solution (0.005 mol/L, 20 mL) and was stirred for 30 min. The final mixture was poured into a 100 mL hydrothermal autoclave and kept at 220 °C for 12 h. After cooling the autoclave, the liquid was removed by centrifuge and the remaining was washed with EtOH and deionised water and dried at 60 °C. The synthesis route for pure CeO₂, used in this work, was similar to the mentioned approach without adding WS₂ nanoflakes.

2.2. Characterisation

Scanning electron microscopy (SEM) images were obtained using a TESCAN MIRA3 microscope (TESCAN Ltd., Czech Republic). X-ray diffraction (XRD) patterns were recorded with a SmartLab X-ray diffractometer (Rigaku Co., Japan, via a Cu Kα radiation source). Raman spectroscopy was recorded by the ANDOR Kymera-328i apparatus (AndorTech. Ltd., United Kingdom, at 532 nm excitation wavelength with 50 × objective, in the range of 100–2000 cm⁻¹). Transmission electron microscopy (TEM) and TEM-based elemental mapping and electron dispersive spectroscopy (TEM-EDS) were all recorded by a JEOL 2100 instrument coupled to an energy-dispersive X-ray analyser (EDX, JEOL Ltd, Japan).

2.3. (Photo)electrochemical measurements

Fluorine-doped tin oxide (FTO) glass with an area of 1.0 × 1.0 cm² was used as a substrate for the preparation of the working electrode. First, 20 mg of each catalyst sample was dispersed for 45 min in a solution including 1 mL of DI and 3 mL of isopropanol. Then, the FTO was washed and activated by diluted acid (HNO₃). 80 μL of stable dispersed catalyst was slowly drop-casted on the FTO and heated to 120 °C on a hotplate for 15 min.

An OrigaFlex-OGF01A Potentiostat/Galvanostat (France) was used to record the electrochemical analysis data. The electrochemical setup included a 0.5 mol/L Na₂SO₄ electrolyte, an FTO-based working electrode, a platinum plate with an area of 2.0 × 1.0 cm² as the counter electrode, and a reference electrode of saturated calomel electrode (SCE). Prior to each electrochemical test, the electrolyte solution was degassed by nitrogen bubbling for 20 min.

The electrochemical properties of samples were tested through the photocurrent test by cyclic chronoamperometry (CA) under both dark and light conditions, the EIS, and Mott-Schottky plots to determine the energy of flat band (E₃). Mott-Schottky plots were recorded at a frequency of 1000 Hz and the voltage range of −1 ~ +1 V vs SCE in dark. The EIS results were obtained using an AC voltage of ± 5 mV at open circuit potential (OCP) and 300 mV vs SCE in a frequency range from 100 kHz to 100 mHz. Photocurrent behaviours were tested under consecutive light on–off cycles (each cycle time: 100 s) for 600 s at 1000 mV vs SCE.

2.4. Computational settings

Spin polarised density functional calculations were performed using VASP code [29,30] with the projector augmented wave method technique [31]. The electronic correlation-exchange energy was approximated with general gradient approximation within the Perdew-Burke-Ernzerhof formalism [32,33]. The energy cutoff value and the fast Fourier transform mesh were generated by setting the precision key to Accurate. Ad hoc Hubbard terms, based on the Dudarev implementation [34], were added to C, O, Na, and F 5d electrons to account for the strong correlation. For Ce, U and J values were 4.20 eV and 0.00 eV, respectively. For W, U and J values were 2.87 eV and 0.00 eV, respectively. These values were reported to improve the electronic description of CeO₂ [35] and WS₂ [36], respectively. Van der Waals dispersion energy correction was applied based on the DFT-D3 method [37]. Only Γ point was used for the Brillouin zone sampling. For geometry optimisation, in addition to the atomic coordinates, the lateral lattice parameters, a and c, were also allowed to relax to forces smaller than 0.01 eV/Å. The Bader charge analysis code [38] was used to analyse charge localisations.

2.5. Formic acid photocatalytic oxidation

For formic acid photooxidation, 15 mg of the catalyst was initially dispersed and sonicated for 1 min in 5 mL of a formic acid aqueous solution (5 vol%, Merck, >98 %) in a Pyrex glass test tube (34 mL) and then bubbled with O₂ gas for 30 min. The glass tube was sealed with a rubber septum and photo-irradiated by a solar simulator (San-Ei Electric, >300 nm, 1000 W m⁻²), stirring at 800 rpm. The amount of evolved CO₂ in the headspace of the sealed tube was determined by a Shimadzu GC-2010 plus gas chromatograph equipped with a barrier ionisation discharge (BID) detector.

3. Results and discussion

3.1. Materials characterisation

We present the synthesis of ceria by the hydrothermal growth through intercalating Ce⁶⁺ in the interlayer space of WS₂, exfoliated by sonication in an aqueous solution. According to the XRD pattern, shown
in Fig. 1a, the synthesised material indicates a clear set of peaks corresponding to the CeO$_2$, WS$_2$ and CeS structures. Furthermore, given the non-equilibrium growth regime, intense nanostructuring and random growth of CeO$_2$ crystallites, the XRD pattern appears with strong background noise and some unidentified peaks, most likely belonging to the W-S-Ce-O alloys with nonstoichiometric compositions for which we do not have a reference structure for refinement. However, we attempted to refine the identified peaks using the Rietveld refinement Fullprof Suite [39] and the Match! package [40]. With acceptable quality parameters of Bragg factor of 20.3 and a $\chi^2$ of 7.5, the content was found to be 76.86 % (±0.03 %) CeO$_2$, 7.00 % (±0.02 %) WS$_2$, and 16.14 % (±0.02 %) CeS. The lattice parameters of these phases were found to be $a = 5.414598$ Å (±0.000527 Å) for the cubic CeO$_2$, $a = 2.970194$ Å ($\pm 0.005109$ Å) and $c = 7.579407$ Å ($\pm 0.009297$ Å) for the hexagonal WS$_2$, and $a = 5.799615$ Å (±0.004254 Å) for the cubic CeS. Also, the XRD pattern of physically mixed CeO$_2$ and WS$_2$ is shown in Fig. S1. We further investigated the changes in the vibrational modes originating from the heterojunction of CeO$_2$ and WS$_2$ using Raman spectroscopy (Fig. 1b). Accordingly, the peaks at 799, 801, 705, 317, 260, and 122 cm$^{-1}$ in WS$_2$'s spectra with a slight shift in some to lower wavenumbers and a decrease in intensity have appeared again in the CeO$_2$@WS$_2$ heterostructure. The 456 cm$^{-1}$ peak in CeO$_2$'s spectra is characteristic of the CeO$_2$ structure, which was also shifted lower to 442 cm$^{-1}$ and decreased in intensity in the final CeO$_2$@WS$_2$ heterostructure. Eventually, a new peak appeared at 912 cm$^{-1}$ which is not originating from either WS$_2$ or CeO$_2$ and is assignable to the newly formed Ce-S bond [41]. Therefore, the Raman spectra prove that there can be a covalent bonding between Ce and S species in the interface of CeO$_2$ and WS$_2$.

As shown in Fig. 1c-g, we studied morphology and the structure of the CeO$_2$-intercalated WS$_2$ (CeO$_2$@WS$_2$) through SEM and TEM. In TEM and SEM micrographs (Fig. 1d-h), we can see an agglomeration of uniform nanorods in each particle, hinting to the successful heterostructure formation of CeO$_2$ and WS$_2$ within each nanorod, as all these nanorods are approximately of the same size and shape. Phase separation would have probably caused different nano-shapes for WS$_2$ and CeO$_2$ as these phases have different crystal symmetry. The HRTEM in the inset of Fig. 1g shows two distinct lattice structures belonging to CeO$_2$ and WS$_2$ within the matrix, confirming the presence of the CeO$_2$@WS$_2$ heterostructure. The observed and specified $d$ values in the HRTEM image can be assigned to the planes with Miller indices of CeO$_2$ (1 1 1) and WS$_2$ (1 0 0) [42-44], indicating the interface in the heterostructures is normal to these planes. TEM-EDS of a selected area under a TEM microscope (Fig. S2) further confirms the co-presence of the related elements in a single particle, showing that the heterostructures have successfully interconnected. TEM-based elemental mapping further proves the presence of the Ce, O, W, and S elements in one particle (Fig. S2).

3.2. (Photo)electrochemical results

Appropriate separation of photogenerated charge carriers at the surface of particles is one of the most critical factors in photocatalytic performance. Photoluminescence (PL) is a valuable method to investigate the charge separation efficiency in materials. As reported before [45], CeO$_2$ possesses a board emission band from 400 to 700 nm with the most intensity in the 470 ~ 570 nm region. The charge transfer in the CeO$_2$ originated from the electron transfer between the Ce 4f energy level and O 2p orbitals [46]. Therefore, this board peak appears due to the existence of many defect energy levels between the mentioned orbitals [47]. According to our observation in the previous report [15], a remarkably diminished CeO$_2$ emission band appears after heterostructure formation with WS$_2$, converting into CeO$_2$@WS$_2$, attributable to the promoted charge separation, which is absent in CeO$_2$ alone. These good charge separation and adagio recombination rates between the photo-induced electron-hole pairs are the main origins of the boosted
photocatalytic efficiency. Moreover, according to our previous study, the CeO$_2$@WS$_2$'s bandgap obtained from Tauc's plots (2.9 eV) [15,48] is narrower than CeO$_2$ (~3.02 eV) and WS$_2$ (3.05 eV) [49]. Lastly, we ought to address the likely lack of contribution from the unintentional CeS phase toward the observed optical properties. CeS has a band gap of ~ 3.6 eV [50] which is wider than both WS$_2$ and CeO$_2$'s band gaps, falling outside the visible range and, thus, is not likely to contribute to photocatalysis.

The charge transfer efficiencies of samples were measured by the EIS since it directly influences charge transfer resistance ($R_{ct}$). As shown in Fig. 2a, the Nyquist plot of WS$_2$ includes a wide semi-circle diameter, demonstrating its higher resistance to charge transfer than other samples. CeO$_2$ also has a greater diameter, showing a high charge transfer resistance. However, the CeO$_2$@WS$_2$ heterostructure revealed a significant reduction in the charge transfer resistance by looking at the diameter of semi-circles which decreases. The $R_{ct}$ of WS$_2$ was found to be ~ 35000 $\Omega$ cm$^{-2}$, and for CeO$_2$, the $R_{ct}$ value was ~ 4500 $\Omega$ cm$^{-2}$. Eventually, the CeO$_2$@WS$_2$ heterostructure's $R_{ct}$ was significantly lower (45 $\Omega$ cm$^{-2}$) than both CeO$_2$ and WS$_2$ (inset of Fig. 2a). Interestingly, the physical mixture of WS$_2$ and CeO$_2$ showed an $R_{ct}$ of 1500 $\Omega$ cm$^{-2}$, confirming that the chemically bonded interface of WS$_2$ and CeO$_2$ plays a substantial role in the electronic structure of the heterostructure. In other words, the charge transport conductivity of the chemically bonded heterostructure (22.23 mS cm$^{-2}$) is by far higher than WS$_2$, CeO$_2$, and their physical mixture of CeO$_2$-WS$_2$ (0.67 mS cm$^{-2}$), which confirms the importance of chemical bonding of these two structures at the interface.

The transient photocurrent response vs time was measured for each photocatalyst sample as an index of their charge separation and transfer efficiency, as shown in Fig. 2b. In this investigation, the lowest response was observed for WS$_2$ inefficient e$^-$/h$^+$ pairs separation. Albeit, a similar behaviour was obtained for CeO$_2$. As predicted, a higher response for CeO$_2$@WS$_2$ heterostructure was observed, which signifies the heterojunction efficiency in the photoelectrocatalytic performance. However, when WS$_2$ was physically mixed with CeO$_2$, the photocurrent response had a significantly lower response than even the bare CeO$_2$. This observation was further evidence highlighting the role of a stable interface between CeO$_2$ and WS$_2$ through chemical bonding between Ce and S species.

The Mott-Schottky method helps identify the type of semiconductors (p or n) and their flat-band energies ($E_{fb}$). The Mott-Schottky plots of WS$_2$, CeO$_2$, and CeO$_2$@WS$_2$, depicted in Fig. 2c, show all semiconductors are n-type due to the potential-C$^-$ plots’ positive slope. Furthermore, the $E_{fb}$ can be determined by interrupting the liner part of potential-C$^-$ plots with the potential x-axis. The values of $E_{fb}$ and our previously reported bandgaps ($E_g$) [15] for these materials are listed in Table S1. In n-type semiconductors, $E_{fb}$ can convert to the conduction band (CB) energy using the $E_{CB} = E_{fb} - 0.2$ V [51]. Thus, the $E_{CB}$ of ~0.61, ~0.46, and ~0.69 V were obtained for WS$_2$, CeO$_2$, and CeO$_2$@WS$_2$, respectively. For calculating the valence band (VB) energy, at first, the $E_{CB}$ values convert to the normal hydrogen electrode (NHE) values using $E_{NHE} = E_{CB} + 0.241$ V [52]. Then, the $E_{VB}$ can be obtainable through the $E_{VB} = E_{CB} + E_{g}$. All described values are listed in Table S1. Considering the CB and VB levels as depicted in Fig. 2d, a plausible type (II) heterojunction can be proposed for the CeO$_2$@WS$_2$ heterostructure. In such a heterojunction, the photogenerated electrons (e$^-$) in CeO$_2$'s VB migrate to WS$_2$'s CB and make it the main reactive CB site. In contrast, the photogenerated holes (h$^+$) in CeO$_2$'s VB migrate to WS$_2$'s VB and make it a more reactive VB site [53,54]. Furthermore, the bandgap narrowing in the CeO$_2$@WS$_2$ sample in type (II) heterojunction is also justifiable. It is worth noting that the experimentally-obtained bandgap for CeO$_2$@WS$_2$ through the Tauc equation (2.9 eV) equals a value from CeO$_2$'s $E_{CB}$ to WS$_2$'s $E_{VB}$, which further confirms the type II heterojunction [15].

### 3.3. Theoretical insights

Here, we study the interface between CeO$_2$ and WS$_2$. In constructing our model, we considered the HRTEM image of the CeO$_2$@WS$_2$ heterostructure in Fig. 1h. We also restricted our models to high-symmetry and low lattice mismatch configurations. To construct the interface at the heterostructure, we first cleaved the WS$_2$ hexagonal structure (downloaded from Materials Project [55], compound id: mp-224) along
We then constructed a supercell with (2u × √2v) \( R_{30}^\circ \) dimensions out of the cleaved surface. The resulting surface had an orthogonal cross-section suitable to be interfaced with cubic CeO\(_2\) with \( u' = 6.381 \) Å and \( v' = 5.527 \) Å. We then cleaved the conventional CeO\(_2\) structure (\( a = 5.415 \) Å) along the [0 0 1] direction. We then interfaced these two surfaces together by expanding WS\(_2\) along the [0 0 1] direction to be three sheets deep and expanding CeO\(_2\) along the [1 0 0] direction to be 12 atomic layers deep. Since we intended to have only one interface in the supercell, we added an ample vacuum slab of 20 Å to avoid artificial interactions at the non-interfacing facets in the supercell. To reduce the lattice mismatch, we allowed the lateral cell parameters to relax during the geometry optimisation. The lattice mismatch in the relaxed structures had an acceptable average value of ~ 5.4 \%. 

Chemically there are two types of interfaces; either an oxygen-cleaved CeO\(_2\) facet interfaces with WS\(_2\), or a Ce-cleaved facet forms the interface with WS\(_2\). The first case has only one high-symmetry configuration, shown in Fig. 3a. The second scenario has two configurations, shown in Fig. 3b and c, respectively. In Fig. 3b, each Ce ion at the interface is coordinated by 3 S ions, while in Fig. 3c, each Ce ion is coordinated by 4 S ions. The Ce-coordinating S ions are marked in the upper row of Fig. 3. Among these three possible interfaces, configuration C was the most stable with total DFT energy of -531.610 eV, while configurations A and B each had higher total energy of -531.209 and -531.178 eV, respectively. In configuration A, the negatively charged facets at the interface create a Coulombic repulsion that reduces stability. The partial charges borne on S and O ions at the interface are given in Fig. 3a-ii. For configuration B, Ce’s undercoordination may be the origin of instability compared to Configuration A, as Ce\(^{4+}\) in a compound is more stable when coordinated by eight anions instead of seven [56].

Further examination of the most stable interface of configuration C in Fig. 3c-ii shows that the interface separation between CeO\(_2\) and WS\(_2\) is 2.74 Å, and the Ce–S bond is 2.93 Å long. This bond length is very similar to the Ce–S bond length in CeS, which is 2.89 Å [57]. Furthermore, the electronic localisation function (\( \eta \)) along the Ce–S bond (Fig. 3d, e) indicates two peaks around both Ce and S centres. This \( \eta \) profile deviates from a perfect ionic bond where \( \eta \) approaches 1 near the anion while approaching 0 near the cation [58]. This profile, however, is not perfectly covalent either. In covalent bonding, \( \eta \) is maximum at the bond centre and tapers off at both ends [58]. Consequently, we conclude that the bonding nature at the CeO\(_2\)@WS\(_2\) interface is only partially ionic (or partially covalent).

The partial density of states of the interfacing layers in Fig. 3f shows that the Ce 4f states are all empty and located above the Fermi level (marked with a green circle). However, some of the Ce 5d states are still occupied and located below the Fermi level (marked with a cyan arrow), explaining the less than + 4 oxidation state indicated by Bader charge analysis (Fig. 3c-ii). Similarly, some of W’s 5d states are also below the Fermi level, as marked by a blue arrow, indicating a deviation from the pure ionic + 4 oxidation state. This deviation is probably caused by the covalency between S and W. Partial oxidation of W and S, in turn, raises the Fermi level to the bottom of the conduction band, intercepting W’s 5d states and creating n-type carriers, facilitating the observed photocatalytic activity.

Fig. 3. The top (upper rows) and side (lower rows) views of the CeO\(_2\)@WS\(_2\) interface configurations are shown (a), (b), and (c). The interface in (c) was found to be the most stable. (d) The electronic localisation function (\( \eta \)) at the interface region in (c). (e) The \( \eta \) line profile of the Ce–S bond at the CeO\(_2\)@WS\(_2\) interfaces. (f) The partial density of states of the interface shown at (c).
3.4. Photocatalytic experiments

We studied the impact of the heterostructure in the WS$_2$ intercalated CeO$_2$ layered materials for the photocatalytic formic acid decomposition. When the heterostructure of two or more different structures is constructive, the photocatalytic activity boosts due to their longer electron/hole lifetime and efficient charge separation. Consequently, the photocatalytic activity improves. The oxidation of formic acid into CO$_2$ under photocatalytic conditions is a benchmark reaction that can be useful to judge the photocatalytic capability of the semiconductors that are supposed to be photocatalysts. This photocatalytic test is also suitable for comparing the photocatalysts under identical conditions.

The photocatalytic activity of CeO$_2$@WS$_2$ was investigated under UV–vis range irradiation. The formic acid oxidation power of the CeO$_2$@WS$_2$ was first investigated in the absence and then the presence of light (Fig. 4a). We observed that, within 90 min, the dispersion of CeO$_2$@WS$_2$ results in 6.7 µmol (or 446.7 µmol g$^{-1}$) CO$_2$ under UV–vis irradiation and 2.2 µmol (146.7 µmol g$^{-1}$) CO$_2$ in the dark, three fold higher CO$_2$ higher evolution rate originating from light irradiation. After 30 min, when there was no light irradiation, the reaction has minor progress and almost stops while in the presence of light; CO$_2$ continued to evolve, further proving that CeO$_2$@WS$_2$ is photo-catalytically active under UV–vis range irradiation. In the next step, we tried to understand the photoactivity of CeO$_2$@WS$_2$ under visible light irradiation. Formic acid photooxidation under the visible range is almost similar to dark conditions (Fig. 4a). This observation indicates that the photocatalytic activity is minimal under the visible range. Therefore, we can claim that the photocatalytic activity of CeO$_2$@WS$_2$ majorly originates from the UV range irradiation.

Lastly, we compared the photocatalytic activity of CeO$_2$@WS$_2$ with CeO$_2$ and WS$_2$ on their own (Fig. 4b). We also studied the effect of different amounts of CeO$_2$ loading on WS$_2$ (Fig. 4c). We realised that CeO$_2$ loaded on WS$_2$ (15 wt%) causes more photocatalytic activity than the 5 wt% and 10 wt% loading amounts. Accordingly, the CO$_2$ production rates for CeO$_2$ and WS$_2$ were 2.9 µmol and 3.5 µmol in 90 min, respectively, which are significantly lower than the ceria-loaded WS$_2$. At last, the produced CO$_2$ in this work is comparable to the previous reports [59–61], e.g., anatase TiO$_2$, layered titanate, protonated layered titanate, and 2D layered titanate-based photocatalysts [59,61]. In another example [60], a newly developed titania-based catalyst (namely, Ti@PMO-Bipy) reports the production of 5.5 µmol CO$_2$ in 90 min under optimal conditions while our developed catalyst produces a greater value (6.7 µmol) of CO$_2$ within 90 min.

4. Conclusions

WS$_2$ once exfoliated through ultrasonic waves, could efficiently form chemical bonds with CeO$_2$ during the hydrothermal synthesis, creating a promising heterostructure. The chemical bonding between Ce and S at the heterojunction was determined by Raman spectroscopy and XRD. Our density functional calculations could identify the most stable CeO$_2$/WS$_2$ interface configuration, further confirming the covalence bonding at the interface. Our simulation predicted a 2.7 Å interface separation between phases with a 2.93 Å Ce–S bond length. The density of states at the interface showed the formation of n-type carriers, matching with that of Mott-Schottky plot. This ultrasonically-synthesised CeO$_2$@WS$_2$ heterostructure emerged as a superior photocatalyst compared to WS$_2$, CeO$_2$, and their physical mixture. Using the Mott-Schottky plots and comparing the $E_F$ of the heterostructure with the pure phases through the Tauc plots, we showed that the CeO$_2$@WS$_2$ heterojunction was type (II). We speculate that several other transition metal oxides can be synthesised in the interlayers of WS$_2$, further building on the work presented here.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors acknowledge the University of Tabriz and the National Institute for Materials Science (NIMS) for their support. Especially, the authors gratefully appreciated the central laboratory of University of Tabriz for all its support. Also, E.D. acknowledges the TÜBİTAK and Horizon-2020 Marie Sklodowska Curie for providing financial support in Co-Funded Brain Circulation Program (Project No. 128057) framework.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2022.106245.

References

[1] F. Arcudi, Ł. Dorożewicz, N. Schweitzer, S.I. Stupp, E.A. Weiss, Selective visible-light photocatalysis of acetylene to ethylene using a cobalt molecular catalyst and water as a proton source, Nat. Chem. 14 (9) (2022) 1007–1012.
[2] T.P. Yoon, M.A. Isehaya, J. Du, Visible light photocatalysis as a greener approach to photochemical synthesis, Nat. Chem. 2 (7) (2010) 527–532.
H. Luo, J. Shi, C. Liu, X. Chen, W. Lv, Y. Zhou, M. Zeng, J. Yang, H. Wei, Z. Zhou, X. Liu, Q. Jia, Y. Fu, T. Zheng, Exfoliation of metal-organic framework nanosheets

G. Chatel, J.C. Colmenares, Sonochemistry: from Basic Principles to Innovative Applications, Top. Curr. Chem. 375 (2017) 8.

R. Browning, P. Plachinda, P. Padigi, R. Solanki, S. Rouvimov, Growth of multiple II-VI layered metal chalcogenide nanocrystals, Chem. Soc. Rev. 42 (2013) 2581.

P. Li, X. Zhao, L. Gao, L. Qiao, H. Jiang, X.-X. Li, W. Huang, Y.-H. Wang, H.-L. Lu, D.W. Zhang, Fabrication of a micro-electromechanical system-based electrochemical sensor gas sensor using CeO$_2$ nano-doped TiO$_2$ nanowires, ACS Appl. Mater. Interfaces 12 (2020) 14095-14104.

Y. Wang, Z. Yang, Y. Song, L. Liu, X. Sun, Z. Chen, H. Zhang, J. Zhang, Y. Li, Z. Zhao, H.-L. Lu, M. Wang, T. Guo, Q. Shen, Formation of disinfection byproducts from chlor(am)amines, Catal. Sci. Technol. 6 (2016) 3594-3605.

C. Gunawan, M.S. Lord, E. Lovell, R.J. Wong, M.S. Jung, D. Oscar, R. Mann, R. Amal, Oxygen-Vacancy Engineering of Cerium Oxide Nanoparticles for Antioxidant Activity, ACS Omega 4 (5) (2019) 9473-9479.

C. Yang, Q. Li, Y. Xiu, X. Jin, Y. Zhang, Enhanced visible light photocatalytic CO$_2$ reduction performance of ZnIn$_2$S$_4$ microcrystals by using CeO$_2$ as cocrystal, Appl. Surf. Sci. 464 (2019) 388-395.

L. Wang, F. Meng, K. Li, F. Li, Characterization and optical properties of poly-like nano-CeO$_2$ synthesized by a facile hydrothermal method, Appl. Surf. Sci. 286 (2013) 269-274.

M. Aslam, M.T. Qamar, M.T. Soomro, I.M.I. Ismail, N. Salah, T. Almeelbi, M. Gondal, A. Hameed, The effect of sunlight induced surface defects on the enhanced photocatalytic performance of cerium sesquioxidographite oxide composite for electrochemical application with high power density and energy density, Phys. B Condens. Matter 624 (2022) 413359.

C. Sirt, R.D. Jethva, R.V. Kashid, D.A. More, A.A. Joshi, M. Dharmadhikari, J. Jagtap, B. Khandke, V. Ramakrishna, N. Vattulina, Theoretical insights into the structural, chemical, and optical properties of cerium dioxide film prepared by atomic layer deposition on TiN and Si substrates, Thin Solid Films 636 (2017) 17953-17958.

M. Washington, S.K. Nayak, D.J. Late, Superior Field Emission Properties of Atomically Thin, Holey, Metal-Oxide Nanosheets for Tuning Band Alignment, Adv. Mater. 27 (2015) 250055.

Y. Kang, Z. Mao, Y. Wang, C. Pan, M. Ou, H. Zhang, W. Zeng, X. Ji, Design of a two-dimensional interplanar heterojunction for catalytic cancer therapy, Nat. Commun. 3 (2012) 1290.

K.T. Wong, S.C. Kim, K. Youn, C.E. Choong, I.W. Nih, B.-H. Jeon, Y. Moon, M. Jang, Understanding the band potential and band gap lifetime for Z-scheme and type-II heterojunction mechanisms for effective micropollutant mineralization: Comparative experimental and DFT studies, Appl. Catal. B 273 (2020) 110604.

A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, APL Mater. 1 (2013) 011002.

R. Mofarah, E. Adibifarozijad, R. Pardekhahram, M.H.N. Assadi, M. Hintze, R. Shahmiri, G. Bahmanrokh, S. Bhattacharyya, M.C. Spadaro, J. Arbiol, S. Lim, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, APL Mater. 1 (2013) 011002.

R. Asadi, G. Banakar, S. Yang, X. Wang, C. Li, J. Zhao, T. Ji, H. Wang, J. Zhang, A. You, J. Xi, P. Cao, The effect of ultrasound on synthesis and energy storage mechanism of Ti$_3$C$_2$Tx MXene, Ultrason. Sonochem. 89 (2022), 106122.

R. Hassandost, A. Koth, Z. Movafagh, M. Esfahani, R. Guengan, S. Endo, W. Jevasuwan, N. Fukata, Y. Sugahara, A. Khataee, Y. Yamauchi, Y. Ide, A. Savin, B. Silvi, F. Colonna, Topological analysis of the electron localization function, J. Phys. Chem. C 123 (2019) 3862-3868.

P.E. Blochwitz, Projector augmented-wave method, Phys. Rev. B 50 (1994) 19793-19799.

J.P. Fjerd, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865-3868.

J.P. Fjerd, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple (Phys. Rev. Lett. 77, 3865 (1996)), Phys. Rev. Lett. 79 (1997), 1396-1396.

G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169-11186.

G. Kresse, J. Furthmüller, Efficiency of ab-initio total-energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1) (1996) 15-50.
photocatalyst embedded with Fe$_3$O$_5$, Inorg. Chem. Front. 8 (19) (2021) 4423–4430.

[60] A. Ahadi, H. Alamgholiloo, S. Rostamnia, X. Liu, M. Shokouhimehr, D.A. Alonso, R. Luque, Layer-Wise Titania Growth Within Dimeric Organic Functional Group Viologen Periodic Mesoporous Organosilica as Efficient Photocatalyst for Oxidative Formic Acid Decomposition, ChemCatChem 11 (19) (2019) 4803–4809.

[61] M. Esmat, A.A. Farghali, S.I. El-Dek, M.H. Khedr, Y. Yamauchi, Y. Bando, Y. Fukata, Y. Ide, Conversion of a 2D Lepidocrocite-Type Layered Titanate into Its 1D Nanowire Form with Enhancement of Cation Exchange and Photocatalytic Performance, Inorg. Chem. 58 (2019) 7989–7996.