Selective isolation of the electron or hole in photocatalysis: ZnO–TiO$_2$ and TiO$_2$–ZnO core–shell structured heterojunction nanofibers via electrospinning and atomic layer deposition
Selective isolation of the electron or hole in photocatalysis: ZnO–TiO₂ and TiO₂–ZnO core–shell structured heterojunction nanofibers via electrospinning and atomic layer deposition†

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Heterojunctions are a well-studied material combination in photocatalysis studies, the majority of which aim to improve the efficacy of the catalysts. Developing novel catalysts begs the question of which photo-generated charge carrier is more efficient in the process of catalysis and the associated mechanism. To address this issue we have fabricated core–shell heterojunction (CSHJ) nanofibers from ZnO and TiO₂ in two combinations where only the ‘shell’ part of the heterojunction is exposed to the environment to participate in the photocatalysis. Core and shell structures were fabricated via electrospinning and atomic layer deposition, respectively which were then subjected to calcination. These CSHJs were characterized and studied for photocatalytic activity (PCA). These two combinations expose electrons or holes selectively to the environment. Under suitable illumination of the ZnO–TiO₂ CSHJ, e/h pairs are created mainly in TiO₂ and the electrons take part in catalysis (i.e. reduce the organic dye) at the conduction band or oxygen vacancy sites of the ‘shell’, while holes migrate to the core of the structure. Conversely, holes take part in catalysis and electrons diffuse to the core in the case of a TiO₂–ZnO CSHJ. The results further revealed that the TiO₂–ZnO CSHJ shows ~1.6 times faster PCA when compared to the ZnO–TiO₂ CSHJ because of efficient hole capture by oxygen vacancies, and the lower mobility of holes.

Introduction

Heterostructure catalysts for the oxidative degradation of environmental pollutants or chemical conversions are well known for their efficiency where the photo-generated charge carriers are driven apart before recombination.1–11 Understanding the catalysis mechanism is vital for the design of new functional materials to be a part of an environmentally friendly technology. The catalytic process on the surface of a semiconductor has been proposed by Izumi et al.12 and Matthews.13 To begin the process of catalysis, the formation of the hydroxyl radical is crucial, which is feasible through (a) electrons and/or (b) holes. Izumi et al.12 suggested that the processes (a) and (b) are both possible, while Matthews13 proposed only the process (b). The design strategy requires that the new generation catalysts should prolong the lifetime of the photo-generated charge carriers to elevate their participation in photocatalytic activity (PCA). For such designs, use of heterostructures is an ideal option, where an electron reservoir from a noble metal14,15 or another semiconductor (heterojunction)16,17 is brought into contact. The former case is exploited in core–shell18,19 nanocomposites2,9,10 formats, in which the photo-electrons from the conduction band (CB) of the semiconductor are transferred to the noble metal and then to the catalysis process, while the holes react from the valance band (VB) of the semiconductor. In the latter case, photo-generated e/h pairs diffuse across the heterojunction and electron and/or hole take part in the catalysis from CB and VB of each semiconductor, respectively.4,6 For example, in the ZnO/ZnSe (ref. 5) heterojunction, the PCA takes place at the VB of ZnSe and CB of ZnO. It is notable that most studies on this topic aim to enhance the PCA, while on the other hand understanding the roles of the electron and hole is equally important to design the new generation catalysts.

In all the above cases, both the charge carriers (electron and hole) are involved in catalysis, which makes it rather hard to determine unambiguously the individual role of each, apart from in the intrinsic surface chemistry16 of the materials. However, it is notable that the charge exchange process and hence the mechanism of PCA at heterojunction is still unclear.

† Electronic supplementary information (ESI) available: Additional SEM image of the CSHJ, XPS spectra and mechanism demonstrating PCA at the surface of pure TiO₂. See DOI: 10.1039/c3nr06665g
even after the decades of research. Nevertheless, if one of the charge carriers can be effectively isolated from the catalysis then this would offer useful insights for future studies on the design of new catalytic materials. In this direction, we have exploited the fundamental behavior of photo-generated charge carriers in semiconductor heterojunctions, and fabricated ‘core–shell’ nanofibers where only one of the semiconductors participates in the PCA, while the counter semiconductor allows the diffusion of either an electron or hole depending on the band alignment. For such a combination, we have considered two potential materials which have attracted a lot of attention in nanostructures for photo as well as thermal catalysis. For a better understanding of the roles of the semiconductor, respectively. To be more precise, the present design enabled the selectivity of either electrons or holes at the TiO2 or ZnO surfaces, respectively. These core–shell heterojunction (CSHJ) nanofibers were fabricated at the nanoscale via combining electrospinning and atomic layer deposition (ALD). It is notable that similar structures were studied, however, for their O2 (ref. 24 and 25) and NO3 (ref. 25) sensing characteristics. In an earlier article by Agrawal et al.,28 spherical core–shell structures were studied only in one combination (ZnO–TiO2) for their PCA. Pd@CeO2 hollow core–shell catalysts were studied for photo as well as thermal catalysis. In both cases, however, the charge carrier separation and their individual roles were not addressed. Recently, an interesting study appeared in literature in which photo-generated e/h pairs from a [Ru(bpy)3(CO2H4)]2+ based visible-light-sensitizer were separated via Co3O4–SiO2 core–shell nanoparticles.29 The separated holes are migrated through the SiO2 shell into the Co3O4 core and the electrons directly participate in the catalysis. Other investigations on core–shell structures include PbTiO3–TiO2,30 (Ba,Sr)TiO3–TiO2 (ref. 28) etc. These studies emphasize the need for a better understanding of the roles of the electron and hole in the catalysis. In the present case the CSHJs were structurally well characterized and their optical properties were studied in conjunction with intrinsic defects where it is generally accepted that the oxygen vacancies (V0) influence the PCA. Structurally, the case with TiO2 is interesting where the phase dependent band gap has shown its effects on the PCA.2,28,29 By considering this, a single (anatase) phase material was synthesized to reduce the complexity of the analysis, which enabled the precise determination of the individual role of each photo-generated charge carrier in the PCA.

Experimental section

Materials

Poly(vinylpyrrolidone) (PVP, Mw ~1.3 × 106, Sigma-Aldrich), titanium[IV]isopropoxide (TTIP, 97%, Sigma-Aldrich), zinc acetate dihydrate (ZnAc, reagent grade, Sigma-Aldrich), ethanol (≥99.8%, Sigma-Aldrich), glacial acetic acid (100%, Merck) and N,N,N-dimethylformamide (DMF, Pesticanal, Riedel) were used in electrospinning. Tetraakis(dimethylamido)titanium (TDMAT, Sigma-Aldrich), diethylzinc (DEZn, Sigma-Aldrich), and HPLC grade water (H2O) were used in the ALD processes. Methylene blue (MB, Sigma-Aldrich, certified by the Biological Stain Commission) was used as a model organic dye to evaluate the PCA of the ZnO–TiO2 and TiO2–ZnO CSHJ nanofibers. Deionized (DI) water is obtained from a Millipore MilliQ system. All the chemicals were used as received.

Electrospinning of PVP–ZnAc and PVP–TTIP nanofibers

PVP–ZnAc solution. PVP (0.4 g) was dissolved in an ethanol (2 mL)/DMF (2 mL) solvent mixture for 1 h. Then 1.4 g ZnAc was added to this PVP solution and stirred for 2 h to yield a homogeneous PVP–ZnAc solution.

PVP–TTIP solution. TTIP (2.88 mL) was stirred in a glacial acetic acid (2 mL)/ethanol (2 mL) solvent system for 15 min, and PVP (0.6 g) solution in ethanol (3 mL) was added to the above. The resulting mixture was constantly stirred for 2 h, and the yellowish PVP–TTIP solution was obtained.

The above two precursor solutions were taken into two separate syringes fitted with metallic needle (~0.6 mm of inner diameter). Each of the syringes was placed horizontally on a syringe pump (KD Scientific, KDS 101). An electric field of ~15 kV (Spellman, SL Series) was applied across the syringe needle and stationary metal collector (covered with a clean aluminum foil). The tip to collector distance was between 10 and 12 cm. Electrospinning was carried out in an enclosed chamber at ~25 °C and 10% relative humidity. Then an ALD process was implemented on these electrospun PVP–ZnAc and PVP–TTIP nanofibers to yield TiO2 and ZnO shell structures, respectively.

Atomic layer deposition of TiO2 and ZnO

TiO2 and ZnO depositions on the electrospun PVP–ZnAc and PVP–TTIP nanofibers, respectively, were carried out at ~200 °C in a Savannah S100 ALD reactor (Cambridge Nanotech Inc.). N2 was used as a carrier gas at a flow rate of ~20 scm. 500 cycles TiO2 and 144 cycles ZnO were applied using the exposure mode (a trademark of Ultraceh/Cambridge Nanotech Inc.) where the dynamic vacuum was switched to static vacuum before each precursor pulse by closing the valve between the reaction chamber and the pump, and switched back to dynamic vacuum for purging excess precursor molecules and gaseous by-products. This allows the substrate to be exposed to precursor molecules for a certain amount of time (i.e. exposure time). For the TiO2 deposition, one ALD cycle was as follows: valve OFF/N2 flow set to 10 sccm/TDMAT pulse (0.1 s, TDMAT heated to ~75 °C)/exposure (10 s)/valve ON/N2 purge (20 scm, 10 s)/valve OFF/N2 flow set to 10 sccm/H2O pulse (0.015 s)/valve ON/N2 purge (10 s)/valve OFF/N2 flow set to 10 sccm/TDMAT pulse (0.1 s)/valve ON/N2 purge (10 s). For the ZnO deposition, one ALD cycle consists of the following steps: valve OFF/N2 flow set to 10 sccm/H2O pulse (0.015 s)/valve ON/N2 purge (20 scm, 10 s)/valve OFF/N2 flow set to 10 sccm/DEZn pulse (0.015 s)/valve ON/N2 purge (20 scm, 10 s).

ZnO–TiO2 and TiO2–ZnO core–shell heterojunction nanofibers

TiO2 coated PVP–ZnAc (PVP–ZnAc–TiO2) and ZnO coated PVP–TTIP (PVP–TTIP–ZnO) nanofibers were calcined at ~500 °C for 3 h in order to remove polymeric precursors. This process
enabled the formation of inorganic cores in both cases, yielding the final CSHJ structures to be ZnO–TiO₂ and TiO₂–ZnO.

Characterization techniques

A scanning electron microscope (SEM, FEI – Quanta 200 FEG) was employed to investigate the morphology and dimensions of the nanofibers before and after the calcination. A nominal 5 nm Au/Pd was sputtered on the samples prior to the observation under SEM. About 100 measurements were considered to determine the average fiber diameter (AFD) from the SEM images. CSHJ nanofibers were subjected to transmission electron microscopy (TEM, FEI-Tecnai G2 F30) where the sample was dispersed in ethanol and a tiny droplet was analyzed from a holey carbon coated TEM grid. TEM-EDX spectra were also recorded for both of the samples. X-ray diffraction (XRD) patterns were recorded in the range of 2θ = 10–100° using PANalytical X’Pert Pro Multi Purpose X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The bonding states of the constituent elements at the surface of the samples (400 μm spot size) were investigated by X-ray photoelectron spectroscopy (XPS, Thermoscientific K-Alpha, Al Kα radiation, hv = 1486.6 eV) with a flood gun charge neutralizer. For the core-level spectra, the pass energy and step size were set to 30 eV and 0.1 eV, respectively. VB spectra were also recorded with a pass energy of 30 eV in energy steps of 0.2 eV. Spectral deconvolutions of the XPS data were performed through the Avantage software. A Horiba Scientific FL-1057 TCSPC was used for the photoluminescence (PL) measurements performed at an excitation wavelength of ~360 nm.

Photocatalytic activity of core–shell heterojunction nanofibers

The photo-induced degradation efficiency of the CSHJ samples (~5.7 mg each) was analyzed by immersing them individually into quartz cuvettes containing MB aqueous solution (0.25 mM). The cuvettes were placed at a distance of ~10 cm from the UV source (8 W, UVLMS-38 EL) operating at a wavelength of 365 nm. Dye concentrations in the cuvettes were measured using a UV-Vis-NIR spectrophotometer (Varian Cary 5000) at regular time intervals. Each CSHJ sample was immersed down at the bottom of the cuvette during the UV-Vis measurement and therefore did not interfere with the data acquisition.

Results and discussion

Fig. 1 is a schematic diagram depicting the fabrication of the CSHJ nanofibers, where the various processes and sequence of the steps are described. ZnO–TiO₂ and TiO₂–ZnO CSHJs were fabricated via a three-step process where electrospinning was followed by atomic layer deposition (ALD) and calcination. In the first step, we prepared precursors via electrospinning²¹–²₄ for the cores of the CSHJ nanofibers, where the precursors were mixtures of PVP and ZnAc or TTIP. In the second step, these nanofibers were used as substrates and TiO₂ or ZnO shell was grown through ALD. Finally, the nanofibers were calcined where the organic component (PVP) is removed to form ZnO or TiO₂ in the core of the CSHJs. The adopted calcination temperature and duration yielded single phase and high quality samples.

In any ALD process, it is important to consider the compatibility between the precursor and polymer as the former can degrade the latter by chemically reacting with it; see the case with the ALD of Al₂O₃ on a nylon-6 polymer.²⁵ On the other hand, in the case of poly(propylene) fibers, an Al₂O₃ base layer is employed to deposit ZnO, where the former protects the diffusion of DEZn into the polymer.²⁶ Apart from these limitations ALD in fact can yield coral,²⁷ core–shell²⁸ like complex nano-structures, which are potential materials for photocatalytic applications.²⁹–³⁰ Hence we applied this technique in combination with electrospinning to produce core–shell structured nano-entities.

The SEM images of the nanofibers before and after calcination are depicted in Fig. 2. Prior to the calcination and after the ALD process, the AFD are 320 ± 120 and 600 ± 340 nm for PVP–ZnAc–TiO₂ and PVP–TTIP–ZnO nanofibers, respectively (Fig. 2a and b). It is generally accepted that electrospun polymer fibers do possess wide range of diameters, while a rough surface occurs for certain polymers in electrospinning depending upon the solvent and its characteristics.³¹–³⁴ After the calcination, the structural integrity of the nanofibers was preserved, while we note a decrease in the AFD values which is expected due to the decomposition and removal of PVP. The final CSHJs, ZnO–TiO₂ and TiO₂–ZnO, have diameters in the range of 100–650 nm and
50–740 nm with AFD of 270 ± 110 nm and 200 ± 120 nm respectively (Fig. 2c and d). If we compare the AFD before and after calcination, the differences across ZnO–TiO2 and TiO2–ZnO can be attributed to the varying PVP content. In the present case the morphological appearances and changes after calcination are similar to earlier observations.18,19,33 After calcination CSHJ nanofibers show a rough surface, see Fig. S1 of the ESI†. We will see the similarity in the next section, where the samples were analyzed under TEM.

The CSHJ samples were subjected to TEM characterization (Fig. 3). The core–shell structure can be seen clearly for both of the samples (Fig. 3a and b), where uniformities of the TiO2 and ZnO shell layers should be pointed out, despite the relatively large surface area of the nanofibers. We have measured the thickness of the shell from these TEM images yielding ~50 nm and ~70 nm for TiO2 and ZnO, respectively. Furthermore, the grainy structure of shell is explicit from the TEM images, which has been shown to possess single crystallinity as evidenced by the high resolution images (Fig. 3c and d). The interplanar distances were measured for the shell regions, and the values match with the literature. We have annotated these values on Fig. 3c and d for TiO2 and ZnO, respectively. We have also recorded EDX on CSHJs from TEM and the results are given in S2 of the ESI†. For both the cases a signal from Zn and Ti is seen as expected, however, the signal from the shell region dominates. From these spectra, the presence of Ti and Zn is confirmed. The quantification of the elements occurring in the spectra are not given as the signal level from the ‘core’ part of the structure depends on the characteristics of ‘shell’ material as the latter encloses the former completely.

The crystalline phase of TiO2 should be identified as precisely as possible, given the type II band alignment (band gaps of rutile and anatase are 3.03 eV and 3.20 eV, respectively) and its influence on PCA.29,30 Importantly given the penetration depth of X-rays, the XRD data contain ZnO and TiO2 characteristic peaks in both of the heterojunction nanofibers. A list containing the peak positions and the corresponding Miller indices, (hkl), for the three cases (anatase TiO2, rutile TiO2 and ZnO) has been tabulated in S3 of the ESI†. The XRD pattern relevant to TiO2 will be discussed for the ZnO–TiO2 CSHJ (Fig. 4a). We have annotated the Miller indices for the anatase and rutile phases of TiO2 on Fig. 4a and the peaks corresponding to ZnO are identified on Fig. 4b for brevity. For example (010), (002) and (011) reflections of ZnO can be seen in Fig 4a, indicated by arrows. Furthermore, the diffraction pattern on a log scale (not shown here) was scrutinized for shape changes and asymmetries. A careful inspection of the peak positions (S3 of the ESI†) and the data (Fig. 4a) suggest that the pattern matches well with the anatase phase polycrystalline TiO2 within the detection limits of XRD. An investigation on
pure TiO₂ nanofibers (results not shown here) confirmed the formation of an anatase phase (i.e. without the ZnO shell, subjected to the same thermal treatments). The peaks in the diffraction pattern are consistent with the literature. The lattice parameters were calculated for tetragonal TiO₂ \( a = b = 3.7847 \text{ Å, and } c = 9.5173 \text{ Å} \) and yielded a crystal volume of 136.33 Å³, which is comparable to the standard value of 135.25 Å³. However, in the literature lattice contraction is evidenced under the influence of \( V_{\text{OS}} \). In the case of TiO₂ when an O atom is removed, the three nearest Ti atoms tend to relax away from the vacancy in the process of strengthening their bonding with the rest of the lattice. In the present case, most probably because of the low density of \( V_{\text{OS}} \), a negligible effect on the bond lengths/cell volume is seen. Moving onto the XRD pattern of the TiO₂-ZnO CSHJ sample, we have identified reflections of the hexagonal (wurtzite) ZnO and annotated the corresponding Miller indices on Fig. 4b. Note that it contains peaks from anatase TiO₂ which were not annotated on Fig. 4b. The XRD pattern indicated a polycrystalline ZnO which was found to be consistent with the literature. The lattice parameters were derived and the \( c/a \) ratio of \( \sim 1.6 \) further supports the wurtzite structure and successful formation of ZnO. Since we have collected the nanofibers on Al foil and calcined them after the ALD process, a background of aluminum oxide is evidenced in the TiO₂-ZnO CSHJ (designated with "*" on Fig. 4b).

The surface characterization of the semiconductors such as ZnO⁴⁰,⁴¹,⁴⁷ and TiO₂ (ref. 48 and 49) is of prime importance not only in the context of PL but also in conjunction with the PCA. Interestingly, both of these properties are dependent on the ionic state of the chemisorbed surface oxygen,⁴⁰,⁴¹,⁴⁷−⁵¹ which can be realized precisely with XPS. Note that the physisorbed oxygen can be desorbed under ultra high vacuum conditions. CSHJ samples were subjected to XPS analysis for Ti 2p or Zn 2p, O 1s and the VB. The spectral locations of the deconvoluted peaks are annotated on the image for each of the spectra. A Ti 2p core-level spectrum obtained from ZnO–TiO₂ CSHJ is shown in Fig. S4a of the ESL.† The spectral locations of the peaks corresponding to Ti 2p½ and Ti 2p½ are consistent with the literature and the expected spin-orbit splitting of 5.7 eV is observed. It is also notable that we have not noticed any signatures of Ti⁴⁺ or Ti⁵⁺ in the Ti 2p spectrum. The core-level spectrum of Zn 2p from the ZnO–TiO₂ CSHJ is shown in Fig. S4b of the ESL and the peaks 2p₃/₂ and 2p₁/₂ indicated a wurtzite structured ZnO where the spin orbit splitting and satellite peak are consistent with the literature.⁴⁰,⁵₂

In the context of the core-level spectrum of O 1s from TiO₂ (ZnO–TiO₂ CSHJ), a major peak centered at \( \sim 530.4 \text{ eV} \) and a minor peak at \( \sim 532.2 \text{ eV} \) can be seen which correspond to the oxygen in TiO₂ and chemisorbed oxygen, respectively (Fig. 5). The presence of oxygen species such as OH, CO, adsorbed H₂O and/or O₂ on the surface generally produces a peak at 532.3 eV. Similar to the earlier case, the O 1s spectrum of ZnO (TiO₂–ZnO CSHJ) can be deconvoluted into two peaks as shown in Fig. 5. The spectrum obtained from the ZnO ‘shell’ has shown a major peak centered at \( \sim 530.5 \text{ eV} \) corresponding to the oxygen in zinc oxide, which is in line with the literature. The other minor peak appearing at \( \sim 531.9 \text{ eV} \) corresponds to the chemisorbed oxygen at the lattice defect sites. The peak at 531.5 eV is attributed to O⁻ and O₂⁻ ions in the oxygen deficient regions on the surface.⁵¹−⁵⁵

Due to the fact that TiO₂ and ZnO possess typical oxygen related defects, the defect sites are subjected to the chemisorption of the above ions while sharing the lattice electron(s).⁵¹−⁵⁵ Furthermore, the grain boundaries (as seen in the TEM images) are obvious locations for electron deficient species to chemisorb. Depending on the availability of free electron(s), the sharing can be partial with the above species which has produced relatively broad binding energies peaking at \( \sim 532.2 \text{ eV} \) or \( \sim 531.9 \text{ eV} \). Among these two samples, it can be seen that the chemisorbed oxygen related to the ZnO–TiO₂ sample shows relatively higher binding energy, obviously because of the differences in the origin of the chemisorbed oxygen. While keeping these differences aside, a variation in the relative area of peaks is demonstrated, where TiO₂–ZnO CSHJ has shown nearly 2.6 times higher area than its complimentary CSHJ. This confirms that a larger fraction of oxygen-defect regions is present in the surface layer for TiO₂–ZnO compared to ZnO–TiO₂.

Furthermore, VB spectra (Fig. S5 of the ESL) of both CSHJs were investigated for any alterations in the edge of the band corresponding to the ‘shell’ semiconductor. The VB edges were at \( \sim 2.35 \text{ eV} \) and \( \sim 2.42 \text{ eV} \) for ZnO–TiO₂ and TiO₂–ZnO, respectively. By the given TiO₂-anatase phase band gap of 3.20 eV, the CB edge should be placed around \( \sim 0.85 \text{ eV} \). It is notable that the VB edges were found to be in the range of 2.4–3.1 eV with band gaps within the range of 3.67–3.2 eV. In the case of ZnO, the CB edge was found to be around \( \sim 0.88 \text{ eV} \) according to its typical band gap of 3.3 eV. A number of studies have already shown the importance of the lattice defects in conjunction with PCA either in the case of pristine or heterojunction catalysts, where they can be identified through optical properties. We have performed PL spectroscopy on the CSHJ nanofibers (Fig. 6) and the
origin of defect-related emission is overlaid on the corresponding spectrum. When CSHJs were illuminated with energies higher than their band gaps, the majority of the absorption takes place within the ‘shell’ region. Hence the emission from the CSHJs is mainly due to the shell region of the heterojunctions, where the visible emission occurs from the surface recombination.41,60,63 In both the cases, a largely similar visible emission indicates a dominant defect density such as VOs. Importantly, despite the visible emission peaks appearing at almost the same wavelength for both the CSHJs, the energetic location of the VOs for TiO2 and ZnO are not the same. These spectra will be discussed independently with reference to the plausible defects in the following sections and subsequently juxtaposed with the PCA. Although the majority of the emission is from the ‘shell’, it should be noted that the emission and its intensity are influenced by the presence of the ‘core’ where there might be a recombination route (radiative/non-radiative) for the photo-generated charge.

In the case of the ZnO–TiO2 sample, the emission from the interband transition is seen at ~3.2 eV. This band arises due to the e/h recombination across the band gap of TiO2, while the broad visible emission centered at ~2.4 eV is due to the surface recombination associated with VOs defects.44,49 XPS has indicated that there is chemisorbed oxygen on the surface of the CSHJ which further supports the defects related to oxygen vacancies. The energetic locations of these defects are discussed in the literature.44,49 which were schematized on the emission spectrum (Fig. 6). The electrons in VOs (also known as F centers) are localized because of Madelung potential of the highly ionic crystal.44 This state can be occupied by O2− by capturing one or two ‘free’ electrons from the crystal, and hence the energetic cost of the vacancy is minimized.44 These localized electrons form a donor level 0.75–1.18 eV below the CB of TiO2,44,49 specifically the donor level at 1.18 eV below the CB is due to V0+54. Furthermore, the band arising because of VOs can be broad enough to merge with the CB in the case of sufficiently highly defective TiO2 of either the anatase or rutile phase,44 and hence a significant shift in Fermi level toward high energies can be expected. We believe that this has not happened in the present case where an explicit peak corresponds to the interband transition from TiO2 and there is a relatively low concentration of VOs (as evidenced in XPS measurements). On the other hand, the VOs can cause the redistribution of excess charge among the nearest neighboring Ti atoms (Ti4+/Vo − Ti3+ or Ti2+) which form a shallow donor state below the CB.55,66 However in the core-level XPS analysis of the Ti 2p spectrum (Fig. S4a of the ESI†) no explicit indication of these ionic states is present, as mentioned previously.

In the case of TiO2–ZnO, the emission spectrum from ZnO consists of the least controversial UV-emission (interband transition) which occurred at ~3.2 eV and debatable visible emission centered at ~2.5 eV. Interestingly, the visible emission is attributed to the VOs, similar to the TiO2 case. However, this green emission consists of two transitions as depicted in Fig. 6. The VOs exist in the bulk grain region (BGR)60 as well as depletion region (DR)44 with different ionic states. In the BGR, V0+ captures an electron from CB and forms Vo* 0.86 eV below the CB and in DR, V0+ captures a hole from VB and forms V0++ 1.16 eV above the VB. While the energetic locations of VOs in TiO2 range from 0.75 eV to 1.18 eV below the CB,44,49 however, notably V0++ is 1.18 eV below the CB.44,49 In the context of TiO2–ZnO, the BGR of ZnO is not accessible to the PCA, hence only the DR, which is on the surface of the CSHJ, takes part in the PCA by capturing a hole from the VB. The optical quality can be compared across the CSHJ by taking the intensity ratios of the interband transition to the visible (IUV/IVis)46,47 yielding ~0.3 for TiO2 and ~0.5 for ZnO for ZnO–TiO2 and TiO2–ZnO CSHJs, respectively. These ratios suggest that the optical quality of ZnO is better than TiO2.

In the case of TiO2, various chemical species (–OH, –CO, H2O or O2) were found to be chemisorbed on the surface which are not the same as in the ZnO case (O− and O2−). Although the species adsorbed on either of the surfaces were not exactly identified, it is clear that for TiO2 chemisorption occurred at a higher energy than ZnO, i.e. the surface adsorbents of TiO2 bind to the lattice more strongly than those of ZnO, which explains the differences in the relative intensities of visible emission among TiO2 and ZnO. In the case of TiO2, since the surface adsorbents are strongly bound to the lattice they can successfully capture an electron from the CB and give rise to visible emission. In contrast, for the case of ZnO, despite their relatively high density, the surface adsorbents are loosely bound and hence under equilibrium, they have relatively lower probability to stay at the defect site and thus to give visible emission.

Furthermore, we would like to comment on the visible emission from the CSHJ. Within the interfacial region between the semiconductors, there is a certain possibility of so called ‘interfacial states’ which may arise due to the lattice mismatch or other related effects. These states can be radiative or non-radiative in nature, which can enhance or subdue the visible-intensity,
respectively. We have not considered the possible emission from the interface, as the oxide hetero-interfaces are not completely understood yet.\(^\text{15}\) Nevertheless, the present design enables future studies to identify the role of each charge-carrier for oxidation processes of various organic compounds, see ref. 50 and 72–81 in ref. 16 and the recent study as well.\(^\text{1}\)

Having discussed the influence of defects on the optical properties, the involvement and role of \(V_{\text{OS}}\) in the interface of heterojunctions is still debatable;\(^\text{48}\) on the other hand since no catalysis takes place at the interface, the dynamics and consequent charge exchange process are out of the scope of the present article. Essentially if \(V_{\text{OS}}\) in TiO\(_2\) exist inside the lattice then they may serve as recombination centers, however this may reduce the PCA.\(^\text{67}\) In a recent article, the importance of oxygen vacancies in TiO\(_2\) and their influence on the PCA has been emphasized.\(^\text{48}\) Prior to the discussion on PCA, it should be noted that no charge carrier is excited to the defect states directly as we have employed a monochromatic UV source (365 nm) and hence the defect sites can capture electrons or holes depending on their energetic location within the band gap.

It is useful to revisit the photocatalysis mechanism\(^\text{12,13}\) to which we will be referring in the context of PCA for each CSHJ. This process is shown as follows after Izumi et al.\(^\text{12}\) and Matthews.\(^\text{13}\) The key for the photocatalysis is the formation of the hydroxyl radical (‘OH), which can be through (a) an electron generated at the CB (\(e_{\text{CB}}\)) and/or (b) a hole generated at the VB (\(h_{\text{VB}}\)). Process (a) contains multiple steps (see below), which are mediated by superoxide anions (‘\(O_2^-\)’) as proposed by Izumi et al.\(^\text{12}\) Initially, molecular oxygen traps the \(e_{\text{CB}}\) and forms ‘\(O_2^-\)’ ions (a1-1), while the second step involves formation of H\(_2\)O\(_2\) (a2-1 through a2-4) followed by its cleavage by superoxide anions (a3-1, 2 or 3) as shown below:

\[
e_{\text{CB}} + O_2 \rightarrow \cdot O_2^- \quad \text{(a1-1)}
\]

\[
\cdot O_2^- + H^+ \rightarrow \cdot HO_2 \quad \text{(a2-1)}
\]

\[
2\cdot HO_2 \rightarrow H_2O_2 + O_2 \quad \text{(a2-2)}
\]

\[
\cdot O_2^- + \cdot HO_2 \rightarrow \cdot HO_2^- + O_2 \quad \text{(a2-3)}
\]

\[
\cdot HO_2^- + H^+ \rightarrow H_2O_2 \quad \text{(a2-4)}
\]

\[
H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + \cdot OH^- + O_2 \quad \text{(a3-1)}
\]

(or)

\[
H_2O_2 + e_{\text{CB}} \rightarrow \cdot OH + OH^- \quad \text{(a3-2)}
\]

(or)

\[
H_2O_2 \xrightarrow{h^+} 2\cdot OH \quad \text{(a3-3)}
\]

On the other hand, in process (b),\(^\text{13}\) ‘OH radicals are formed mainly from the \(h_{\text{VB}}\) in the presence of either adsorbed H\(_2\)O (b-1) or the OH\(^-\) groups on the surface (b-2).

\[
h_{\text{VB}}^+ + H_2O \rightarrow \cdot OH + H^+ \quad \text{(b-1)}
\]

Finally, in any case the ‘OH radical oxidizes the dye (‘OH + dye → oxidized products) when generated by a photo-electron or photo-hole.

Moving on to the context of the CSHJ, its functionality depends on fundamental physical parameters such as band offset, where there exists a profound effect on the carrier confinement and electronic transport along and across the interface.\(^\text{37}\) Further complicating the process of charge transfer, the oxide hetero-interfaces are not well understood yet.\(^\text{17}\) In the present case initial precursor nanofibers of ZnO or TiO\(_2\) were produced, then the counter semiconductor is deposited. This intermediate level heterostructure was subjected to calcination, producing the hetero-oxide interface with a structural distortion along with a probability of chemical bonds and charge distribution across the junction. The present calcination parameters yielded anatase TiO\(_2\) in both of the heterojunctions. On the other hand, it is acknowledged that mixed phase TiO\(_2\) yields a higher PCA;\(^\text{29,10,68}\) however, we aim to determine the individual roles of electrons and holes in the process of catalysis. In the mixed phase TiO\(_2\), the energetic alignment of band edges suggests a flow of conduction electrons from rutile to anatase.\(^\text{16}\) Keeping this in the background, we chose to produce a single phase TiO\(_2\) to study the catalytic mechanism. On the other hand, defect disorders in either TiO\(_2\) or ZnO play a significant role in the PCA. Hence we refer to the discussion of PL from TiO\(_2\) and ZnO, and correlate it with the PCA of ZnO–TiO\(_2\) and TiO\(_2\)–ZnO CSHJ, respectively.

PCA is compared across the CSHJ while considering the degradation of MB without any catalyst (Fig. 7). The photocatalytic activities of the ZnO–TiO\(_2\) and TiO\(_2–ZnO\) core–shell heterojunction nanofibers. Exponential decay fits and constants are shown when compared with the pristine methylene blue (MB) without any catalyst.
Hinshelwood model. In any photocatalysis involving a semiconductor, the efficiency of the process depends on the balance between the interfacial charge transfer (semiconductor to dye) and charge carrier recombination lifetime. In the present investigation, the degradation time constants yielded from an exponential fit for each CSHJ are given on Fig. 7. In the absence of a catalyst, MB did not show any degradation at a noticeable level while ZnO–TiO2 and TiO2–ZnO CSHJs yielded ~3.11 h and ~1.95 h decay times, respectively. These decay times indicate how fast the catalysts can oxidize the dye which is being tested.

Interestingly, the time constant shown by the TiO2–ZnO CSHJ is nearly 1.6 times faster than that of the ZnO–TiO2 CSHJ. It is vital to understand the diffusion of electrons or holes across the CSHJs prior to the explanation of the variation observed in the PCA.

In Fig. 8 we have shown a schematic diagram which replicates the semiconductors with energetic locations with respect to vacuum for both CSHJs. Previously discussed processes are annotated on the figure, i.e. (a) and (b) while considering the nature of defect. In the context of ZnO and TiO2, these defect-related bands are shown to depict improved catalytic activity.8,16,44,48,49,59

**Role of electrons**

Under illumination of the ZnO–TiO2 CSHJ, electron and hole pairs are created in the TiO2 shell region. If we consider the alignments of the band as shown in Fig. 8 (left panel), it is clear that the holes can be diffused into the core (ZnO), while the electrons can participate in the PCA at the CB or VB of TiO2. However, there is also a possibility that eCB may be transferred to VO* (BGR) and/or VO** (DR) in ZnO due to the TiO2 core–shell heterojunction and energetic locations with respect to vacuum for both CSHJs. Previously discussed processes are annotated on the figure, i.e. (a) and (b) while considering the nature of defect. In the context of ZnO and TiO2, these defect-related bands are shown to depict improved catalytic activity.8,16,44,48,49,59

![Proposed catalysis mechanism.](image)

**Fig. 8** Proposed catalysis mechanism, where either electrons from the TiO2 or holes from the ZnO are engaged from the ZnO–TiO2 (left panel) and TiO2–ZnO (right panel) core–shell heterojunction nanofibers. The energetic band locations of TiO2 were obtained from the references as follows (1),50 (2),44,46 (3),44,49,64 and (4),70 while for the ZnO case (5),71 (6),50,51 (7),50,51 and (8).72 The band gaps of TiO2 and ZnO were taken as 3.2 eV (ref. 30) and 3.3 eV,72 respectively. The processes (a) and (b) stand for acceptor → acceptor and donor → donor, respectively. eCB and hCB stand for electron and hole capture, respectively.

In the present context, we are discussing the VO*S that are limited to the surface of the TiO2 and the electrons at such defects have almost no mobility to reach the VO** or VO*S of ZnO. Photo-generated electrons in the VB of TiO2 find the VO* state energetically favorable, however physically not reachable, because VO* lies in the bulk of the ZnO. Hence the electron has to take part in the PCA before the recombination. However the electrons in the VO*S of TiO2 can reach the DR (grain boundaries of ZnO), which might hinder the PCA. Furthermore, if VO*S exist inside the lattice then they may serve as recombination centres.77 Since the holes are most likely diffuse into ZnO, they may not play a major role in the PCA. The above argument assumes that e/h pairs are not created in ZnO, where TiO2 absorbs almost all of the UV illumination. However, in the case that they are generated in ZnO dominantly, eCB may migrate to the CB of TiO2 and participate in the PCA. Hence the active site for the PCA at the TiO2 surface are CB and VO*S as designated by process (a) on Fig. 8, left panel. In the case of TiO2, the existence of VO*S creates unpaired electrons or TiO** centres (though not evidenced in the XPS), which could form donor levels and also the e/h recombination process is affected causing a change in chemical rates.8,16,44,48,49,59

If we look at the mechanism of catalysis for pure TiO2 under suitable illumination, the photo-generated electrons either at the CB or VO*S are captured by O2, producing O2* radical groups where the adsorption energies are ~0.94 and ~2.52 eV, respectively.77 As discussed earlier, these radical groups are the key for the oxidation of the test dye. Notably, a high density of VO*S can induce vacancy electronic states below the CB73 and an improved PCA is noticed under the visible light. Since charge migration is a physical process, it may be possible that some of the holes, which are not migrated to the core, can participate in the PCA as indicated with (b)* on Fig. 8, left panel, however with negligible activity. Deconvolution of the visible emission (not shown here) from TiO2 suggests that the emission from the optical transition from VO** to the VB has relatively lower intensity when compared to that from VO (which are 0.75 eV below the CB) to the VB, which implies that the defect density of VO** is relatively less. Hence the electron capture from the CB is dominated by VO, which is 1.18 eV below the CB.44,49,62 see left panel of Fig. 8, black coloured (a). Furthermore, similar to the molecular oxygen, H2O can involve in the PCA when disassociated at a defect site, e.g. VO (energetically more favourable73), while on a perfect TiO2 surface H2O is physically adsorbed.73–75

**Role of holes**

In contrast to the previous CSHJ, the present heterojunction favours electrons to migrate to the TiO2-core leaving the holes at the VB to participate in the PCA. Otherwise, this photo-generated electron can be captured by VO* which can further diffuse into the TiO2-core by accessing VO*S therein, as shown in the Fig. 8, right panel. Hence the active holes at the surface of the ZnO-shell take part in the PCA and the above-discussed mechanism can be taken into account to understand the oxidation process. Since the surface layer is only ZnO, it has been revealed that VO*S can behave as important adsorption and active sites for...
catalysis, which strongly influence the reactivity of metal oxides.\textsuperscript{77} Notably, $V_{O}^{−}−$ forms after capturing a hole from the VB. Hence by involving H$_2$O to form 'OH the dye is oxidized as shown earlier in eqn (b-1) and (b-2). Similar to the earlier case, it may be possible that some of the electrons, which are not migrated to the core, can participate in the PCA. However, the activity with such electrons is negligible and shown with grey coloured (a)* on Fig. 8, right panel.

The higher PCA for the TiO$_2$–ZnO CSHJ can be because of various reasons, including a high density of surface defects and lower binding energy of the surface adsorbents, which can exchange the charge carrier and participate in the PCA. In ZnO, under biased and illuminated conditions,\textsuperscript{99} the mobility of the hole (10 cm$^2$ V$^{-1}$ s$^{-1}$) would be much lower when compared to unbiased conditions such as those used here. From the earlier described processes (a) and (b), it is clear that 'OH radical forms with O$_2$ (primary/electrons and/or H$_2$O/hole. In the case of ZnO–TiO$_2$, electrons are the main participants in the PCA, hence the availability of the O$_2$ can be a limiting factor. On the other hand, for the TiO$_2$–ZnO CSHJ, the vast availability of H$_2$O is an advantage to yield higher efficiency. Therefore in the context of an aqueous solution holes may yield a higher PCA than electrons.

In the case of TiO$_2$, the charge carrier generation under suitable illumination takes place in the order of fs, and subsequent processes such as charge carrier trapping and recombination take place in 0.1–10 ns and 10–100 ns, respectively (Fig. S6 of the ESI†). We can see that trapping is 10 times faster and the trapped charge has to participate in recombination.\textsuperscript{10} Also, it is suggested that the electron transfer to oxygen may be the rate determining step, see ref. 43, 86 and 87 in Hoffmann et al.\textsuperscript{10} Depending on the surface chemistry, there is a possibility that there exists more than one type of binding. For example, in the case of CHCl$_3$ interacting with Degussa P25 at pH 5, two different sites of non-uniform binding energies are identified. The stronger binding site dominates sorption at concentrations <1 mM, and the weaker binding site is considered mostly for concentrations >1 mM, see ref. 50 in Hoffmann et al.\textsuperscript{10} It is thought that high density of defects would lead to a higher PCA; however, this is the case only when we have loosely bound species at the lattice. As in the case of TiO$_2$, although there are significant defects, they are occupied with strongly bound adsorbents and hence may not be easily brought into the catalysis process where an exchange of charge is required. Although we have not considered the effect of pH, it is notable that water disassociation equilibrium depends on the pH of the solution, which is quite complex in the context of UV-irradiated TiO$_2$. On the other hand, pH also determines the surface charge of TiO$_2$ with respect to its point of zero charge (pzc, ~6.5), as well as the ionization state of the organic reactant and of its metabolites.\textsuperscript{79} If the pH is higher than the pzc, the surface becomes negatively charged, the opposite is valid for pH < pzc. In the present case, since MB is a cationic dye, the most favorable adsorption occurs at pH < pzc, where the adsorption is the basic requirement\textsuperscript{80} for the reaction to take place.\textsuperscript{80} We believe that the integral effect of above reasons caused photogenerated holes from ZnO to have higher efficiency than electrons from TiO$_2$.

Conclusions

In this study we have attempted to determine the individual roles of electrons and holes in photocatalysis, which are photo-derived from a core–shell structured semiconducting heterojunction, where the design enables only the ‘shell’ part of the CSHJ to be exposed for the PCA. These CSHJs were characterized for their structural integrity, which revealed the formation of pure, single-phase anatase TiO$_2$ in both CSHJs. TEM analysis suggested well-developed grains, which in principle influence the PCA by forming grain boundaries. XPS has evidenced typical $V_{S8}$ on the surface hosting various oxygen-related species. The optical properties of the CSHJs were studied and discussed with reference to the intrinsic defects. We have not considered the interfacial defects between core and shell regions, however, the interface is not directly accessible for the PCA anyway. In the case of ZnO the visible emission occurs from the surface, and hence considering the defects limited to the surface does not undermine the analysis. Crucially, under suitable illumination, e/h pairs are created mainly in the shell region of the CSHJs, and holes and electrons migrate to the core of the structure for ZnO–TiO$_2$ and TiO$_2$–ZnO structures, respectively, as governed by the band alignment.

In the ZnO–TiO$_2$ CSHJ e/h pairs are created in TiO$_2$ and electrons take part in catalysis at the CB of TiO$_2$ while holes migrate to the core of the structure. The PCA in this heterojunction is an integral effect of catalysis taking place at the VB and $V_{S}$ sites on the surface, where the photo-generated holes are eliminated. In the TiO$_2$–ZnO CSHJ, e/h pairs are created majorly in ZnO, and electrons are diffused into the core while holes at the VB of ZnO involve in PCA. The results suggested that TiO$_2$–ZnO CSHJ has shown higher PCA than the other combination. It might be because of surface chemistry and the intrinsic characteristics of the photo-generated charge carriers. The density of the $V_{S8}$ for ZnO-shell is higher than TiO$_2$-shell (XPS), which might have enhanced the hole capture process thereby contributing to the PCA. The densities of oxygen related defects differ by a factor of 2.6, causing an improvement of nearly 1.6 times in the PCA. Apparently, this is not linear scaling because of the differences in the chemical nature of the defects. Finally the higher PCA for ZnO shell can be because of high density of defects, lower binding energy of surface adsorbents, and comparatively lower mobility of the holes in the VB.

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Notes and references
