

Literature Review

2.1 Degradation of industrial dyes – materials and brief literature review.

The importance of clean water cannot be dwindled today due to shortage of clean water. One of the areas in industry that utilizes a huge amount of water is the dyeing industry where the untreated chemical substances pose heavy threats to the ecosystem dependent directly and indirectly. (Saquib, Abu Tariq et al. 2008, Yang, Dong et al. 2010) These are mostly consisting of non-biodegradable substances. The following literature survey presents the various works carried out by other researchers in the field.

TiO₂ is a preferred choice of material for researchers due to its low cost, easy availability, non-toxicity and ease of tunability. Pu et al., have used TiO₂ in composition with graphene oxide (GO) for degradation of rhodamine 6G and observed good interaction of TiO₂ and GO. (Pu, Zhu et al. 2017) This effect added the photocatalytic degradation by 3.5 times greater than bare TiO₂ with observed 100% degradation in 90 mins. Park et al., prepared nitrogen (N) doped TiO₂ graft copolymerization for visible photocatalysis of methyl orange, degrading over 70% in 60 min (Park, Kim et al. 2017). In order to utilize the full spectrum of UV and visible, Hu et al., created a three dimensional MoS₂ and TiO₂ nanosheets on GF (graphitic fibers) for degrading 90% methyl orange in 30 min (Hu, Zhao et al. 2017). In another study, Panomsuwan et al., reported black TiO₂ for reducing methylene blue up to 90% in 180 min which they attributed to large surface area and oxygen vacant sites (Panomsuwan, Watthanaphanit et al. 2015). Laishram et al., have also reported hydrogenated HfO₂ doped TiO₂ for degradation of several common industrial dyes among which methylene blue was reportedly 90% degraded as fast as 10 mins under basic pH (Laishram, Shejale et al. 2018). These results indicate the importance of absorption in the UV and visible region of the solar spectrum and also the ambience at which the reaction is carried and further studies is needed to ensure fast and complete degradation of the dyes.

2.2 Catalytic Soot Oxidation – materials and brief literature review.

Clean air is an essential human requirement. Indoor and outdoor air pollution have resulted in 6.5 million deaths according to estimates given by the World Health Organisation (WHO). A major portion accounting for 90 % of this occurs in South East Asia and Western Pacific regions belonging to middle- and low- income families. ((WHO) 2016) Some of the major diseases that can be directly correlated to air pollution includes lung diseases, and cardiovascular diseases. Of the many pollutants categorized under air pollutants - soot having 2.5 μm size is a dangerous component to environment and health. Soot is defined as a particulate matter having deep black colour of carbon produced mainly by incomplete combustion of organic matter. (Weidman and Marshall 2012, Oxford 2020) Diesel and petrol engines and industrial chimneys are some of the places that contributes mainly to soot pollution. Diesel particulate filters having catalytic converters are installed in the engines to oxidise the soot particulates to gaseous products. The most used catalyst is Pt, however, it is highly expensive and tends to suffer from catalytic poisoning mandating frequent replacement of the catalytic converter (Zhang, Hou et al. 2017). Replacements of Pt are being done by cost reliable materials such as CeO₂, ZSM, NiO, perovskites, SiO₂, Al₂O₃ and composites of CeO₂ with other metal and rare earth oxides. (Guo, Meng et al. 2013, Giménez-Mañogil, Bueno-López et al. 2014, Wagloehner, Baer et al. 2014, Laishram, Shejale et al. 2018, Sudarsanam, Hillary et al. 2018, Aneggi, Llorca et al. 2019, Jampaiah, Velisoju et al. 2019, Martínez-Munuera, Zoccoli et al. 2019, Tran, Martinovic et al. 2020)

Aneggi et al., reported the importance of oxygen vacancies in soot oxidation using CeO₂ and ZrO₂ based catalyst. They also emphasized on the role of ZrO₂ stabilizing the performance and also increasing the number of active oxygen sites (Aneggi, de Leitenburg et al. 2006). They also

reported light off temperature T_m as low as ranging from 263 °C to 380 °C with tightly milled catalyst at different time from 10 min to 10 h. Krishna et al. also carried out studies relating to rare earth and Pt doped to CeO_2 where Pt and Re doped Ce were found to be more active which they attributed to improved CO to CO_2 conversion and the presence of Pt metal (Krishna, Bueno-López et al. 2007). Zawadki et al. prepared cobalt alumina spinel catalyst for soot combustion reaction, however high T_{50} was observed ranging from 520 °C to 590 °C for different composition of alumina with different metals such as Pt, Zn, and Co. Liang et al suggests ceria doped with Cu and Mn to have T_m as low as 356 °C to 368 °C when doped which they attributed to the formation of solid solutions of the constituent metals promoting oxygen vacant sites and increases chemisorption by surface oxygen (Liang, Wu et al. 2008). Zhang et al synthesized perovskites that are macroporous comparable to supported Pt catalysts with T_{50} of 336 °C when Temperature Programmed Oxidation (TPO) was performed (Zhang, Zhao et al. 2009). Soot oxidation is a technique that can be improved by enhancing the interfacial connection of the soot and the catalyst. This is especially because the reaction occurring involves a gas-solid-solid interface which is highly dependent upon the contact the soot makes with the catalyst being used (Voskanyan and Chan 2018).

2.3 Carbon nanomaterials for energy and environmental-based applications – materials and brief literature review.

Carbon in its various forms has been extensively and exhaustively studied for various applications. Very recently multiwalled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) and graphene have caught enormous attention due to its admirable properties. Literature reports the use of such carbons in energy harvesting applications in solar cells as photoanode materials to enhance properties like conductivity and electrocatalytic activity. Mehmood et al. synthesized Al_2O_3 impregnated TiO_2 MWCNT and used it as photoanode for DSSC and obtained an efficiency of 7.02 % compared to 5.02 % of the pristine TiO_2 (Mehmood, Malaibari et al. 2016). Jang et al synthesized a carbonized TiO_2 layer over the traditional TiO_2 DSSC with both sides (photoanode and counter electrode) of DSSC based solar cell having carbonised TiO_2 at both ends which recorded efficiency of 5.21 % (Jang, Xin et al. 2012). Graphene and MWCNT based 3-D architecture was proposed by Yen et al, which recorded an increase in 31 % higher than conventional DSSC with PCE of 6.11 %. They attributed this to the reduced pi-pi interaction due to the incorporation of MWCNTs (Yen, Hsiao et al. 2011). However, there are literature reports where using MWCNTs has affected negatively up on the cell performance by hindering the absorption of dyes (Yen, Lin et al. 2008). Moreover, incorporation of MWCNTs does not account for strong contact points because of the morphological and structural variations. (Brennan, Byrne et al. 2011)

Other carbon-based materials of varying morphology are being developed for its use in applications relating to energy storage such as batteries – lithium-ion and sodium-ion and supercapacitors. For example, Yun et al synthesized ultra-thin hollow carbon with 3 nm thick carbon walls which was used for sodium-ion symmetric pseudocapacitors that recorded specific capacitance of 186 Fg^{-1} . (Yun, Cho et al. 2015) Similar hollow carbon with double-shelled was prepared by Xu et al using block co-polymer and TEOS as templates with high surface area > 600 m^2/g . they reported after 100 cycles a specific discharge capacity of 920 mAh/g at 0.1 A/g current density (Xu, Niu et al. 2018). Furthermore, these N doped Carbon were used for CO_2 capture application, such as, Li et al. electrospun carbon nanofibers dispersed with NiO to form a free-standing film with high surface area which was used for CO_2 uptake and electroreduction. Additionally, these were used for studying the performance of electrochemical supercapacitors having 850 F/g specific capacitance (Li, Guo et al. 2018). Zhu et al used microwave solvothermal synthesized carbon spheres as Pt replacement for counter electrode and observed comparable efficiency of 6.28 % (Zhu, Wang et al. 2016). Thus, new carbon-based materials such as nitrogen-doped core shell, hollow and solid spheres are highly being used for various applications. One of which is the adsorption of heavy metal and toxic ions such as Pb^{2+} and Cd^{2+} (Yuan, An et al. 2018). Apart from this, the N doped porous carbon are used for

biomedical applications, for example, Hu et al. synthesized nitrogen-doped mesoporous carbon and graphene and used it as nanoenzymes for peroxidase mimicking (Hu, Gao et al. 2018). Taking into account the importance of new nanocarbon structure, it is important to study the catalytic activity, interaction with other dopants to better understand for effectively utilizing in similar and other advanced applications.

2.4 All Inorganic CsPbBr₃ perovskites – increase stability by protecting with metal oxides and making composite with graphitic carbon nitride (GCN)

The importance of perovskite quantum dots has risen over recent years due to its luminescent and enhanced photoelectrochemical properties which have opportunities in optoelectronic applications such as displays, LEDs, solar cells, lasers and photocatalysis etc (Kim, Yassitepe et al. 2015, Wang, Li et al. 2015, Swarnkar, Marshall et al. 2016, Xu, Yang et al. 2017). Protesescu et al. synthesized halide perovskites using the hot injection method (Protesescu, Yakunin et al. 2015). In this method in a solution of containing PbBr₂ under inert atmosphere and certain temperature, cesium oleate is injected. However, the instability issues with exposure to ambient atmosphere, light and moisture which makes it ineffective for use in fabrication and device (Zhou, Xu et al. 2018). The outer coating of a protective layer has been suggested as a facile and potential means of addressing the instability issue, for example, Chen et al. prepared photonic crystals of organic halide perovskite coated with PDMS. They were able to achieve stability in contact with water after 24 h (Chen, Schünemann et al. 2017). Apart from this, inorganic oxides such as Al₂O₃ have been used. Loiudice et al. used Atomic Layer Deposition (ALD) to deposit AlO_x on CsPbBr₃ quantum dots and showed stability when exposed to air for at least 45 days (Loiudice, Saris et al. 2017). Huang et al. synthesized silica encapsulated CH₃NH₃PbBr₃ quantum dots using tetraethyl orthosilicate in toluene (Huang, Li et al. 2016). However, the coating materials are insulators that does not conduct electrical charges which further objects to the use of these materials for various optoelectronic applications. Therefore, metal oxides encapsulation is used for used as coating shell for the halide perovskite. Liao et al. synthesized CsPbBr₃ nanocrystals in composition with metal oxides of Ti, Si and Sn which they further characterized using photoelectrochemical application to study the mobility of charge carriers and generated current density (Liao, Xu et al. 2018). Further, it was illustrated by Chen et al. that by varying the constituent cation and anions there can be wide tunability of which can cover entire up to the visible spectrum, such as changing the halide compound from Br⁻ to I⁻ the emission can be tuned from green to red luminescence (Chen and Chen 2019). Thus, successfully forming a stable perovskite compound will facilitate good charge transport and collection from the perovskite material and increase the stability as well. This will be immensely useful application relating to display technology, photodetectors, solar cells, etc.

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