

Perspective

Heterogeneous Photocatalysis Scalability for Environmental Remediation: Opportunities and Challenges

Sherif A. Younis ^{1,2}  and Ki-Hyun Kim ^{1,*} 

¹ Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seoul 04763, Korea; sherifali_r@yahoo.com

² Analysis and Evaluation Department, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt

* Correspondence: kkim61@hanyang.ac.kr

Received: 4 September 2020; Accepted: 24 September 2020; Published: 25 September 2020



Abstract: Heterogeneous photocatalysis is an ecofriendly technique for purifying organic pollutants in environmental systems. While pilot-scale photoreactors have explored photocatalytic system upscalability, their practical implementation is restricted for various reasons. These include feed composition alteration, complicated photoreactor designs, high operation and synthesis costs, photocatalyst poisoning, low quantum yield under solar irradiation, fast exciton recombination, and low reuse or regeneration capabilities. In this paper, we highlight the photocatalyst scalability challenges for real-world applications. We also provide an in-depth discussion on photocatalyst opportunities for effective air and water pollution control. Lastly, we offer a contemporary perspective on photocatalysis scale-up for the real environmental treatment.

Keywords: heterogeneous photocatalysis; environmental remediation; application challenges; scaling-up

1. Introduction

Heterogeneous photocatalysis (HPC) is a photoactivated chemical reaction that became popular after Fujishima and Honda discovered the UV-driven photoelectrochemical water splitting reaction with a TiO₂-based photoanode in 1972 (Figure 1). The effectiveness of HPC has been studied in many diverse fields, including environmental remediation [1,2], energy production [1], chemical engineering [3], medicine/biochemistry [4,5], agriculture [6], and multidisciplinary research areas [7] (Figure 1).

The HPC process is an advanced, ecofriendly approach to purify a wide range of gaseous and refractory pollutants in both air and water environmental systems [2,8]. Upon light irradiation, the HPC process harnesses photon energy when it is equal to or exceeds the bandgap energy (E_g). The absorbed photon energy induces electron (e^-) photoexcitation, followed by interfacial valence band (VB “hole (h^+) creation”) charge transfer to the conduction band (CB; i.e., e^-/h^+ pairs separation) and activation of surface redox reactions [1]. The photogenerated e^-/h^+ pairs possess a high redox potential that can convert oxygen/water (O_2/H_2O) molecules adsorbed on the hydrated catalyst surface to a reactive oxidative species (ROS) such as free excitons (e^-), superoxide radical anions ($\bullet O_2^-$), and/or hydroxyl/hydroperoxyl radicals ($\bullet OH/HO_2\bullet$) [9]. ROS radicals play a vital role in accelerating the oxidative/reduction reactions on the surface of the photocatalysts, such as converting adsorbed organic/inorganic pollutants into less harmful compounds [10]. However, the rapid reverse reaction, fast e^-/h^+ pair recombination, is a major limitation on scaling HPC technology to real-world conditions. Further, most of the newly developed photocatalysts, such as metal–organic frameworks (MOFs), metal-oxides, and nanocomposites, exhibit low quantum efficiency (<1%) and poor photonic stability under UV–visible/solar lights [1,11]. In this respect,

MOF-based photocatalysts exhibited low photonic stability under normal environmental conditions due to the potential destruction of the coordination connectivity between a ligand and metal nodes in the presence of water molecules [1]. Such deformation in the MOF molecular structures can lead to a decrease in the photocatalytic activity with the disruption of the photogenerated charge mobility/separation mechanism (between ligand and metal nodes). Depending on the solution pH, ZnO photocatalyst can also be subjected to photodissolution during HPC reaction in the aqueous media (i.e., direct attack of the photon on the surface of Zn-O bonds, followed by the release of Zn ions (at pH = 3–5) or Zn hydroxide (at pH = 10)) [12]. Likewise, the photonic stability of ATP/TiO₂/Ag₃PO₄ composite could be deteriorated as a result of the photoreduction of Ag⁺ (in the Ag₃PO₄) into metallic Ag ($\text{Ag}^+ + e^- + h\nu \rightarrow \text{Ag}$) during the HPC reaction [13]. In addition, the use of HPC technology for air purification (e.g., ventilation and air conditioning (HVAC)) faces challenges of (i) poor effectiveness removing low (sub-ppm)-concentration hazardous pollutants (e.g., volatile organic compounds (VOCs)), (ii) high energy consumption (UV-A light use), (iii) long reaction duration, and (iv) difficult photocatalytic reactor optimization (photon and mass transfer control) [14].

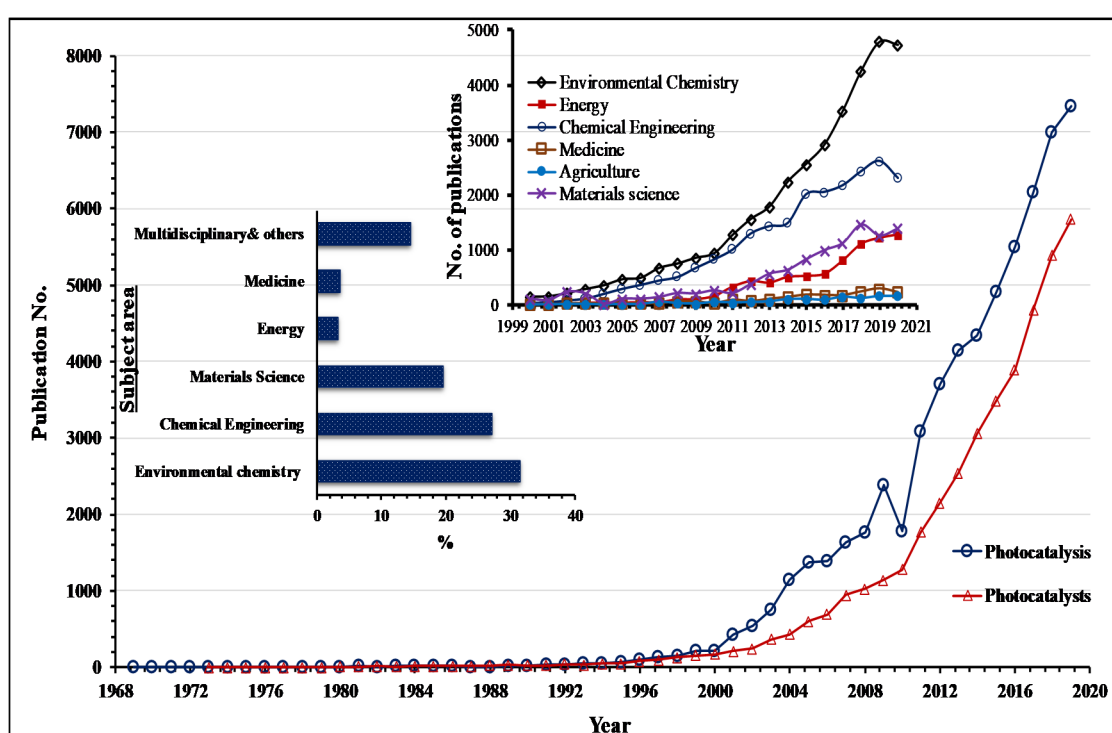


Figure 1. A meta-analysis of the Scopus research database for publications with “Photocatalysis” or “Photocatalyst” keywords between 1970 and August 2020 (inset: no. of publications per research area).

In this work, we highlight the main technical challenges restricting photocatalysis applications in environmental fields and address solutions based on up-to-date advances. We also discuss HPC-based photoreactor scalability in water and air purification systems.

2. Photocatalysis: Challenges vs. Opportunities

Many photocatalysts have been proposed for water and air decontamination applications, with ZnO and TiO₂ nanoparticles being the preferred options. These include MOFs, carbon or organic-based materials, nanocomposites, and metal oxide semiconductors and are based on criteria such as commercial availability, cost-effectiveness, conditional stability, high catalytic activity, and non-toxicity [15,16]. Nonetheless, the scalability of ZnO and TiO₂-based HPC systems is debatable due to the shortcomings of (i) a large bandgap energy (TiO₂ and ZnO have an E_g of 3.1–3.3 eV) reduces quantum efficiency under sunlight, (ii) high energy consumption (high photon energy below 400 nm (UV-A) wavelength) induces e^-/h^+ pair generation, (iii) ROS reduction due to rapid e^-/h^+

pair recombination on active surface sites decreases photocatalytic activities, (iv) limited ability to scale up due to a complicated modification process required to improve solar-driven photocatalysis, (v) fast active surface site deactivation/poisoning via interaction with intermediated byproducts that lowers the kinetic reaction rate, (vi) natural scavenger presence (e.g., antioxidant systems including halides and polyphenols) that can impair the photocatalytic process via photogenerated ROS radical interactions, (vii) low photocatalyst chemical stability that shortens its reuse-cycle service lifetime, (viii) spent solid photocatalyst disposal as secondary solid waste, and (ix) low photocatalytic/photonic efficiency against high concentrations of mixed pollutants at high air and water flow rates.

When using HPC technology, photon absorption on photocatalyst surfaces may diminish due to catalysts aggregation and/or light reflection/scattering, especially in high-salinity water with solid suspension or color products [1]. The spent photocatalysts remain suspended in the mobilized photoreactors unless there is a suitable recovery system such as filtration. There are many diverse photoreactor types, including immobilized photoreactors, photocatalytic membrane reactors (PMRs), and hybrid membrane slurry photoreactors. These were designed to help resolve problems mentioned above, but they suffer from technical drawbacks such as catalyst efficiency and membrane fouling/scaling [16]. The photon and mass transfer limitations are also other engineering problems that restrict the implementation of HPC-based photoreactors in the industrial scale. In most photoreactors, it is not easy to achieve uniform irradiance over the entire photocatalyst surface, especially when loading large amounts of a catalyst. Further, part of the emitted photon cannot reach the photocatalyst surface due to simultaneous light absorption/diffraction during traveling through the fluid/gas media containing target reactants (or reagent species). Such a consumption of photon light could require an increase in photon energy level for the activation of the photocatalyst. The limited mass transfer of the pollutant molecules over the restrained photocatalyst layer (due to the alteration of flow rates, amount of slurry photocatalyst, and total suspension volume) is also recognized as major impediments for the industrialization of fluidized bed photoreactors. An overview of the photoreactors design and their challenges (in terms of photon and mass transfer limitations) has been given elsewhere [17–20]. Moreover, HPC technology has been used to address diverse outdoor and indoor air VOC pollutants via painting buildings, roofs, bridges, pavement, and ceramic surfaces with TiO₂ photocatalysts. A recent study also proposed using three flat/tubular UV-based TiO₂ photoreactor configurations: bench-scale, semi-pilot, and full pilot (Figure 2a) for indoor air treatment [21]. However, the reaction rate of the photocatalytic system for outdoor/indoor air purification is affected by the combined effects of various factors, including substrate or platform configuration used for coating the semiconductors, light irradiance, VOC pollutants (types and concentration), temperature, photoreactor design, mass/air velocity, and moisture level [22].

Since 2016, 1500 studies have focused on the technical defects mentioned, with various prospects for enhancing environmental photocatalysis use. For example, many pre-/post-synthesis modification strategies have been utilized to improve the optical response and photoactivity of bulk photocatalysts in the visible/sunlight spectrum. Some strategies found that photocatalysts doped with heteroatoms like O, N, S, P, and B are more efficient due to a dipole moment increase. Such an increase in the dipole moment facilitates electron transfer kinetics from VB to CB and shifts the optical response to the visible spectrum [23]. Photocatalyst properties such as bandgap, Fermi level, charge transport, spin density, localized electronic state, and optical/magnetic characteristics can be tuned by doping the semiconductor crystal lattice with low-cost/abundant transition metals like Fe, Ni, Ti, Zn, and Co or alkali metals such as Li, Na, and K [24]. Metal-oxide photocatalyst defect formation (oxygen vacancies) is another effective option for enhancing photocatalyst activity [25].

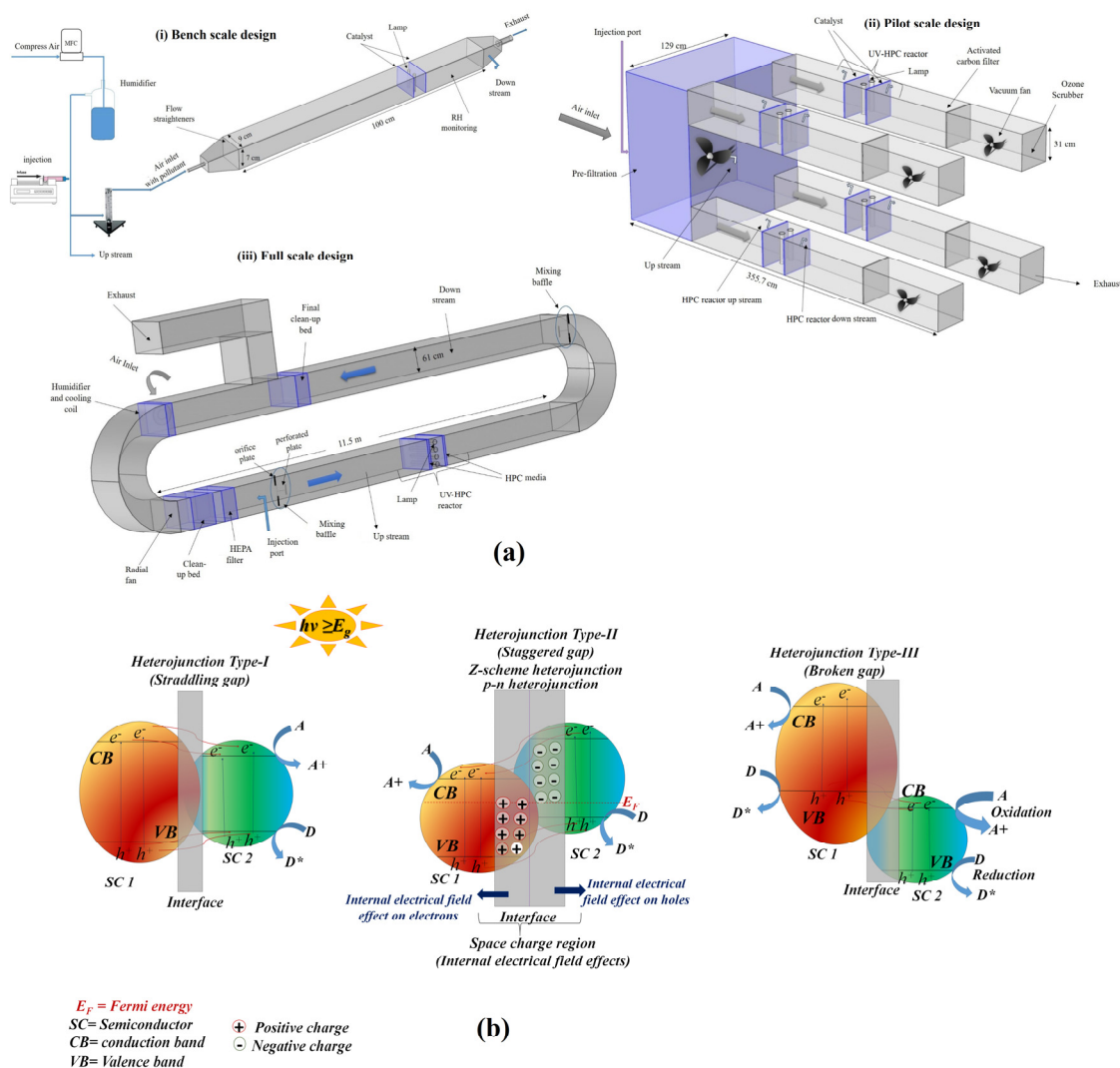


Figure 2. Schematic of (a) the indoor air photoreactor design (Reprinted from [21], with permission of Elsevier) and (b) semiconductor photocatalyst e^-/h^+ pair separation between heterojunction surfaces.

Based on the bandgap alignment concept, the design of semiconductor coupling (heterojunction or Z-scheme photocatalyst) can be chosen to increase photogenerated charge lifetimes for photocatalytic performance enhancements in the visible light spectra [9]. At the heterojunction interface, photogenerated electrons in the CB can migrate from more to less negative Fermi energy (E_F), whereas the VB demonstrates a hole transfer from more to less positive E_F (Figure 2b) [16,26]. This charge transfer mechanism decreases the charge recombination rate so that the redox potential of the constructed heterojunction system can promote catalytic activities under solar irradiation. For example, AgFeO_2 -graphene/ $\text{Cu}_2(\text{BTC})_3$ MOF, as a ternary heterojunction photocatalyst (with good reusability cycles of up to 4 runs), has recently been developed to enhance sunlight-driven photocatalytic degradation of pharmaceutical pollutants [27]. Due to the low E_F (-0.08 V vs. SHE) of graphene, the photogenerated electrons in the CB of AgFeO_2 (-0.50 eV) and $\text{Cu}_2(\text{BTC})_3$ MOF (-0.18 eV) migrated to the graphene layer (i.e., acting as a trapping site to increase the lifetime of e^-/h^+ pairs). Likewise, several types of TiO_2 -based Z-scheme photocatalysts (e.g., $\text{Au@CdS}/\text{IO-TiO}_2$, CdS-Ag-TiO_2 , $\text{TiO}_2/\text{WO}_3/\text{Au}$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S-MWCNT-TiO}_2$ systems) have been synthesized [28]. As mentioned above, these TiO_2 -based Z-scheme photocatalysts possess multiple merits such as: (a) low bandgap energy, (b) spatial separation of redox-active sites, (c) effective migration/separation rate for the e^-/h^+ pairs, and (d) high redox ability to thermodynamically enhance visible-driven HPC reactions towards CO_2 reduction, H_2 production (e.g., water splitting), and degradation of organic contaminants

under visible irradiation. The detailed information on the basic principles of Z-scheme heterojunction photocatalysts, along with their types and synthesis strategies, can be found elsewhere [28,29].

Similar to a Z-scheme heterojunction photocatalyst (Type II, Figure 2b), plasmonic photocatalysts can enhance solar-driven HPC applications. The system's enhanced performance is due to plasmon resonance energy transfer from the plasmonic metal (e.g., Ag or Au) to the semiconductor through dipole–dipole interaction and/or hot electron injection [24]. Due to high noble metal costs (e.g., Ag and Au), more abundant plasmonic elements (e.g., Bi, Al, or Cu) are recommended. Enormous effort has been made to overcome single photoreactor obstacles by optimizing the operating parameters and integrating hybridized photoreactor systems through a combination of PMRs and immobilized/suspended photocatalysts (e.g., enhancing performance at reduced operation cost) [16,30]. To increase photocatalytic performance in the hybridized mode, the cross-flow mode for the feed stream is recommended for reducing catalyst/substrate accumulation on the membrane surface (cake formation). Both mechanochemical and hydrothermal synthesis methods are promising ecofriendly methods for reducing the cost of scaled-up production for solar photocatalysts. In particular, the mechanochemical synthesis has been proposed for the upscale production of various catalytically active materials (e.g., metal oxides, MOFs, and nanocomposites) due to its simple operation under milder conditions, short reaction period, solvent-free solid-state reaction (under dry milling), and high reproducibility. Based on the applied friction force during grinding, a variety of defects/changes can be introduced in the crystal lattice of the synthesized photocatalysts, leading to improved photoreactivity [31]. In the hydrothermal synthesis, an aqueous phase (e.g., ecofriendly, low-cost solvent) is used as the main reaction medium for catalyst synthesis under high temperature/pressure conditions. The hydrothermal approach has been adopted preferably for the sustainable production of zeolite catalysts (from kaolinite) in industry, with the high yields [32]. During the hydrothermal reaction, the properties of water (e.g., density, viscosity, dielectric/ionization constant, surface tension, and vapor pressure) are changed as a function of applied temperature/pressure. Accordingly, water can act as a solvent, chemical component, or a puffing accelerator for the rates of hydrolysis and ionic reactions as water properties change with the increases in applied temperature/pressure [33]. Synthesis and operation costs are, however, dependent on many other factors involved in the use of catalyst (e.g., individual component costs, energy consumption, regeneration process, and long-term stability).

3. Future Photocatalysis Perspective and Upscaling Recommendations

As discussed above, diverse approaches offer promising opportunities for increasing photocatalyst environmental applications. However, most HPC research was conducted using bench-scale setups under unrealistic controlled conditions that are far from real feed streams. Only limited efforts have assessed photocatalytic performance using real water and air feed streams [21,27,34]. However, it should be noted that there are many impractical/inconsistent data in the existing research regarding HPC application for environmental remediation. This is due to the frequent use of (i) deionized water (or pure air stream) as a reaction medium (e.g., ignoring the impact of background constituents on HPC system), (ii) longer reaction period (>3 h; i.e., unrealistic time), (iii) single pollutant system (i.e., far away from reality), and (iv) optimized batch reactor system (relative to practical continuous mode) to control the mass transfer process. Further, HPC technology scalability has barely been explored for industrial purposes like wastewater treatment or outdoor/indoor air purification. In addition, the photocatalytic water splitting to hydrogen (as renewable energy) is still suspected to be impractical in that it requires high-expensive sacrificial agents or electron donors (e.g., glucose, glycerol, triethanolamine, ethylene glycol, lactic acid, isopropanol, acetonitrile, and methanol) relative to the commercial route of H₂ generation [35]. Besides, it is crucial to design photoreactors capable of continuous evacuation/separation of coevolved explosive O₂ and H₂ gas mixture during upscaling of the HPC-based water splitting in order to (i) prevent photocatalyst inactivation by evolved O₂, (ii) reduce operation cost, and (iii) avert the possible reverse reaction (i.e., recombination of H_{2(g)} and O_{2(g)}) in the presence of active photocatalysts. As a fact, relatively little is known about catalyst deactivation mechanisms with respect to the application of HPC technologies under the

real-world conditions. Most importantly, the performance of the integrated hybrid photoreactor is expected to be reduced if applied at the industrial scale due to many interfering variables (e.g., natural scavengers, sunlight intensity variation, feed quality, and side reactions (between mixed contaminants)). Further, the generation of the byproducts is generally ignored when assessing HPC performance (catalyst poisoning and quantum yield) under simulated lab-scale conditions.

In the upscaled fields, Purifics Photo-Cat is recognized as the only commercialized UV-driven HPC system for the real wastewater treatment although the many solar-driven photocatalysts have been proposed in the literature [24]. Photo-Cat is a closed-loop UV-driven TiO₂ slurry-based photocatalytic system with a high flux ceramic membrane for continuous water purification/decontamination from organic/biological pollutants, inorganic (or heavy metals), and submicron particulate matters (<https://www.purifics.com/photo-cat>). A good number of HPC-based life projects (e.g., PhotoPAQ (LIFE08 ENV/F/000487: 2010–2014), MINOX-STREET (2013–2018), and EQUINOX (IFE12 ENV/ES/000749: 2019), co-funded by European Union's) have been carried out to confirm the feasibility of photocatalytic cementitious coating materials for outdoor air pollutant remediation (e.g., NO_x, O₃, VOCs, and airborne particles) [22]. Nonetheless, it is still challenging to predict HPC performance in the field due to the following possibilities: (i) photocatalyst aging processes when coated on roads and pavement for outdoor traffic, (ii) seasonal environmental parameter variations such as solar irradiation, wind, temperature, and humidity, and (iii) photocatalyst exposure conditions like air volume to photocatalytic surface ratio. There are additional challenges for solar-driven photocatalytic purification systems, which are required to remain in continuous, 24-h operation, at nighttime. These challenges require smart photocatalyst development, with operational flexibility under both solar and LED light, as well as self-cleaning behaviors to reduce surface deactivation. In this regard, TiO₂ has been utilized as a self-cleaning material in industrial projects such as coated liquid suspension for building materials (e.g., HydrotechTM by TOTO Ltd., Beijing, China) and in cementitious composites (e.g., TX ActiveTM, TX AriaTM, and TX MillenniumTM by Italcementi SpA Company, Bergamo, Italy) [36]. This supports the premise that TiO₂-based HPC technology is scalable and can be used to improve day–night cycle performance in real-world applications. Combining adsorption and photocatalysis is an alternative option for overcoming light source limitations and extends day–night cycle operational capabilities. A hybrid adsorbent–photocatalyst system will also reduce catalyst deactivation and extend service lifetime by adsorbing undesirable byproducts and accelerating the mineralization process (i.e., adsorbent surfaces can serve as an ⁻OH species source). Future studies should focus on understanding hybridized photoreactor system efficacy and solar-driven photocatalyst performance and stability under real industrial conditions. Accurate cost estimates are also required for hybrid adsorbent–photocatalyst system production in scaled-up industrial operations.

4. Conclusions

We reviewed many reports on HPCs for water and air purification. Despite the number of publications, newly developed solar-driven photocatalysts such as MOF-based nanocomposites and plasmon semiconductors need to be validated for practical applications because of their high production costs and poor kinetic stability. TiO₂/ZnO-based photocatalysis is the preferred real-world application option due to its cost, stability, self-cleaning behavior, and commercial availability. However, more efforts should aim to enhance an optical response and photocatalytic activity in visible light regions, using methods such as heteroatom or transition/alkali metal (as low-cost and abundant elements) doping, adsorption–photocatalysis combinations, and hybrid photoreactor tuning. Future investigations for implementing practical photocatalytic systems at the industrial scale are necessary to (i) select reproducible and easy synthesis protocols for photocatalyst, (ii) optimize the configuration of photoreactors, (iii) mitigate poor photocatalytic performance component materials such as suspended particles, colored components, and natural antioxidants, (iv) reduce photocatalyst deactivation phenomena by suppressing the generation of intermediate byproducts, and (v) reduce operational costs (e.g., relative to conventional treatment options).

Author Contributions: S.A.Y.: Formal analysis, Writing–review & editing, Investigation, Software, and Methodology; K.-H.K.: Writing–review & editing, Project administration, Resources, and Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research acknowledges grant support from the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and Future Planning (Grant No: 2016R1E1A1A01940995).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Younis, S.A.; Kwon, E.E.; Qasim, M.; Kim, K.; Kim, T.; Kukkar, D.; Dou, X.; Ali, I. Metal-organic framework as a photocatalyst: Progress in modulation strategies and environmental/energy applications. *Prog. Energy Combust. Sci.* **2020**, *81*, 100870. [[CrossRef](#)]
2. Durgalakshmi, D.; Rakkesh, R.A.; Rajendran, S.; Naushad, M. *Green Photocatalysts for Energy and Environmental Process*; Rajendran, S., Naushad, M., Ponce, L.C., Lichtfouse, E., Eds.; Environmental Chemistry for a Sustainable World; Springer International Publishing: Cham, Switzerland, 2020; Volume 36. [[CrossRef](#)]
3. Parrino, F.; Bellardita, M.; García-López, E.I.; Marci, G.; Loddo, V.; Palmisano, L. Heterogeneous photocatalysis for selective formation of high-value-added molecules: Some chemical and engineering aspects. *ACS Catal.* **2018**, *8*, 11191–11225. [[CrossRef](#)]
4. Tomás-Gamasa, M.; Mascareñas, J.L. TiO₂-based photocatalysis at the interface with biology and biomedicine. *ChemBioChem* **2020**, *21*, 294–309. [[CrossRef](#)]
5. Zhang, H.; Shan, Y.; Dong, L. A Comparison of TiO₂ and ZnO nanoparticles as photosensitizers in photodynamic therapy for cancer. *J. Biomed. Nanotechnol.* **2014**, *10*, 1450–1457. [[CrossRef](#)] [[PubMed](#)]
6. Sichel, C.; de Cara, M.; Tello, J.; Blanco, J.; Fernández-Ibáñez, P. Solar photocatalytic disinfection of agricultural pathogenic fungi: Fusarium species. *Appl. Catal. B Environ.* **2007**, *74*, 152–160. [[CrossRef](#)]
7. Ibhaddon, A.; Fitzpatrick, P. Heterogeneous photocatalysis: Recent advances and applications. *Catalysts* **2013**, *3*, 189–218. [[CrossRef](#)]
8. Lacombe, S.; Fresno, F.; Lavrenčič Štangar, U. Photocatalysis: New highlights from JEP 2013. *Environ. Sci. Pollut. Res.* **2014**, *21*, 11111–11115. [[CrossRef](#)]
9. Pedanekar, R.S.; Shaikh, S.K.; Rajpure, K.Y. Thin film photocatalysis for environmental remediation: A status review. *Curr. Appl. Phys.* **2020**, *20*, 931–952. [[CrossRef](#)]
10. Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R.; et al. Photocatalytic Degradation of organic pollutants using TiO₂-based photocatalysts: A review. *J. Clean. Prod.* **2020**, *268*, 121725. [[CrossRef](#)]
11. Byrne, C.; Subramanian, G.; Pillai, S.C. Recent Advances in Photocatalysis for Environmental Applications. *J. Environ. Chem. Eng.* **2018**, *6*, 3531–3555. [[CrossRef](#)]
12. Han, J.; Qiu, W.; Gao, W. Potential dissolution and photo-dissolution of ZnO thin films. *J. Hazard. Mater.* **2010**, *178*, 115–122. [[CrossRef](#)] [[PubMed](#)]
13. He, H.; Jiang, Z.; He, Z.; Liu, T.; Li, E.; Li, B.-W. Photocatalytic activity of attapulgite–TiO₂–Ag₃PO₄ ternary nanocomposite for degradation of Rhodamine B under simulated solar irradiation. *Nanoscale Res. Lett.* **2018**, *13*, 28. [[CrossRef](#)] [[PubMed](#)]
14. Boyjoo, Y.; Sun, H.; Liu, J.; Pareek, V.K.; Wang, S. A review on photocatalysis for air treatment: From catalyst development to reactor design. *Chem. Eng. J.* **2017**, *310*, 537–559. [[CrossRef](#)]
15. Rafique, M.S.; Tahir, M.B.; Rafique, M.; Shakil, M. Photocatalytic nanomaterials for air purification and self-cleaning. In *Nanotechnology and Photocatalysis for Environmental Applications*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 203–219. [[CrossRef](#)]
16. Wetchakun, K.; Wetchakun, N.; Sakulsermsuk, S. An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO₂- and ZnO-based photocatalysts used in suspension photoreactors. *J. Ind. Eng. Chem.* **2019**, *71*, 19–49. [[CrossRef](#)]
17. Sundar, K.P.; Kanmani, S. Progression of photocatalytic reactors and it's comparison: A review. *Chem. Eng. Res. Des.* **2020**, *154*, 135–150. [[CrossRef](#)]
18. Sohrabi, S.; Keshavarz Moraveji, M.; Iranshahi, D. A review on the design and development of photocatalyst synthesis and application in microfluidic reactors: Challenges and opportunities. *Rev. Chem. Eng.* **2020**, *36*, 687–722. [[CrossRef](#)]

19. Van Gerven, T.; Mul, G.; Moulijn, J.; Stankiewicz, A. A review of intensification of photocatalytic processes. *Chem. Eng. Process. Process Intensif.* **2007**, *46*, 781–789. [[CrossRef](#)]
20. McCullagh, C.; Skillen, N.; Adams, M.; Robertson, P.K.J. Photocatalytic reactors for environmental remediation: A review. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1002–1017. [[CrossRef](#)]
21. Shayegan, Z.; Haghghat, F.; Lee, C.S. Photocatalytic oxidation of volatile organic compounds for indoor environment applications: Three different scaled setups. *Chem. Eng. J.* **2019**, *357*, 533–546. [[CrossRef](#)]
22. Feroso, J.; Sánchez, B.; Suarez, S. Air purification applications using photocatalysis. *Nanostructured Photocatal.* **2020**, 99–128. [[CrossRef](#)]
23. Fernandes, A.; Makoś, P.; Wang, Z.; Boczkaj, G. Synergistic effect of TiO₂ photocatalytic advanced oxidation processes in the treatment of refinery effluents. *Chem. Eng. J.* **2020**, 391. [[CrossRef](#)]
24. Djurišić, A.B.; He, Y.; Ng, A.M.C. Visible-light photocatalysts: Prospects and challenges. *APL Mater.* **2020**, *8*. [[CrossRef](#)]
25. Li, T.; Shen, Z.; Shu, Y.; Li, X.; Jiang, C.; Chen, W. Facet-dependent evolution of surface defects in anatase TiO₂ by thermal treatment: Implications for environmental applications of photocatalysis. *Environ. Sci. Nano* **2019**, *6*, 1740–1753. [[CrossRef](#)]
26. Koe, W.S.; Lee, J.W.; Chong, W.C.; Pang, Y.L.; Sim, L.C. An overview of photocatalytic degradation: Photocatalysts, mechanisms, and development of photocatalytic membrane. *Environ. Sci. Pollut. Res.* **2020**, *27*, 2522–2565. [[CrossRef](#)] [[PubMed](#)]
27. El-Fawal, E.M.; Younis, S.A.; Zaki, T. Designing AgFeO₂-Graphene/Cu₂(BTC)₃ MOF heterojunction photocatalysts for enhanced treatment of pharmaceutical wastewater under sunlight. *J. Photochem. Photobiol. A Chem.* **2020**, *401*, 112746. [[CrossRef](#)]
28. Qi, K.; Cheng, B.; Yu, J.; Ho, W. A review on TiO₂-based Z-scheme photocatalysts. *Cuihua Xuebao/Chin. J. Catal.* **2017**, *38*, 1936–1955. [[CrossRef](#)]
29. Xu, Q.; Zhang, L.; Yu, J.; Wageh, S.; Al-Ghamdi, A.A.; Jaroniec, M. Direct Z-Scheme Photocatalysts: Principles, synthesis, and applications. *Mater. Today* **2018**, *21*, 1042–1063. [[CrossRef](#)]
30. Zheng, X.; Shen, Z.P.; Shi, L.; Cheng, R.; Yuan, D.H. Photocatalytic membrane reactors (PMRs) in water treatment: Configurations and influencing factors. *Catalysts* **2017**, *7*, 224. [[CrossRef](#)]
31. Xu, C.; De, S.; Balu, A.M.; Ojeda, M.; Luque, R. Mechanochemical synthesis of advanced nanomaterials for catalytic applications. *Chem. Commun.* **2015**, *51*, 6698–6713. [[CrossRef](#)]
32. Abdullahi, T.; Harun, Z.; Othman, M.H.D. A review on sustainable synthesis of zeolite from kaolinite resources via hydrothermal process. *Adv. Powder Technol.* **2017**, *28*, 1827–1840. [[CrossRef](#)]
33. Yang, G.; Park, S.-J. Conventional and microwave hydrothermal synthesis and application of functional materials: A review. *Materials* **2019**, *12*, 1177. [[CrossRef](#)] [[PubMed](#)]
34. El-Fawal, E.M.; Younis, S.A.; Moustafa, Y.M.; Serp, P. Preparation of solar-enhanced alzo@carbon nano-substrates for remediation of textile wastewaters. *J. Environ. Sci.* **2020**, *92*, 52–68. [[CrossRef](#)] [[PubMed](#)]
35. Chowdhury, P.; Malekshoar, G.; Ray, A.K. Dye-sensitized photocatalytic water splitting and sacrificial hydrogen generation: Current status and future prospects. *Inorganics* **2017**, *5*, 34. [[CrossRef](#)]
36. Petronella, F.; Truppi, A.; Ingrosso, C.; Placido, T.; Striccoli, M.; Curri, M.L.; Agostiano, A.; Comparelli, R. Nanocomposite materials for photocatalytic degradation of pollutants. *Catal. Today* **2017**, *281*, 85–100. [[CrossRef](#)]

