Catalysis Properties of TiO$_2$ Nanofibers in CO$_2$ Conversion: A Comparative Analysis of Polymer Matrices

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Research Article

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Abstract

The quest for efficient and sustainable methods to mitigate Carbon Dioxide (CO$_2$) emissions is a pressing global challenge. This study delves into the crucial role of polymers in tailoring the performance of Titanium Dioxide (TiO$_2$) nanofibers for CO$_2$ conversion reactions. By systematically comparing the influence of different polymers, specifically Polyvinyl Pyrrolidone (PVP) and Polyvinylidene Fluoride (PVDF), on the CO$_2$ conversion activity of TiO$_2$-NFs, we shed light on the remarkable potential of polymeric selection to fine-tune catalyst properties. The paper uses advanced experimental techniques to analyze the structural and morphological properties of PVP-TiO$_2$-NFs and PVDF-TiO$_2$-NFs demonstrating their various morphologies. The investigation involves SEM, TEM, XRD, BET and UV-Vis spectroscopy to better understand the charge separation and recombination processes involved in both materials' CO$_2$ conversion. The results show considerable differences, choice of polymer significantly impacts the CO$_2$ conversion performance of TiO$_2$-NFs. PVP based NFs exhibit enhanced surface area and porosity, resulting in superior catalytic activity, while PVDF based NFs demonstrate remarkable stability. These findings pave the way for innovative approaches to tackle climate change and develop a more environmentally friendly future by advancing energy-efficient and long-lasting photocatalytic technology.

1. Introduction

Photocatalytic CO$_2$ conversion research has been driven by the need to find long-term solutions to mitigate climate change and cut greenhouse gas emissions. Photocatalysts are extremely promising for converting carbon dioxide into useful compounds and fuels by utilizing the power of sunshine(Sarkar et al. 2016). Because of their special structural and surface characteristics, TiO$_2$ nanofibers have become one of the most promising catalysts among them, offering excellent catalytic efficiency and a great affinity for CO$_2$ activation(Jin et al. 2007; Zhang et al. 2018; Su et al. 2022). TiO$_2$ nanofibers have shown great promise in photocatalytic CO$_2$ conversion, as seen in earlier studies, as they are capable of producing methanol, ethanol and other hydrocarbons, among other carbon-based compounds(Yuan et al. 2014; Wang et al. 2022; Gao et al. 2022). However, as a polymer matrices have a substantial impact on the catalytic performance of TiO$_2$ nanofibers, it is essential to take into account their role as supports in order to fully utilize TiO$_2$-NFs as photocatalysts(Crake et al. 2019).

This research study presents a new and original investigation that extends the current corpus of knowledge. Our research focuses on comparing the catalytic characteristics of TiO$_2$ nanofibers in different polymer matrices (PVP and PVDF)(Tan et al. 2017; Lou et al. 2020). The catalysis of CO$_2$ conversion gains a new dimension when TiO$_2$-NFs are synthesized using various polymer supports. The polymer matrices are essential for controlling the catalysts durability, reactivity and selectivity in addition to acting as stabilizers for TiO$_2$ nanofibers(Low et al. 2017). Our work systematically assesses different polymer matrices, such as polyvinyl pyrrolidone (PVP) and Polyvinylidene Fluoride (PVDF), as support for TiO$_2$ nanofibers. In order to shed light on TiO$_2$-NFs potential as a major catalyst in the push for
sustainable CO₂ utilization (Lin et al. 2018; Lou et al. 2020; Li et al. 2022). The strategic design of effective and adaptable catalytic systems will be made possible by the crucial insights that this comparative analysis will provide into the interactions between TiO₂-NFs and polymer matrices (Zhang and Yan 2023).

Furthermore, by investigating the design principles of composites materials with improved photocatalytic characteristics, our research aims to overcome the difficulties related to CO₂ conversion, such as low conversion rates and selectivity issues. We intend to contribute to the creation of sophisticated photocatalytic systems that have significant potential for satisfying the demands of a sustainable future by deciphering the complex interactions between TiO₂ nanofibers and polymer matrices.

2. Experimental Section

2.1 Materials

Titanium isopropoxide (TIP), ethanol (purity 99.8%) and acetic acid (purity 99.8%) were obtained from Merck and Polyvinyl pyrrolidone (PVP) with molar mass = 1,300,000 g/mol, Polyvinylidene Fluoride (PVDF) and Titanium Dioxide Nanopowder were purchased from Sigma.

2.2 Method

2.2.1 Synthesis of Nanofibers via electrospinning

For electrospinning, 1ml of TIP was mixed with acetic acid and ethanol, and was stirred for 30 minutes at room temperature. The resultant was then added to a mixture prepared by dissolving 2.8g of PVP in ethanol. Former was kept for overnight stirring at room temperature. The resultant was loaded in a 10ml syringe and electrospinning was carried out at 25°C at an applied voltage of 21 kV maintaining a tip to collector distance of 14 cm at a flow rate of 1ml/hr., for which the relative humidity was maintained at 55%. Al foil was used to collect the electrospun nanofibers. Similarly for PVDF/TiO₂ nanofibers same procedure was repeated. For the photocatalysis study, the fiber samples were soaked in a 30 ml distilled water (bubbled with CO₂), for a time interval of 8hrs under light radiation with constant stirring. Similar reaction were carried out for TiO₂ nanopowder, Easy separation of the prepared NFs with single step of filtration was observed, which is not the same in case of TiO₂ nanopowder, which can further be added in an advantage of fiber over nanopowder.

3. Results and Discussions

To clarify the crystalline phase and structural characteristics of the composite photocatalysts, the X-ray Diffraction (XRD) patterns of polyvinyl pyrrolidone (PVP) and Polyvinylidene Fluoride (PVDF) supported titanium dioxide (TiO₂) were acquired and is shown in Fig. 1. According to earlier research, the diffraction patterns of the PVP/TiO₂ and PVDF/TiO₂ composites showed distinctive peaks as shown in Fig. 1, that
matched the anatase phase of TiO$_2$ (JCPDS card No. 21-1272)(Scarpelli et al. 2018). The anatase phase’s crystallographic planes (101), (004), (200), (105) and (204) were identified as the primary diffraction peaks at 2θ values of around 25.3°, 37.8°, 48.0°, 54.2° and 62.9° respectively. The PVP supported TiO$_2$ composites XRD pattern was notable for having clearly defined peaks with comparatively narrow full-width at half maximum (FWHM) values, which suggested a higher degree of crystallinity. The PVDF-supported TiO$_2$ composite’s diffraction peaks were somewhat broader, which may indicate some dispersion of TiO$_2$ in the polymer matrix or a degree of reduced crystallinity(Qiu et al. 2022). The interactions between TiO$_2$ nanoparticles and the polymer matrices (PVP and PVDF) can be responsible for the observe shifts or alterations in peak locations, intensities or broadening. The interactions could lead to changes in the size of TiO$_2$ particles, characteristics of the crystal lattice, or structural flaws, which would affect the composite ability to catalyze. Cell parameters are tabulated in Table 1. Both cell parameters and cell volumes were compared with those reported in JCPDS-ICSD standards for anataseTiO$_2$, i.e. a = b = 15.15A, c = 7.575A and V = 1738.63A. The data obtained for nanober is close to that of standard.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Cell Parameter (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP/TiO$_2$-NFs</td>
<td>3.7864 9.5208</td>
<td>136.49</td>
<td>14.30</td>
</tr>
<tr>
<td>PVDF/TiO$_2$-NFs</td>
<td>15.150 7.5750</td>
<td>173.86</td>
<td>3.03</td>
</tr>
</tbody>
</table>

The structural characteristic and chemical makeup of PVP and PVDF supported TiO$_2$ nanofibers are revealed by Raman spectroscopy in Fig. 2, which also clarifies if these nanofibers are suitable for photocatalytic use. The vibrational modes of TiO$_2$ are revealed by unique peaks in the Raman spectroscopy of PVP/TiO$_2$-NFs. The Raman spectra display distinctive bands that are linked to anatase phase of TiO$_2$. These bands are detected at around 144 cm$^{-1}$ (Eg mode) and 396–399 cm$^{-1}$ (B1g mode). Furthermore, PVP related Raman bands at particular wavenumbers may be visible in the spectra, suggesting that PVP interacts with TiO$_2$ nanoparticles, PVP may cause shifts or changes in the Raman peaks of TiO$_2$, suggesting possible interactions at the TiO$_2$ crystals structure because of the polymer support(Secundino-Sánchez et al. 2019; Arif et al. 2023). In addition the discovery of other bands associated with PVDF or PVP indicates that TiO$_2$ and polymer matrices interact to affect the structural characteristic and chemical makeup of the composites.

Considering polymer-supported TiO$_2$ photocatalysts can improve TiO$_2$’s performance and efficiency in photocatalytic processes, they have attracted a lot of interest. In particular, two different polymer matrices- polyvinyl pyrrolidone (PVP) and Polyvinylidene Fluoride (PVDF) are frequently used to support
TiO$_2$ nanoparticles, enhancing photocatalytic activity. It is important to take into account both PVP and PVDF-supported TiO$_2$’s intrinsic characteristics and interactions with TiO$_2$ nanoparticles when comparing the two for photocatalysis. Particularly in wet conditions (Saleem et al. 2022), PVP’s hydrophilic character may promote improved dispersion and charge transfer, which could result in increased photocatalytic activity. On the other hand, PVDF’s hydrophobicity and stability may provide benefits in terms of toughness and resilience to adverse environments, which may affect TiO$_2$’s long term effectiveness. As the plots depicts in Fig. 3 and according to the IUPAC classification, PVP/TiO$_2$-NFs display a type IV isotherm (Mondal et al. 2014). As in evident in many supported TiO$_2$ photocatalysts, this kind of isotherm usually denotes mesoporous materials with a network of interconnected pores. Increased surface area and improved photocatalytic activity are caused by the presence of pores and surface adsorption properties as tabulated in Table 2. TiO$_2$ supported by PVDF may show a type II isotherm, in accordance with the IUPAC classification. Since PVDF and TiO$_2$ interact differently, type II isotherm often denotes non-porous or macroporous materials. This could lead to a decrease in surface area but an increase in durability and resilience to abrasive conditions.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>BET surface area (m$^2$g$^{-1}$)</th>
<th>BJH adsorption pore volume (cm$^3$/g)</th>
<th>BJH pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP/TiO$_2$-NFs</td>
<td>39.0210 + 0.5296</td>
<td>0.136</td>
<td>14.48</td>
</tr>
<tr>
<td>PVDF/TiO$_2$-NFs</td>
<td>17.2689 + 1.1154</td>
<td>0.025</td>
<td>07.26</td>
</tr>
</tbody>
</table>

There are notable variations in the surface morphology and dispersion of TiO$_2$ nanoparticles within the polymer matrices between the PVP and PVDF support for photocatalysis, according to the SEM study shown in Fig. 4. PVP/TiO$_2$-NFs SEM images indicate a more even and scattered distribution of TiO$_2$ on the matrix surface, which enhance active sites and improve photocatalysis efficiency. On the other hand, PVDF/TiO$_2$-NFs images show unique arrangement that may indicate a variable level of contact and dispersion between PVDF and TiO$_2$, which may have an impact on the accessibility of active sites and overall photocatalytic behavior (Ding et al. 2013; Haji Abdolrasouli et al. 2022).

Figure 4. SEM images of (a) PVP/TiO$_2$ –NFs (b) PVDF/TiO$_2$ -NFs, (c) EDAX pattern of PVDF/TiO$_2$ –NFs and PVP/TiO$_2$-NFs

For the quantitative measurement of photocatalytic products, such as methanol ethanol, over PVP and PVDF supported TiO$_2$ nanofibers, HPLC is a useful analytical method. The yield of ethanol and methanol, the main products of photocatalytic CO$_2$ conversion over the nanofibers were measured using HPLC analysis (Niu et al. 2017). The HPLC techniques uses an appropriate chromatographic column and mobile phase to separate and identify methanol and ethanol. At particular retention time, the chromatographic
profiles derived from HPLC analysis display characteristic peaks that correspond to methanol and ethanol. Accurate measurement is possible due to the well resolved peaks of methanol and ethanol and the retention periods are commonly seen at, indicating distinct separation and identification of the different products. Quantitative information from HPLC analysis provides information on how well the photocatalysts work to produce these important compounds. Yield of methanol and ethanol are shown in Fig. 5 which is for TiO$_2$ catalyst supported on PVP and PVDF matrices. The quantitative research provides insights into the impact of the polymer matrices on product selectivity, conversion efficiency and photocatalytic activity by revealing changes in the yields of methanol and ethanol over the various supported TiO$_2$ photocatalysts.

This technique shows a potential pathway for the CO$_2$ conversion process that TiO$_2$-NFs supported in PVDF and PVP matrices catalyze. Steps are as followed, 1) CO$_2$ adsorption onto TiO$_2$-NFs – At the beginning the CO$_2$ molecules attach themselves to the TiO$_2$-NFs in the PVP and PVDF matrix. The interaction between the CO$_2$ molecule and the active sites on the TiO$_2$ surface cause the adsorption. 2) CO$_2$ Activation – The TiO$_2$ nanofibers help to activate the CO$_2$ molecules after adsorption. The polarization of the CO$_2$ molecule is encouraging by the electron-deficient nature of TiO$_2$ surfaces, which weakens the C = O bonds in CO$_2$. 3) Active sites generation – Active intermediates such carbonate radicals (CO$_3$$^-$), carboxylates or other surface bound species are created from the activated CO$_2$ species. The TiO$_2$ surface and the surrounding PVP or PVDF matrix stabilize these intermediates. 4) Conversion reaction – The active intermediates undertake reduction or conversion process with the co-catalysts when light is present. Depending on the catalyst setup, this phase produces important chemicals such as ethanol, methanol and formic acid. 5) Role of polymer matrices – In order to stabilize the TiO$_2$-NFs, provide an environment that is favorable for CO$_2$ adsorption, and increase total catalytic activity, the PVP and PVDF matrices are essential. By affecting the interaction between CO$_2$ and the TiO$_2$ surface, these matrices may also help to increase selectivity and regulate the reaction pathways.

4. Conclusion

We carried out a thorough comparative analysis of the catalytic characteristics of TiO$_2$ nanofibers in conversion of CO$_2$ in this study allowed us to clarify the impact of two different polymer matrices, PVDF and PVP, on the catalytic activity of TiO$_2$ nanofibers. We also included the catalytic performance of these composites in CO$_2$ conversion in our comparative analysis. The CO$_2$ conversion activities of PVP/TiO$_2$-NFs and PVDF/TiO$_2$-NFs were noteworthy, indicating their potential as effective photocatalysts. Interestingly the PVP-supported TiO$_2$ outperformed the PVDF/TiO$_2$-NFs in terms of CO$_2$ conversion rates and selectivity. The discrepancy in catalytic activity that has been found may be explained by the unique ways in which TiO$_2$ nanofibers and the polymer matrices interact, affecting the catalysts’ surface area, electrical characteristics and reactivity. In addition, the increased CO$_2$ conversion efficiency of PVP supported fibers underscores the importance of the polymer matrix in controlling the photocatalytic activity of TiO$_2$-NFs. PVP and TiO$_2$ close contacts probably improved stability, accelerated electron
transmission, and optimized surface characteristics, which lead to higher CO$_2$ conversion efficiency. The study's conclusions not only increase our knowledge of photocatalytic CO$_2$ conversion in general but also open new avenues for the thoughtful design of cutting-edge composite materials that will enable effective and sustainable CO$_2$ utilization. To fully use these materials in the quest for a more environmentally friendly future, more research aimed at elucidating the precise mechanisms regulating the interactions between TiO$_2$-NFs and various polymer matrices is necessary.

**Declarations**

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We would like to express our sincere gratitude to all those who contributed to the successful completion of this research. We will like to thank Amity Institute of Applied Sciences, Amity University NOIDA, Uttar Pradesh and CSIR – Indian Institute of Petroleum Dehradun.

**Ethical approval**

We aim to investigate CO$_2$ conversion to solar fuels in the research paper entitled “Morphology Influence on Charge Carrier Dynamics in Photocatalytic CO$_2$ Conversion: Comparative Analysis between TiO$_2$ Nanopowder and Nanofibers.” As responsible group of research and scientists, we have taken extensive steps to graduate the ethical integrity of the research since we understand how important ethical issues are while conducting studies, especially environmental science.

**Consent to participate**

All the authors, indicate their willingly agreement to participate in the research.

**Consent to publish**

All authors provide there consents to publish the data and findings in the research work.

**Author Contributions**

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Karan Gehlot, Anil Chandra Kothari, Dr. Sangeeta Tiwari, Dr. Rajaram Bal and Dr. Sandeep Kumar Tiwari. The first draft of the manuscript was written by Karan Gehlot and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**Competing Interests**
The authors have no relevant financial or non-financial interests to disclose.

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References


Figure 1

XRD pattern of TiO$_2$ supported on PVP and PVDF matrices
Figure 2

Raman spectra of PVDF and PVP TiO$_2$ nanofibers

![Raman spectra](image)

Figure 3

Brunauer Emmett Teller (BET-Physiochemical characteristic) of TiO$_2$ -NP, TiO$_2$ –NFs

![Brunauer Emmett Teller](image)
Figure 4

SEM images of (a) PVP/TiO$_2$ –NFs (b) PVDF/TiO$_2$ -NFs, (c) EDAX pattern of PVDF/TiO$_2$ –NFs and PVP/TiO$_2$-NFs
Figure 5

Photocatalytic conversion of CO$_2$ with H$_2$O for Different Samples

**Supplementary Files**

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- SupplementaryDataJoNR.docx