Development of Photocatalytic Active SiCN-Ti e-Spun Fibers Based on a Polysilazane-Derived Precursor for Hydrogen Generation

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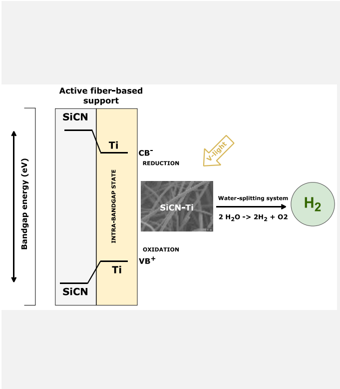


This study focuses on synthesizing novel photocatalytic active Ti-doped SiCN fibers using a Ti precursor (Titanium n-butoxide) and a commercially available polysilazane (Durazane 1800). The Ti-doped SiCN fibers were processed by combining the polymer-derived ceramic route and the electrospinning technique. Water-splitting tests under visible light were performed and analysed regarding the material composition and hydrogen generation. The addition of Ti enhanced the target photoactivated processes and increase the hydrogen generation up to 4-fold compared to pristine SiCN. The enhanced harnessing of visible light on the Ti-doped composites indicates a reduction in bandgap values compared to pristine SiCN. The composites developed herein are promising candidates for visible-light-driven hydrogen generation systems.

Introduction

Nowadays, many efforts are directed toward producing sustainable fuels, targeting environmentally friendly processes, safety, and renewable sources. In this regard, hydrogen is a promising energy source that can be used with a lower carbon footprint [1]. However, clean production, costs, infrastructure, and storage are still challenging tasks. Recent efforts have been made to develop photocatalysts to achieve more efficient systems in this context.

Among the photocatalytic systems, titanium dioxide (TiO_2) has been the most studied material in the literature since its discovery [2]. However, the stringent bandgap associated with TiO_2 (3.0 eV and 3.2 eV for the rutile and anatase phase, respectively) limits its light adsorption efficiency to the spectrum's ultraviolet region (UV) [3]. Therefore, developing heterojunction systems is an exciting alternative to improving optical absorption properties towards the visible-light range to promote an increase in the semiconductor's photoactivity [4].

This study focuses on synthesizing novel photocatalytic active heterojunctions based on Ti-SiCN ceramics fibers. For this, we combine the PDCs technology, using a polysilazane as the SiCN precursor and Titanium n-butoxide as the Ti precursor, with the electrospinning technique. The objective is to investigate the photocatalytic properties under visible light regarding the material composition and structure.

Material and Methods

The electrospinning process was performed based on the methodology proposed by our research group [5]. For this, a liquid oligosilazane (Durazane 1800, Merck KGaA) was first selectively crosslinked to achieve a spinnable solid polymer named HTTS [5]. The HTTS was then solubilized in THF (30 wt%) with different amounts of titania precursor (Titanium (IV) n-butoxide, ThermoFisher (Kandel) GmbH), as described in Table 1.

Table 1. Experimental planning for TiBu loading. The calculation of the TiBu added was based on the HTTS concentration.

Sample	Titanium n-butoxide (wt.%)	HTTS (wt.%)	THF (wt.%)
H70_T30_Ti0	0		
H70_T30_Ti5	5		
H70_T30_Ti10	10		
H70_T30_Ti15	15	70	30
H70_T30_Ti20	20		
H70_T30_Ti25	25		

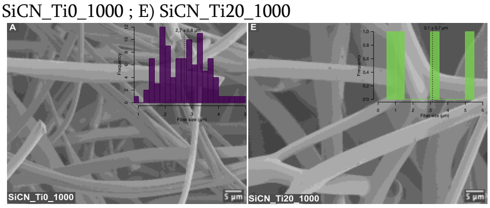
The optimized parameters used for the electrospinning were + 12 kV, - 8 kV, 10 cm, and 1 $mL.h^{-1}$. The e-spun fibers were crosslinked in the air at 70 ºC for 24 h and then pyrolyzed in a tubular furnace under nitrogen flow up to 1000 ºC.

Scanning electron microscopy (SEM) coupled with an EDX detector was used to investigate the ceramic fiber's morphology and elemental composition. Solid-state NMR and XRD were used to characterize the ceramic phase formation. The photocatalytic system for hydrogen generation tests was performed using a methodology adapted from previous work [4].

Results and Discussion

SEM micrographs (Fig. 1) disclose the morphology of the non-woven electrospun fibers after pyrolysis at 1000 °C under N_2. Homogeneous seamless defect-free fibers with an average diameter ranging from 2.2 to 3.1μm were obtained. Adding Ti precursor did not induce appreciable variation in the fiber's morphology, such as peeling, cleavage, or roughness.

Figure 1. SEM images from the fibers pyrolyzed at 1000 °C: A) SiCN_Ti0_1000 ; E) SiCN_Ti20_1000

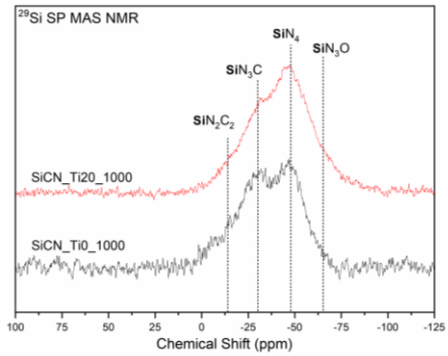


The investigation of the ceramic phase formation during pyrolysis was first conducted using XRD analysis. The XRD patterns reveal that the ceramic material remains amorphous even with the highest amount of Ti precursor (25 wt.%). Similar findings are also available in the literature [6]. In addition, ^{29}Si solid-state NMR was performed (Fig. 2). NMR spectra show the formation of various Si environments as expected for pure PDCs. Interestingly, the formation of SiN_4 sites was more pronounced in the Ti sample.

The reaction mechanism that led to the formation of more SiN_4 phases is still being determined. Nonetheless, the addition of the titanium precursor clearly influences the pyrolysis behavior by inducing the formation of more Si-N bonds. This tendency was also observed in the EDX analysis, which showed a significant increase in the N/Si atomic ratio as the amount of Ti precursor increased.

Finally, the hydrogen generation essays were carried out through methanol-reforming. The SiCN materials showed negligible photocatalytic effect under visible-light conditions, which may result from a wide bandgap. Nevertheless, adding Ti has enhanced the photocatalytic activity under the measured conditions, especially for composition SiCN_Ti20, with an increase in hydrogen generation up to 4-fold compared to pristine SiCN. This impressive result may be associated with decreased bandgap values due to adding Ti heteroatom bonds within the matrix.

Figure 2. NMR spectroscopy of the pristine and Ti-doped SiCN fibers (SiCN_Ti0_1000 and SiCN_Ti20_1000).



Conclusions

In this work, we developed new SiCN-Ti fibers with impressive photocatalytic activity. The ceramic fibers were processed by combining the electrospinning technique with the PDCs technology. Through XRD analysis, no crystalline phase was detected, revealing the formation of an amorphous ceramic. NMR analysis demonstrated that adding titanium precursor modified the pyrolysis behavior, inducing the formation of more SiN_4 phase. Finally, the hydrogen generation tests indicated that Ti enhanced the photoactivated processes. The composites developed herein are promising candidates for visible-light-driven hydrogen generation systems.

Acknowledgments

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