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Nanosponge-C_3N_4 composites as photocatalysts for selective partial alcohol oxidation in aqueous suspensions

P. Lo Meo,[a] E.I. García-López,[a] F. Arcidiacono,[a] A. Di Vincenzo,[a] L. Palmisano,[b] G. Marcì.[b]

[a]Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

[b]"Schiavello-Grillone" Photocatalysis Group. Dipartimento di Ingegneria, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

paolo.lomeo@unipa.it

INTRODUCTION

Nanosponges (NSs) are a class of hyper-reticulated polymers, obtained from supramolecular host molecules such as cyclodextrins or calixarenes. These are suitable materials for applications such as the sequestration of pollutants, drug carrier/delivery systems and also as functional supports for catalysts. In the latter case, the supramolecular host system constituted by the NS is able to capture the substrate to be transformed, and to concentrate it near the photocatalyst active sites, ultimately resulting in significantly improved catalytic performances [1].

In this work, we prepared four composite materials containing thermoesfoliated carbon nitride (TE-C_3N_4) embedded into different NSs based on β-cyclodextrins (βCDs). The composites were tested as photocatalysts for the photodegradation of 4-nitrophenol (4-NP), and for the selective partial oxidation of two alcohols, namely 5-hydroxymethylfurfural (HMF) and veratryl alcohol (VA) to the correspondent aldehydes in aqueous medium.

SYNTHESIS

The TE-C_3N_4 photocatalyst was obtained according to a well-known procedure [2], by a two-step thermolysis of melamine (Figure 1). Four different NSs (N1-N4) were synthesized (Figure 2) according to literature protocols [3]; the relevant composites with TE-C_3N_4 (5% w/w, C1-C4) were obtained by physically mixing the photocatalyst with the reactants before the reticulation reaction.

Figure 1

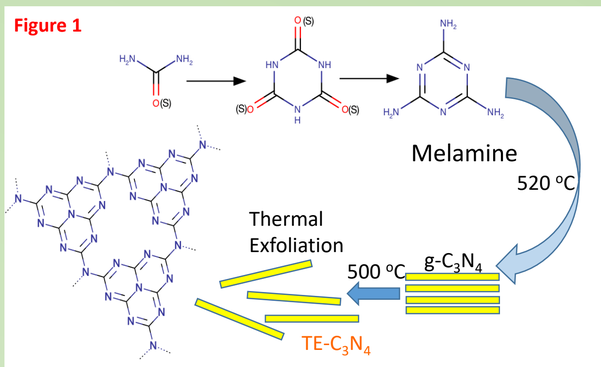
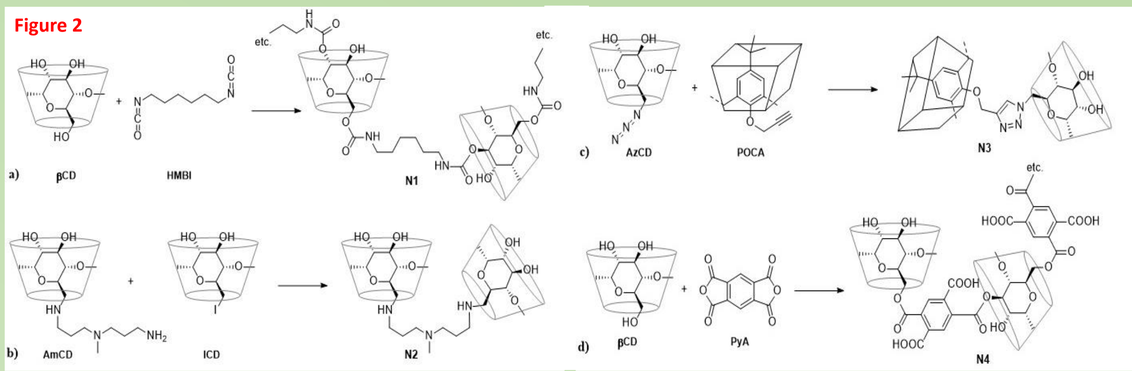


Figure 2



CHARACTERIZATION

Evidence for the accomplishment of the reticulation reaction and the physical entrapment of the TE-C_3N_4 into the NS matrix was achieved by FT-IR (Figure 3) Solid State NMR (Figure 4) and SEM (Figure 5). Tauc diagrams (Figure 6) show that the semiconductor bandgap experienced only minor changes due to embedding.

Figure 3

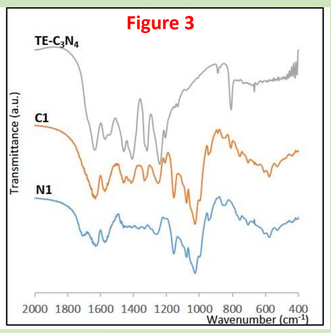
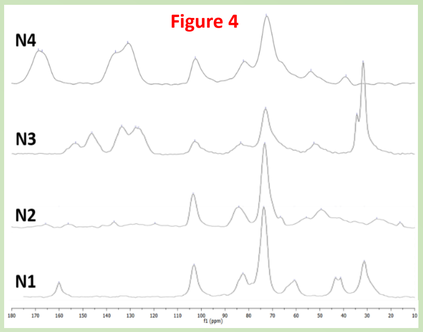


Figure 4



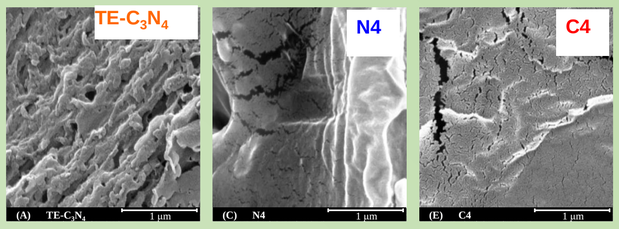
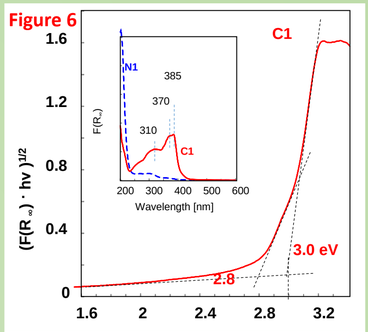


Figure 5. The presence of TE-C_3N_4 is not evident from the SEM pictures of the composites, indicating that the carbon nitride has been incorporated into the nanosponges.

Figure 6



PHOTODEGRADATION of 4-NITROPHENOL

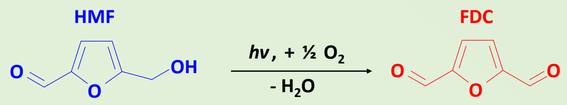
The photooxidative degradation of 4-NP in the presence of air is a sort of gold standard to assess the efficacy of a photocatalyst. The results of photoirradiation experiments carried out in a SOLARBOX apparatus (after equilibration in the dark) of a 4-NP 0.5 mM solution, expressed as initial reaction rates, are summarized in Table 1.

Table 1

material	Initial reaction rate ($\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$)		Normalized initial reaction rate ($\mu mol \cdot h^{-1} \cdot g_{TE-C3N4}^{-1}$)	
	pH = 5.5	pH = 3.7	pH = 5.5	pH = 3.7
TE-C_3N_4	116 ± 6	122 ± 6	116 ± 6	122 ± 6
C1	35.5 ± 1.5	32.2 ± 1.4	710 ± 30	664 ± 30
C2	56.5 ± 1.8	64.6 ± 1.9	1130 ± 40	1290 ± 40
C3	*negligible*	*negligible*	*negligible*	*negligible*
C4	35.3 ± 1.5	*negligible*	710 ± 30	*negligible*

Normalized data positively assess the synergistic enhancement of the catalytic activity due to the matrix local concentration effect in the case of composites C1, C2 and C4. Lack in activity for C3 and C4 at pH 3.7 can be attributed to the largely hydrophobic character of the matrix, resulting in scarce solvent mobility. Large substrate adsorption for material C2 makes results questionable. Hence, materials C1 and C4 were selected for subsequent tests.

PHOTOOXIDATION of 5-HYDROXYMETHYLFURFURAL

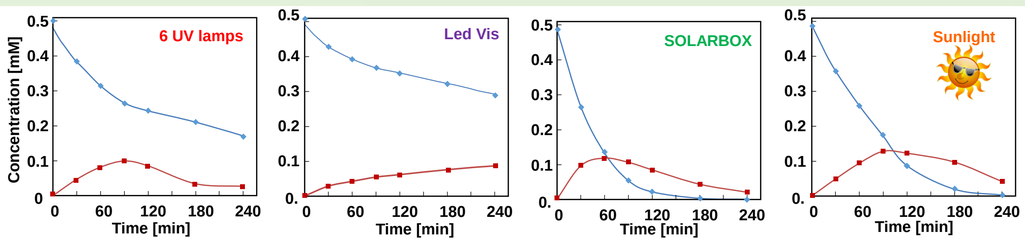


The photooxidation of HMF into the corresponding dialdehyde (FDC) was studied with four different light sources, namely UV (365 nm), visible LED, SOLARBOX and natural sunlight. Although part of the substrate undergoes mineralization, conversion to FDC occurs with good selectivity (Figure 7 depicts trends for TE-C_3N_4 as an illustrative example). The obtained initial reaction rates are summarized in Table 2.

Table 2

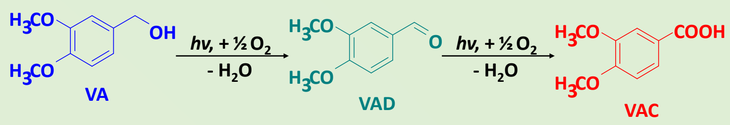
material	Initial reaction rate ($\mu mol\ h^{-1} \cdot g_{cat}^{-1}$)				Normalized initial reaction rate ($\mu mol\ h^{-1} \cdot g_{TE-C3N4}^{-1}$)			
	UV lamp	Vis. LED	Solarbox	sunlight	UV lamp	Vis. LED	Solarbox	sunlight
TE-C_3N_4	150	94	668	386	150	94	668	386
C1	58	*negligible*	60	47	1160	*negligible*	1200	940
C4	125	60	147	212	2500	1200	2940	4240

Figure 7



Again, the favorable reactivity enhancement effect due to matrix-photocatalyst synergism is immediately apparent.

PHOTOOXIDATION of VERATRYL ALCOHOL

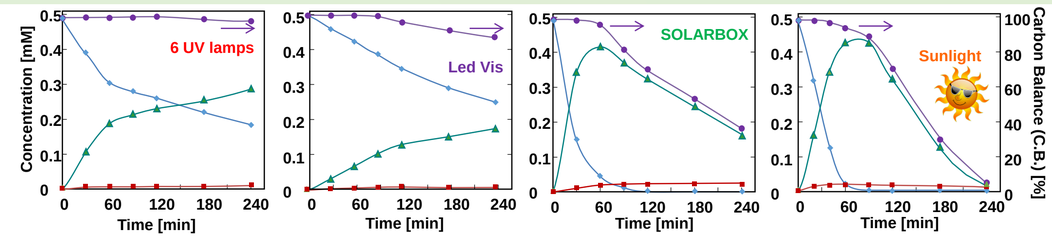


Also this reaction was studied with four light sources (UV 365 nm, visible LED, SOLARBOX and natural sunlight). Again, good selectivity towards the corresponding aldehyde (VAD) is observed (Figure 8 depicts trends for C4 as an illustrative example). The obtained initial reaction rates are summarized in Table 3.

Table 3

material	Initial reaction rate ($\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$)				Normalized initial reaction rate ($\mu mol \cdot h^{-1} \cdot g_{TE-C3N4}^{-1}$)			
	UV lamp	Vis. LED	Solarbox	sunlight	UV lamp	Vis. LED	Solarbox	sunlight
TE-C_3N_4	154	96	1278	327	154	96	1278	327
C1	135	53	480	345	2700	1060	9600	6900
C4	138	59	1023	520	2760	1180	20460	10400

Figure 8



Reaction rates may increase up to 30 times, due to synergism, in the case of C4 with sunlight irradiation. The latter case is also remarkable for the excellent conversion and selectivity achieved.

CONCLUSIONS

- ✓ TE-C_3N_4 can be easily dispersed in a nanosponge matrix, obtained by reticulating cyclodextrin units.
- ✓ Characterization of the obtained composites suggests the occurrence of no specific interaction between the photocatalyst and the nanosponges matrix.
- ✓ The study of the photooxidation of model molecules such as 4NP, HMF and VA confirmed an enhancement of the TE-C_3N_4 photocatalytic activity and selectivity. This improvement can be attributed to the local substrate concentration enhancement provided by the nanosponge.

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