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Introduction

Nitrous oxide is the third most important of the long-lived greenhouse gases. N₂O decomposition into nitrogen and oxygen offers a simple solution for its conversion to natural components of air. The photocatalytic decomposition of N₂O under UV irradiation on photocatalysts is one of the candidate methods for its removal. Graphitized carbon nitride (CN) has attracted a great attention due to its photocatalytic properties. It is an organic polymer, based on heptazine (tri-s-triazine) building blocks. Graphitic carbon nitride is usually obtained by the air-atmosphere pyrolysis of a few simple and cheap organic compounds, e.g. melamine, dicyandiamide, urea, thiourea and their mixtures. However, in as-prepared state, it suffers from certain disadvantages, such as nominal low specific surface area and fast recombination of photoinduced electron - hole pairs. They can be overcome by exfoliation and doping, for instance, with non-metal elements, such as sulfur, phosphorus, nitrogen, and oxygen. CN represents a very promising material for the photocatalytic decomposition of N₂O.

Experiment

Graphitic carbon nitride was synthesized by the melamine heating at 550°C for 4 hours. Modified CN photocatalysts were synthesized by different ways under the same conditions as CN (Table 1). In photocatalytic experiments, the photocatalyst was placed at the bottom of the batch reactor (volume of 184 ml). In both photochemical and photocatalytic experiments, the reactor was filled with N₂O/He mixture (1050 ppm of N₂O) and illuminated by an 8 W Hg lamp ($\lambda_{\max} = 365 \text{ nm}$, 0.665 mW/cm^2).

Results and discussion

The results of the photocatalyst characterizations and the surface elemental composition are summarized in Table 1. The presence of sulfur significantly increased the S_{BET} of CN synthesized from thiourea (S-CN). On the other hand, the derivatization of CN with mesyl chloride (Mes-CN) decreased its S_{BET}. The XPS analysis identified the presence and bonds of C, N, O and S. The pyridinic nitrogen atoms (NC₂) are dominant nitrogen ones in the CN structure and are located at the edges of melem units. The XPS results also indicate lower content of nitrogen which is likely due to surface defects in terms of nitrogen vacancies.

Table 1. Summary of physico-chemical properties of studied photocatalysts and surface elemental composition

Preparation	S _{BET} (m ² /g)	E _g (eV)	Elemental composition					Surface elemental composition					
			C (%)	H (%)	N (%)	S (XRF/EA) (%)	Cl (%)	C (at.%)	N (at.%)	O (at.%)	S (at.%)	H** (at.%)	C/N
CN	11	2.69	34.54	1.72	62.31	-	-	53.37	38.43	7.81	≤0.06	0.33	1.39
S-CN	20	2.63	34.06	1.74	61.15	0.22/n.d.	-	46.93	47.77	5.13	0.08	0.09	0.98
Mes-CN	8	2.66	35.43	2.20	56.36	0.26/0.34	1.43	57.20	28.96	11.73	0.89	1.22	1.98
P25	45*	3.20*	-	-	-	-	-	-	-	-	-	-	-

*Values provided by producer, **Amount of surface hydrogen was calculated to 100%.

The linear decrease of the N₂O conversion with increasing structure protonation was found. This different hydrogen content was likely caused by the substitution of nitrogen with sulfur in the case of S-CN and the addition of -SO₂CH₃ groups in the case of Mes-CN (Figure 1a). Figure 2b clearly demonstrates the decreasing dependence of the N₂O conversion on the C/N atomic ratio. In Figure 2c we observed a significant increase in photoactivity of the photocatalysts as the overall NC₂ portion increases.

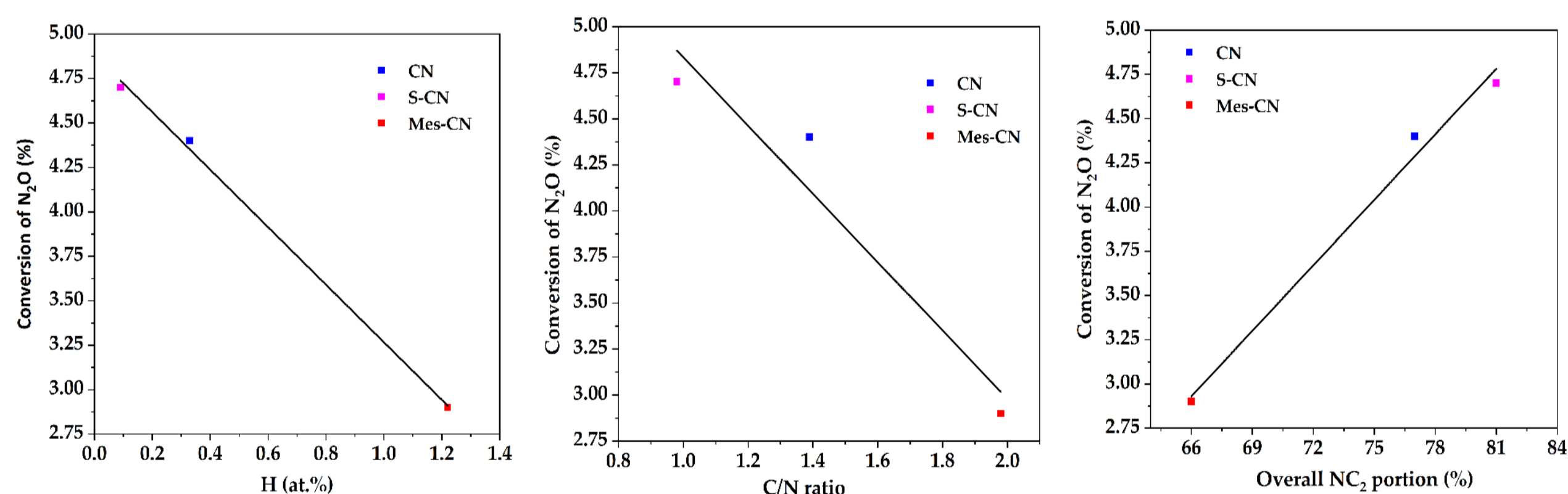


Figure 1. Correlation between the N₂O conversion in the photocatalytic decomposition of nitrous oxide and hydrogen content (a), and C/N atomic ratio (b), and overall NC₂ portion (c) determined by XPS

Conclusions

The N₂O photocatalytic decomposition was performed in the presence of photocatalysts based on graphitic carbon nitride and compared with commercial TiO₂ photocatalysts (Evonik P25) and with photolysis. The choice of the preparation of the CN photocatalysts (it means the precursor type and the sulfur modification) were found to have impact on their physico-chemical properties and photocatalytic activity. The N₂O conversion in the presence or without the photocatalyst (photolysis) decreased in the order to S-CN > CN > TiO₂ (P25) > Mes-CN > photolysis. It was proved that the preparation process influences the degree of carbon nitride condensation. The S-CN photocatalyst with the highest photoactivity had the highest degree of condensation. As the polymerization degree increases and the proton content decreases, the activity of photocatalysts based on graphitic carbon nitride was significantly enhanced. The photoactivity of the CN materials was also influenced by the content of NC₂ nitrogen.

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