# **Electronic Supporting Information**

## Supported Structure-Controlled Graphitic Carbon Nitride Catalyst for

#### Dehydrochlorination of 1,2-Dichloroethane

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#### Table S1.

Pore structure parameters of samples and texture parameters comparison of fresh and spent catalysts.

## Table S2

Surface mass composition (%) of g-C<sub>3</sub>N<sub>4</sub>@AC catalysts, determined by XPS.

	S <sub>BET</sub> (n	n² g-1)	V(cm <sup>2</sup> g <sup>-1</sup> )		
Samples	Fresh	Spent	Fresh	Spent	
g-C <sub>3</sub> N <sub>4</sub>	43.79	9.36	0.13	0.07	
AC	743.99	587.74	0.41	0.26	
1# g-C <sub>3</sub> N <sub>4</sub> @AC	669.35	156.45	0.36	0.084	
2# g-C <sub>3</sub> N <sub>4</sub> @AC	655.97	122.05	0.35	0.071	
3# g-C <sub>3</sub> N <sub>4</sub> @AC	593.38	61.20	0.34	0.03	
4# g-C <sub>3</sub> N <sub>4</sub> @AC	560.57	52.5	0.32	0.02	
$SiO_2$	396.77		0.30		
3# g-C <sub>3</sub> N <sub>4</sub> @ SiO <sub>2</sub>	390.37	358.92	0.30	0.28	
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	187.97		0.13		
3# g-C <sub>3</sub> N <sub>4</sub> - γ-Al <sub>2</sub> O <sub>3</sub>	188.21	189.43	0.13	0.12	

# Table S1 Pore structure parameters of samples and texture parameters comparison of fresh and spent catalysts.

#### Table S2. Surface mass composition (%) of g-C<sub>3</sub>N<sub>4</sub>@AC/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalysts, determined by

			XPS.				
	C 1s (%)	N 1s (%)	O 1s (%)	Al 2p (%)	Si 2p (%)	F1s (%)	Cl2p (%)
AC	79.32	0	20.68				

1# g-C <sub>3</sub> N <sub>4</sub> @AC	74.51	5.01	19.48				
2# g-C <sub>3</sub> N <sub>4</sub> @AC	73.88	5.38	20.84				
3# g-C <sub>3</sub> N <sub>4</sub> @AC	73.31	5.51	21.18				
4# g-C <sub>3</sub> N <sub>4</sub> @AC	72.49	6.12	22.39				
3#-g-C <sub>3</sub> N <sub>4</sub> -SiO <sub>2</sub>	25.3	1.3	50.9		21.8		
3#-g-C <sub>3</sub> N <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub>	22.5	0	48.1	29		0.5	
1# g-C <sub>3</sub> N <sub>4</sub> @AC-500	72.80	5.31	21.89				
1# g-C <sub>3</sub> N <sub>4</sub> @AC-450	74.14	6.08	19.78				
3# g-C <sub>3</sub> N <sub>4</sub> @AC-used	76.3	5.4	17.6				0.7



Fig.S1 TEM figures of the (a) active carbon, (b)  $g\text{-}C_3N_4$ , (c)3#  $g\text{-}C_3N_4@AC$ 



Fig. S2 The GC spectrum and MS of the outlet gas



Fig. S3 (a) XRD pattern of the graphitic carbon nitride. (b) XRD patterns of the Active carbon, 3#-g-C<sub>3</sub>N<sub>4</sub>@AC, T-g-C<sub>3</sub>N<sub>4</sub>@AC,

#### D-g-C<sub>3</sub>N<sub>4</sub>@AC

The difference on the stability maybe due to the dispersion of the obtained carbon nitride derived from them. As the XRD patterns of these catalysts shown in Fig S1, there is a sharp reflection of  $g-C_3N_4$  on the T-g-C<sub>3</sub>N<sub>4</sub>@AC, meaning that the carbon nitride derived from thiourea is more easily to form bulk on the active carbon compared to urea and dicyandiamide.



Fig. S4 XRD patterns of silica and the catalyst 3#-g-C<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>



Fig.S6 Effect of supports (silica 3#-g-C<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> and alumina 3#-g-C<sub>3</sub>N<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>) and precursors (Thiourea T-g-C<sub>3</sub>N<sub>4</sub>@AC and Dicyandiamide D-g-C<sub>3</sub>N<sub>4</sub>@AC) on the catalytic performance of the g-C<sub>3</sub>N<sub>4</sub>@AC catalysts. Reaction conditions: T=290 °C; GHSV (1,2-DCE) = 100 h<sup>-1</sup>.



**Fig. S7** FI-IR spectra of g-C<sub>3</sub>N<sub>4</sub>, 3#-g-C<sub>3</sub>N<sub>4</sub>-AC, 3#-g-C<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> and 3#-g-C<sub>3</sub>N<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> referred to that of Active carbon, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>

The BET results of these catalysts, presented in Table S1, showing that no change in the specific surface area of 3#-g-C<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> and 3#-g-C<sub>3</sub>N<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> can be detected compared with the supports, while for those catalysts with the AC as the support, obvious decrease in BET surface area can be found compared with that for the AC. Aside from that, the FI-IR spectra of 3#-g-C<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub> and 3#-g-C<sub>3</sub>N<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> referred to the supports SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are presented in Fig. S7. The breathing vibration at 808 cm<sup>-1</sup> for triazine units, the skeletal vibration bands at 1243 cm<sup>-1</sup> and 1638 cm<sup>-1</sup> for aromatic C-N and C=N heterocycles, characteristic bands for g-C<sub>3</sub>N<sub>4</sub>,<sup>1</sup> are not present for all the catalyst samples. Compared to the spectra of silica and alumina, there is no characteristic reflection for g-C<sub>3</sub>N<sub>4</sub> is detected in the spectra of the catalysts, indicating that no g- C<sub>3</sub>N<sub>4</sub> formed on either silica and alumina. Furthermore, for the FT-IR spectra of active carbon and 3# g-C<sub>3</sub>N<sub>4</sub> still can be observed, for example, the vibration of 808 cm<sup>-1</sup>, the vibration of 1065 cm<sup>-1</sup> and 1638 cm<sup>-1</sup> corresponding to aromatic C-N and C=N heterocycles.

This was further supported by the XPS analysis of these catalysts, rare reflection of nitrogen was observed in both of these two catalysts (Table S2). This result indicates that active carbon is the optimal support for making the supported graphitic carbon nitride catalysts for dehydrochlorination of 1,2-dichloroethane.



Fig. S8 High-resolution XPS spectra of C 1s for (a) AC, (b) g-C<sub>3</sub>N<sub>4</sub>, (c) 3# g-C<sub>3</sub>N<sub>4</sub>@AC

Fig. S8 shows that both the active carbon and the 3# g-C<sub>3</sub>N<sub>4</sub>@AC catalyst contain the two peaks with binding energies of 284.51eV and 285.26eV in the C1s spectrum corresponding to the original C–C (284.81 eV) and C–OH (285.99 eV) bonds, respectively.<sup>2</sup> Another peak with a binding energy of 288.89 eV can be found in the spectra of both the g-C<sub>3</sub>N<sub>4</sub> and the 3# g-C<sub>3</sub>N<sub>4</sub>@AC catalyst samples, corresponding to the C–N–C bond belonging to the g-C<sub>3</sub>N<sub>4</sub> material, demonstrating the existence of g-C<sub>3</sub>N<sub>4</sub> in the 3# g-C<sub>3</sub>N<sub>4</sub>@AC catalyst.



**Fig. S9** The optimized key structures for dehydrochlorination of trans-1,2-dichloroethane and cis-1,2-dichloroethane respectively. (the unit of bond length is Å). co-adsorbed reactants (co-ads), transition states (Ts), intermediate (Im) and products (Pr). Chlorine, nitrogen, carbon, and hydrogen atoms are depicted in green, blue, gray and white, respectively.



Fig. S10 Optimized structures of Cis- pathway including the reactant (Co-Re), transition states (Ts1 and Ts2) and intermedium (Im) Chlorine, nitrogen, carbon, and hydrogen atoms are depicted in green, blue, gray and white, respectively.



Fig. S11 Possible reaction mechanism for the dehydrochlorination reaction of 1,2-dichloroethane.

A tentative mechanism for a base facilitated dehydrochlorination reaction is proposed in Fig. S11. The co-adsorbed reactants 1 can be attributed to the positive interaction between the pyridine nitrogen atom of  $g-C_3N_4$ , an electron donor due to the lone pairs of electrons, and a hydrogen atom of 1,2-dichloroethane, an electron-acceptor because of the electron-withdrawing effect of a chlorine atom of the compound. The intermediate is formed via the C–H bond cleavage with a vinyl chloride produced. As pictured in Fig. S10, the H1 atom is adsorbed to the N1 atom and the Cl1 atom is adsorbed by the C1 atom at the same time. The adsorbed

hydrogen and chlorine atom undergoes an electron transfer process before forming a hydrogen chloride which desorbed from the catalyst.



450-600°C increase degree of polymerization

Fig. S12. Synthesis route of carbon nitride



Fig.S13 TPD profiles of 1,2-dichloroethane on the catalysts used

Temperature programmed desorption (TPD) of 1,2-dichloroethane was carried out to study the effect of degree of polymerization in the supported carbon nitride catalysts and the results are presented in Fig.S13. It can be seen that all the supported carbon nitride catalysts display high binding strength for 1,2-dichloroethane compared to the active carbon, indicating that the carbon nitride enhances the 1,2-dichloroethane adsorbability on the catalysts. Moreover, the TPD results also show that the catalysts synthesized at lower temperatures present stronger adsorbability to 1,2-dichloroethane, with the desorption peak temperature changing from 138.7

°C for the 1# g-C<sub>3</sub>N<sub>4</sub>@AC catalyst to 158.6 °C for the 1# g-C<sub>3</sub>N<sub>4</sub>@AC-450 catalyst, which is consistent well with the catalytic performance discussed above.



Fig. S14 Highest occupied and lowest unoccupied orbitals of the monomer to the tetramer.

- 1. J. Zhang, M. Zhang, C. Yang and X. Wang, *Advanced Materials*, 2014, **26**, 4121-4126.
- 2. F. Su, M. Antonietti and X. Wang, Catalysis Science & Technology, 2012, 2, 1005-1009.