Supporting information for:

Robust selenium-doped carbon nitride nanotubes for selective electrocatalytic

oxidation of furan compounds to maleic acid

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Fig. S1. Raman spectra of the prepared g-C₃N₄, g-C₃N₄-AC and C_{3.0}N-Se_{0.03}. The g-C₃N₄ and g-C₃N₄-AC only showed some characteristic peaks in the region of 500-3000 cm⁻¹, which corresponded to the stretching vibrations of heptazine heterocyclic ring units in their 2D conjugated framework.



Fig. S2. XPS survey spectra of $C_{3.0}$ N-Se_{0.03}.



Fig. S3. TEM images of the prepared other C_xN-Se_y materials. (a) $C_{0.7}N-Se_{0.002}$, (b) $C_{0.9}N-Se_{0.003}$, (c) $C_{2.1}N-Se_{0.01}$, and (d) $C_{4.2}N-Se_{0.05}$. The morphology of the C_xN-Se_y materials with different C/N ratios was significantly different. $C_{0.7}N-Se_{0.002}$ and $C_{0.9}N-Se_{0.003}$ had a thin nanosheet structure (Fig. S3a and b). Some portions of $C_{2.1}N-Se_{0.01}$ material possessed the hollow column structure (Fig. S3c), while $C_{4.2}N-Se_{0.05}$ showed curved tubular structure with width in the range of about 20 to 50 nm (Fig. S3d). In comparison with the $C_{3.0}N-Se_{0.03}$, the hollow cavity width of $C_{4.2}N-Se_{0.05}$ was smaller and the curvature and agglomeration of tubes were more serious.



Fig. S4. (a) TEM image and (b) SEM image of the prepared g-C₃N₄



Fig. S5. XRD patterns of $C_{0.7}$ N-Se_{0.002}, $C_{0.9}$ N-Se_{0.003}, $C_{2.1}$ N-Se_{0.01}, $C_{3.0}$ N-Se_{0.03}, and $C_{4.2}$ N-Se_{0.05}. $C_{0.7}$ N-Se_{0.002} and $C_{0.9}$ N-Se_{0.003} showed signals of both conjugated tri-s-triazine and graphene-like turbostratic forms, while the typical ordering turbostratic form was observed for the $C_{2.1}$ N-Se_{0.01}, $C_{3.0}$ N-Se_{0.03} and $C_{4.2}$ N-Se_{0.05}. Moreover, a gradual decrease of interlayer distance could be found when more Se was incorprated in the framework.



Fig. S6. (a) XRD patterns, and (b) N₂ adsorption-desorption isotherms of g-C₃N₄ (synthesized from urea) and g-C₃N₄-AC (synthesized from urea and NH₄Cl). A slight shift of single broad diffraction peak at 24.8° the C_{3.0}N-Se_{0.03} (1e) compared with the typical peak (27.8°) in g-C₃N₄ (synthesized from urea) and g-C₃N₄-AC (synthesized from urea and NH₄Cl) can be found, implying the decrease of interlayer distance in C_{3.0}N-Se_{0.03} caused by Se doping. Meanwhile, the peak centered at 13.0° in g-C₃N₄ and g-C₃N₄-AC, which was the characteristic peak for the tri-striazine structure, was not observed in C_{3.0}N-Se_{0.03}, indicating the change of the tri-s-triazine structure owing to the Se doping and the different C/N atomic ratio.



Fig. S7. FT-IR spectra (a) and Raman spectra (b) of $C_{0.7}N$ -Se_{0.002}, $C_{0.9}N$ -Se_{0.003}, $C_{2.1}N$ -Se_{0.01}, $C_{3.0}N$ -Se_{0.03}, and $C_{4.2}N$ -Se_{0.05}. With increasing C/N atomic ratio, the band at 810 cm⁻¹ (ascribed to tritazine rings) in FT-IR spectra became weaker (Fig. S7a), and the graphene-like structure of C_xN -Se_y materials became stronger (Fig. S7b). $C_{2.1}N$ -Se_{0.01}, $C_{3.0}N$ -Se_{0.03} and $C_{4.2}N$ -Se_{0.05} had similar FT-IR and Raman spectra, implying the very close structure of these three materials.



Fig. S8. XPS spectra of the prepared g-C₃N₄. (a) XPS survey spectra, (b) high-resolution XPS spectra of C 1s, (c) high-resolution XPS spectra of N 1s, and (d) high-resolution XPS spectra of O 1s. The strength of C-C and N-(C)₃ bonds in C_{3.0}N-Se_{0.03} was significantly enhanced compared with those in g-C₃N₄, which may be caused by the high content of C atoms in C_{3.0}N-Se_{0.03}.



Fig. S9. XPS survey spectra of $C_{0.7}$ N-Se_{0.002}, $C_{0.9}$ N-Se_{0.003}, $C_{2.1}$ N-Se_{0.01}, $C_{3.0}$ N-Se_{0.03}, and $C_{4.2}$ N-Se_{0.05}. The signals for Se and C became stronger with the increase of the used SeO₂ amount, while the N signals became weaker.



Fig. S10. High-resolution XPS spectra of C 1s. (a) $C_{0.7}N$ -Se_{0.002}, (b) $C_{0.9}N$ -Se_{0.003}, (c) $C_{2.1}N$ -Se_{0.01}, and (d) $C_{4.2}N$ -Se_{0.05}. The content of sp² C-C bond was obviously increased with the increasing amount of the used SeO₂, while the content of sp² C-N-C decreased.



Fig. S11. High-resolution XPS spectra of N 1s for $C_{0.7}$ N-Se_{0.002}, $C_{0.9}$ N-Se_{0.003}, $C_{2.1}$ N-Se_{0.01}, and $C_{4.2}$ N-Se_{0.05}. XPS spectra of N 1s showed that with the increase of Se content, the ratio of graphitic N obviously increased while an opposite tendency was found for pyridinic N.



Fig. S12. (a) Conversion of furfural and yields of various products at different applied potentials over $C_{3.0}$ N-Se_{0.03} in 0.5 M KHCO₃ solution, and (b) Current density and total charge at different electrolysis times at 1.7 V *vs.* Ag/AgCl.



Fig. S13. XPS spectra of fresh and recovered $C_{3.0}$ N-Se_{0.03}.



Fig. S14. LSV curves at a scan rate of 50 mV/s with and without 10 mM Furfural in (a) 0.5 M $(NH_4)_2SO_4$, (b) 1 M of KOH, (c) 1M H₂SO₄, and (D) pH=7 phosphate buffered solution (PBS).

Fig. S15. (a) LSV curves of g-C₃N₄ at a scan rate of 50 mV/s, and (b) Tafel plots of g-C₃N₄ with and without furfural in 0.5 M aqueous KHCO₃ solution.

Fig. S16. (a) The furfural conversion, MA yield and FE at different applied potentials, and (b) Concentrations of furfural and the oxidation products at various electrolysis times over pure g-C₃N₄ electrode at 1.8 V *vs*. Ag/AgCl in 0.5 M aqueous KHCO₃ electrolyte.

Fig. S17. LSV curves of a serious of C_x N-Se_y materials at a scan rate of 50 mV/s without furfural in 0.5 M KHCO₃ solution.

Fig. S18. (a) Charging current density differences plotted against scan rates, and (b) Nyquist plots of g-C₃N₄ and C_{3.0}N-Se_{0.03} in 0.5 M KHCO₃ solution at an open circuit potential.

Fig. S19. Nyquist plots of various C_x N-Se_y electrodes in 0.5 M KHCO₃ solution at an open circuit potential.

Catalysts	Furfural conv. (%)	MA yield (%)	MA selec. (%)	References
C _{3.0} N-Se _{0.03}	99.5	84.2	84.0	This work
Amberlyst-15	>99	11	11	1
Nb ₂ O ₅	>99	5	5	1
ZrO ₂	>99	5	5	1
ZSM-5	>99	2.4	2.4	2
$H_5PV_2Mo_{10}O_{40}$ · xH_2O	98.7	54	55	3
$H_5PV_2Mo_{10}O_{40}{\cdot}xH_2O$	100	41.8	41.8	4
TS-1	100	62	62	5
V ₂ O ₅ /SnO ₂	74.4	38.9	52.3	6
FeT(p-Br)PPCl/SBA-15	53.7	38	70.8	7

Table S1. Furfural oxidation using various heterogeneous catalysts.

Eletrolytes	ъЦ	Potontial (V)	Furfural	MA yield	Furanone yield (%)	FA yield (%)	Selectivity of
	рп	Potentiai (V)	conversion (%)	(%)			MA (%)
0.5 M H ₂ SO ₄	0.42	1.7	98.1	20.8	1.4	< 0.1	21.2
0.5 M (NH ₄) ₂ SO ₄	5.18	1.7	90.7	59.8	3.4	< 0.1	65.9
PBS (pH=7)	7.01	1.7	91.1	15.6	0.27	0.19	17.1
1 M KOH	13.67	1.6	100	37.8	1.1	2.65	37.8

Table S2. Electrochemical oxidation of furfural and distribution of products over $C_{3.0}N$ -Se_{0.03} in various electrolytes with different acidity and alkalinity.

Table S3. Concentration of surface nitrogen species of various electrodes.

Sample	Total N (atom%)	Pyridinic N (atom%)	Graphitic N (atom%)	Oxidized N (atom%)
$g-C_3N_4$	20.6	17.6	2.2	1.8
$C_{0.7}$ N-Se _{0.002}	15.1	9.6	4.4	1.1
C _{0.9} N-Se _{0.003}	14.2	7.8	5.4	1.0
C _{2.1} N-Se _{0.01}	8.0	4.0	3.5	0.5
$C_{3.0}$ N-Se _{0.03}	5.1	2.3	2.4	0.3
C _{4.2} N-Se _{0.05}	3.3	1.1	1.9	0.3

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