

Supplementary materials

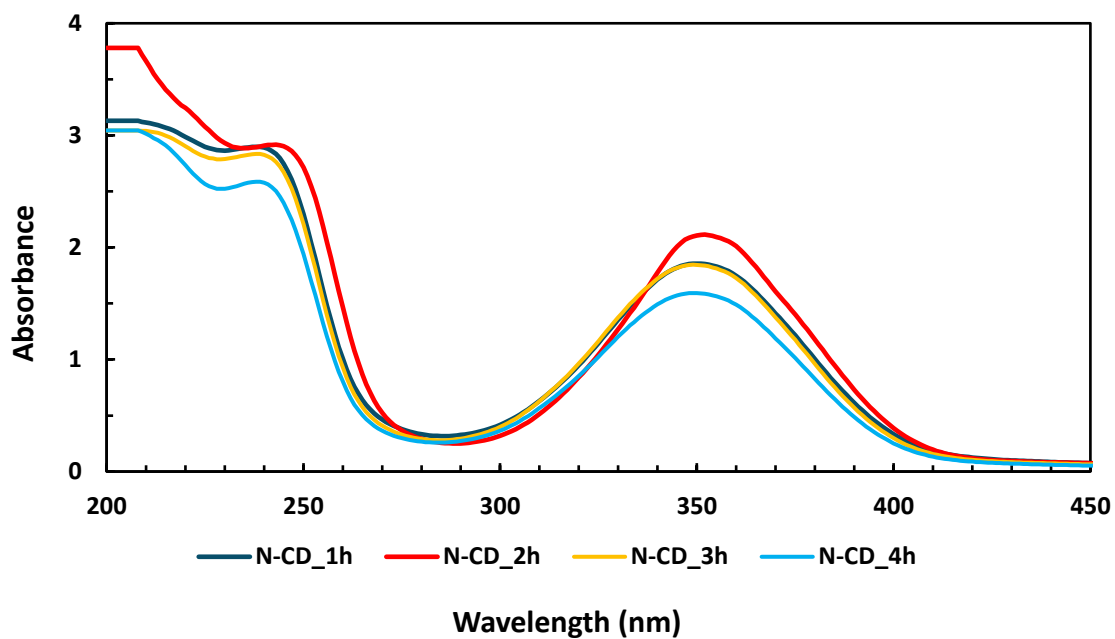


Fig. S1 UV-Visible spectra of N-CDs at different reaction times.

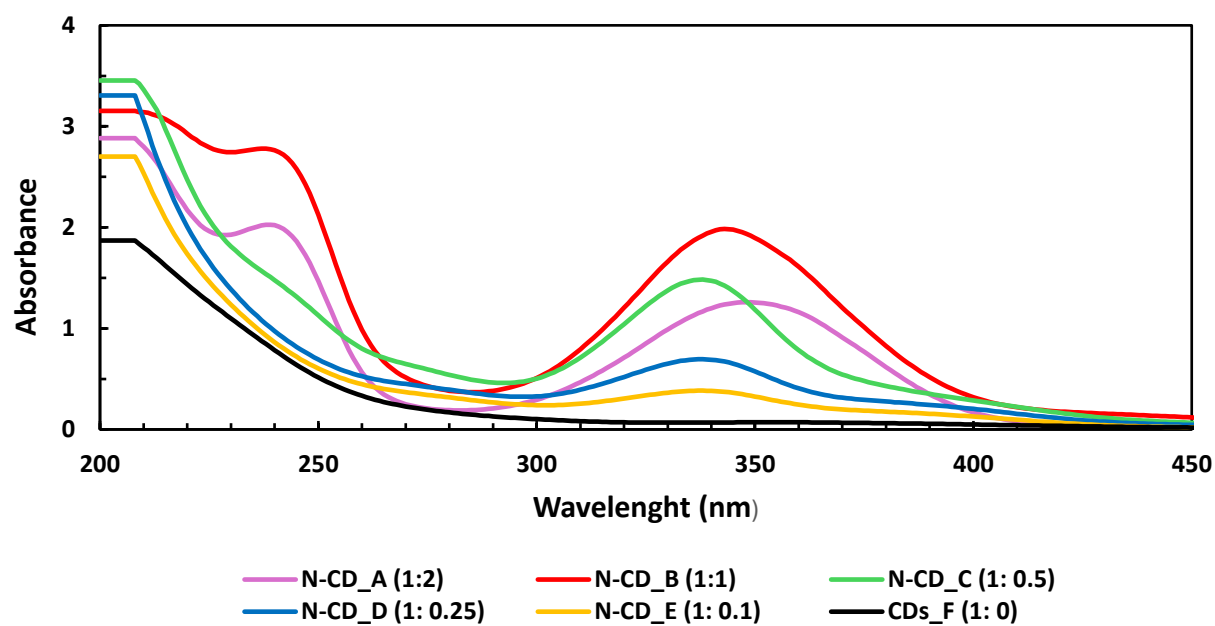


Fig. S2 UV-Visible spectra of N-CDs at different molar ratio of citric acid: EDA.

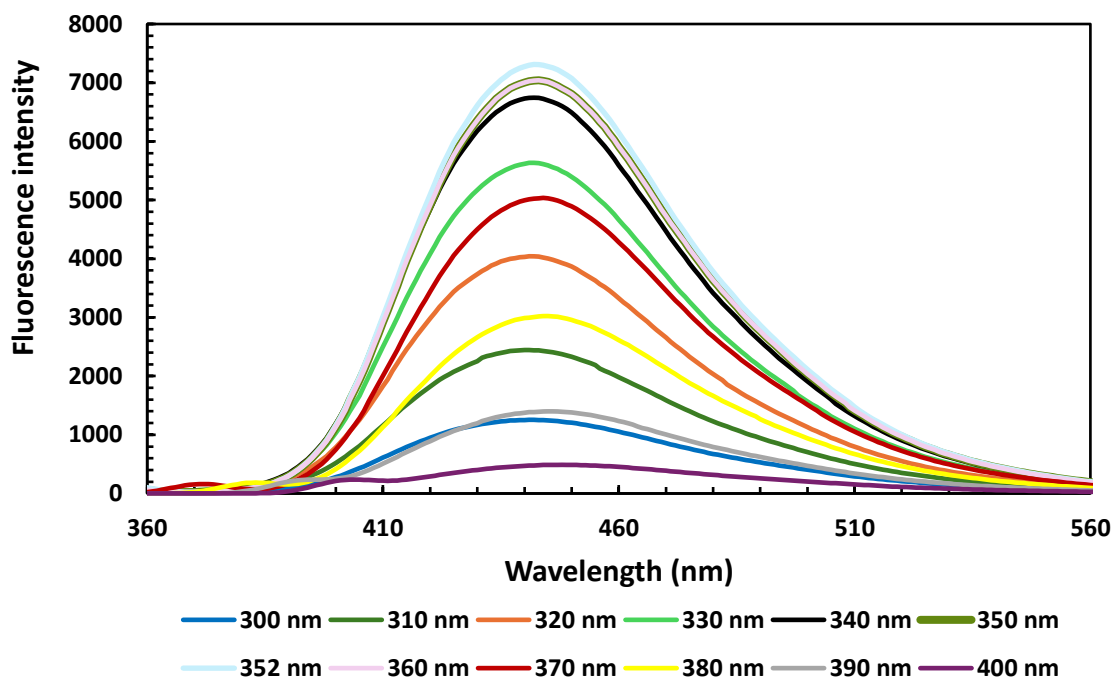


Fig. S3 Fluorescence emission spectra of N-CDs_B (1:1) at different excitation wavelengths.

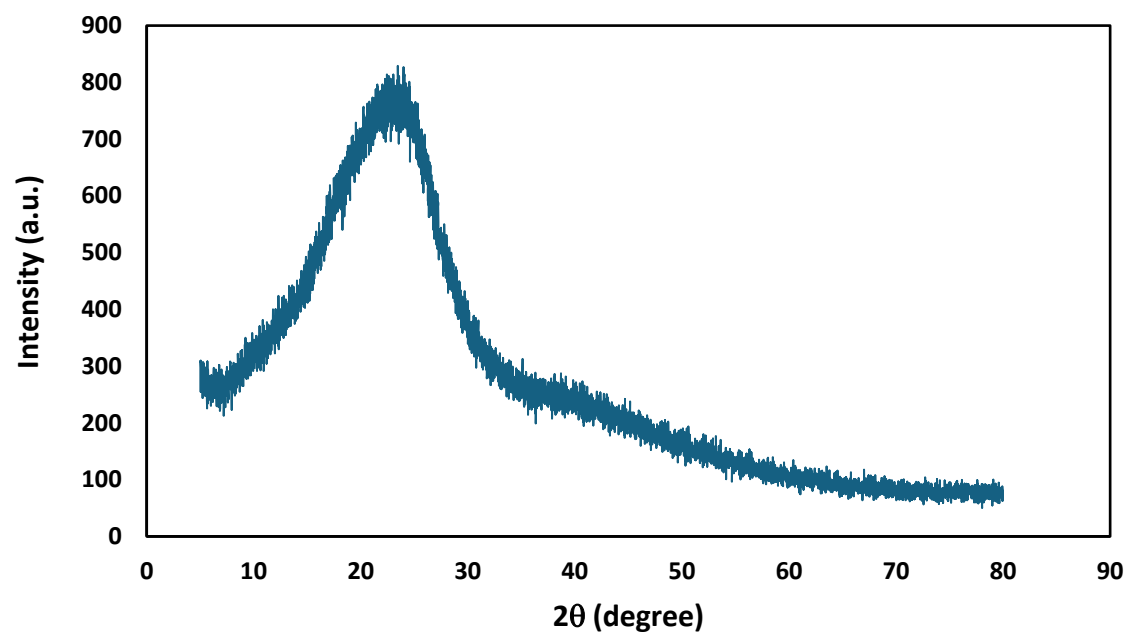


Fig. S4 XRD pattern of N-CDs.

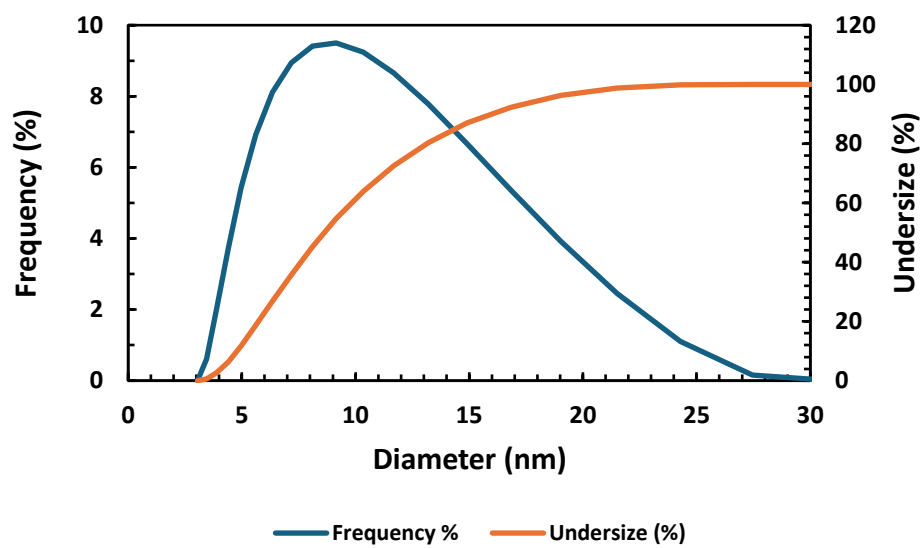


Fig. S5 Particle size distribution of N-CDs.

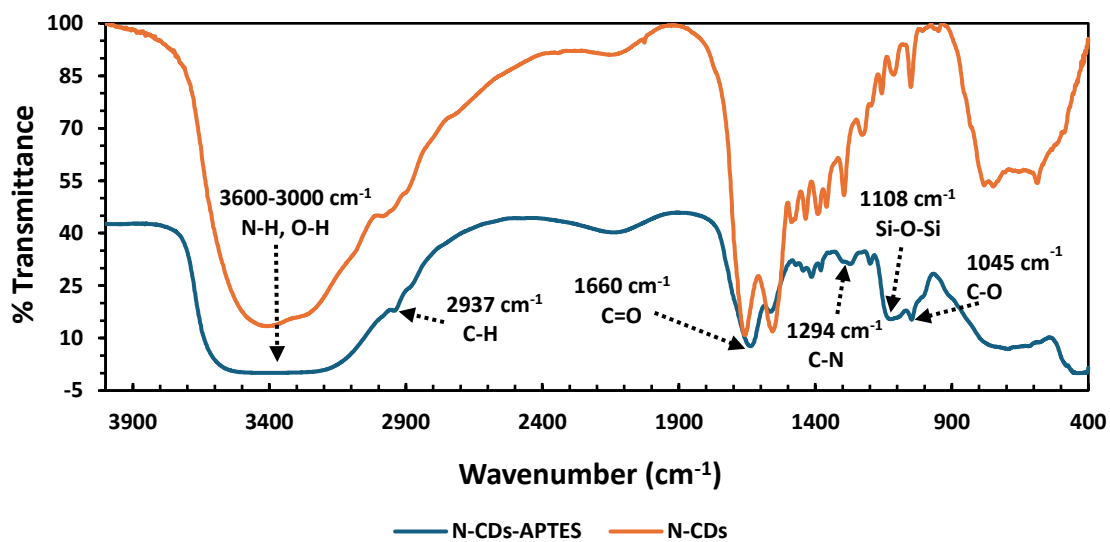


Fig. S6 FTIR spectra of N-CDs and N-CDs-APTES

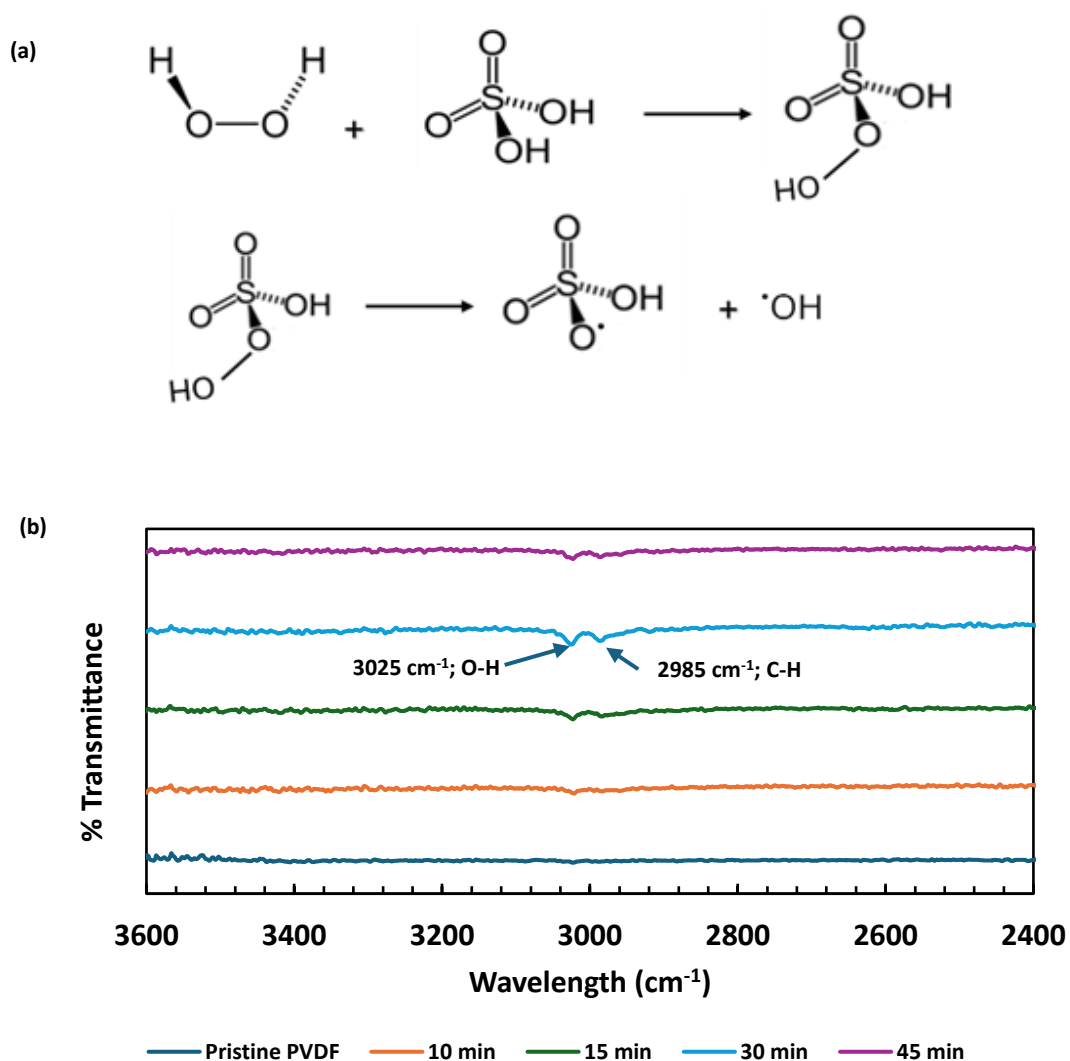


Fig. S7 Modification of PVDF membrane with piranha solution: (a) Formation of hydroxyl radicals via Caro's acid decomposition in piranha solution, and (b) Effect of reaction times on the PVDF membranes treated with piranha solution.

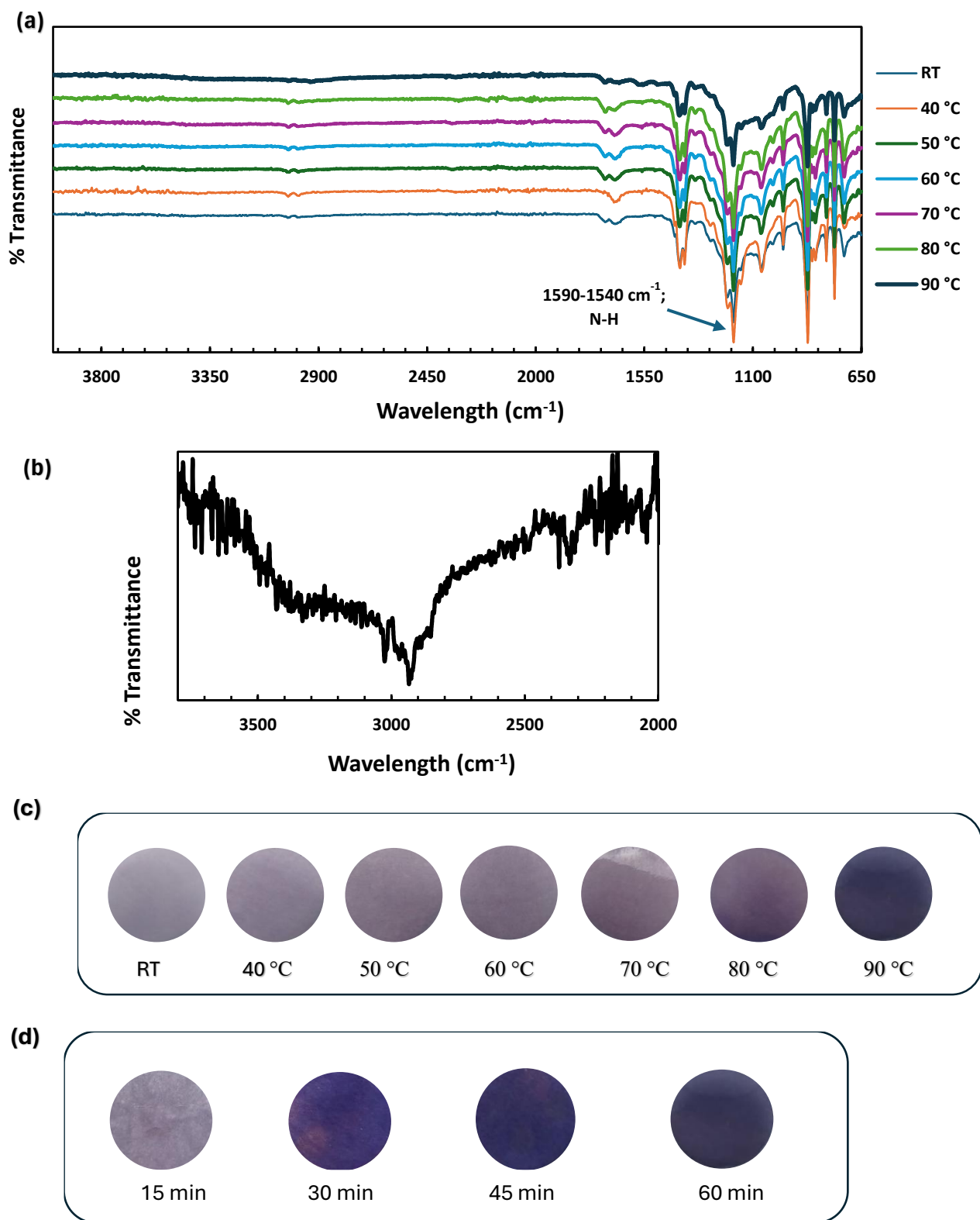


Fig. S8 ATR-FTIR spectra of PVDF-APTES membrane (a) at different temperatures, (b) at 90 °C (zoom in), and Ninhydrin test showing (c) temperature and (d) time-dependent of amine functionalization of PVDF-APTES.

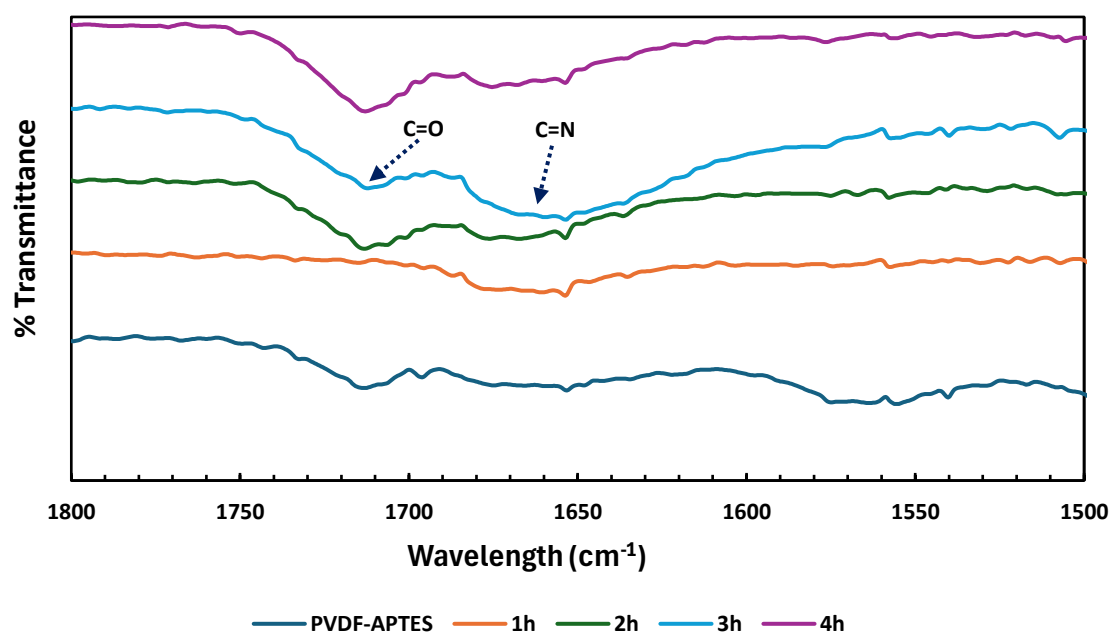


Fig. S9 ATR-FTIR spectra of GA-crosslinked PVDF-APTES membranes treated for different reaction times.

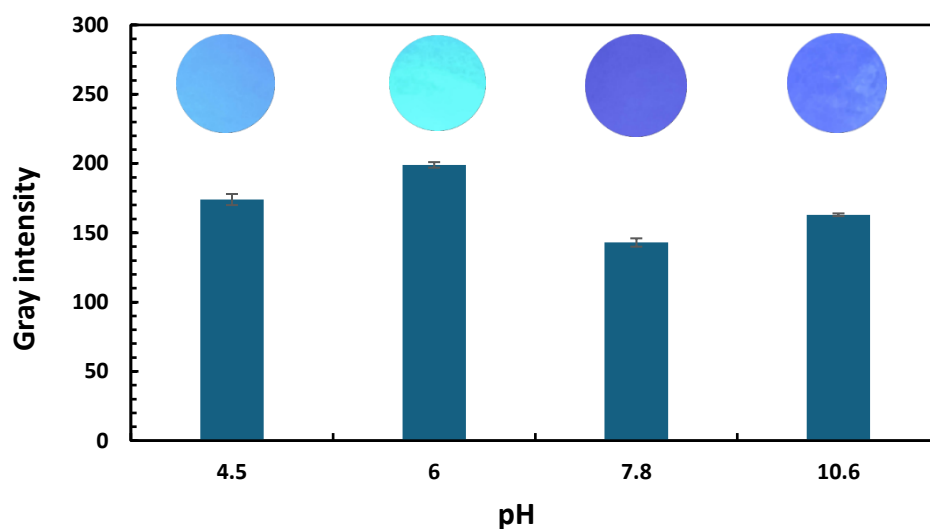


Fig. S10 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP membrane at different pH values.

Table S1 One way ANOVA test for pH optimization

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
4.5	3	523	174.3333	12.33333
6	3	596	198.6667	2.333333
7.8	3	429	143	12
10.6	3	488	162.6667	2.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	4868.666667	3	1622.889	223.8467	4.7E-08	4.066181
Within Groups	58	8	7.25			
Total	4926.666667	11				

P-value ≤ 0.05

k = 4, df = 8, q = 4.53 and HSD = 7.04 ($\alpha = 0.05$)

Table S2 Comparison of the mean differences with Post-hoc Tukey HSD test for pH data

pH of N-CDs	Mean differences	Significant if Mean difference > HSD (7.04)
pH 6.0 – pH 4.5	25	Yes
pH 6.0 – pH 7.8	56	Yes
pH 6.0 – pH 10.6	36	Yes
pH 4.5 – pH 7.8	31	Yes
pH 4.5 – pH 10.6	11	Yes
pH 10.6 – pH 7.8	20	Yes

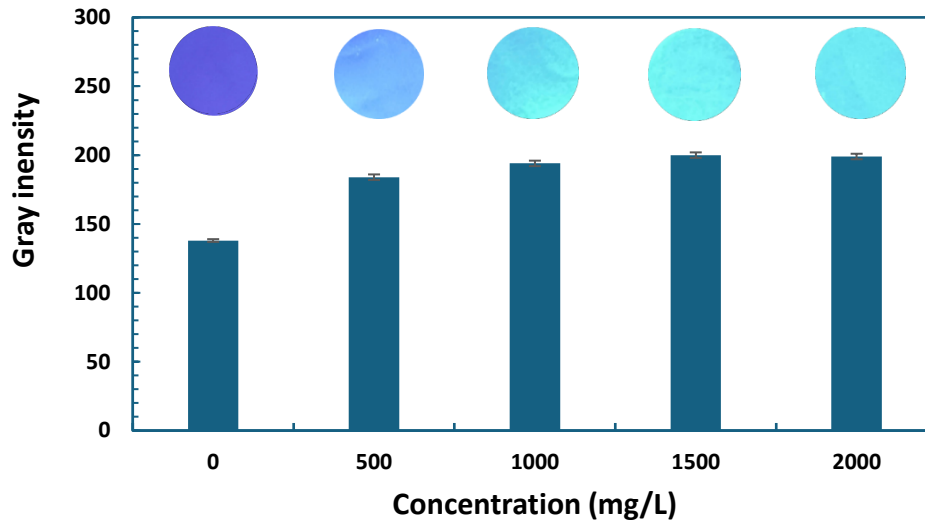


Fig. S11 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP membrane at varying concentration of N-CDs.

Table S3 One way ANOVA test for N-CDs concentration optimization

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
0	3	416	138.6667	2.333333
500	3	551	183.6667	2.333333
1000	3	580	193.3333	2.333333
1500	3	600	200	3
2000	3	597	199	4

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7852.933	4	1963.233	701.1548	3.39E-12	3.47805
Within Groups	28	10	2.8			
Total	7880.933	14				

P-value ≤ 0.05

k = 5, df = 10, q = 4.65 and HSD = 4.49 ($\alpha = 0.05$)

Table S4 Comparison of the mean differences with Post-hoc Tukey HSD test for concentration of N-CDs

Concentration of N-CDs (mg/L)	Mean differences	Significant if Mean difference > HSD (4.49)
1500-0	61	Yes
1500-500	16	Yes
1500-1000	7	Yes
1500-2000	1	No
2000-0	60	Yes
2000-500	15	Yes
2000-1000	6	Yes
1000-0	54	Yes
1000-500	9	Yes
500-0	45	Yes

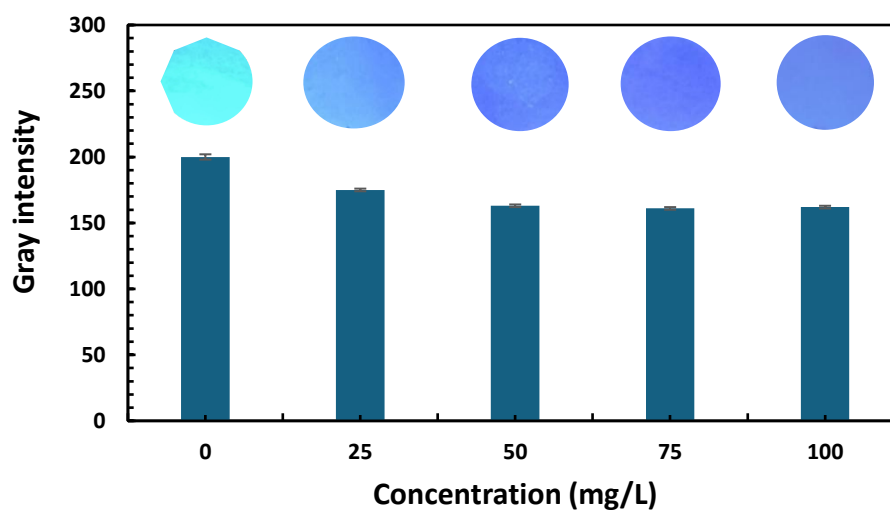


Fig. S12 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP membrane at varying concentration of 2,4-D.

Table S5 One way ANOVA test for 2,4-D concentration optimization

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
0	3	600	200	3
25	3	525	175	1
50	3	489	163	1
75	3	482	160.6667	0.333333
100	3	485	161.6667	0.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3327.6	4	831.9	734.0294	2.7E-12	3.47805
Within Groups	11.33333333	10	1.133333			
Total	3338.933333	14				

P-value ≤ 0.05

k = 5, df = 10, q = 4.65 and HSD = 2.85 ($\alpha = 0.05$)

Table S6 Comparison of the mean differences with Post-hoc Tukey HSD test for concentration of 2,4-D

Concentration of 2,4-D (mg/L)	Mean differences	Significant if Mean difference > HSD (2.85)
75-0	39	Yes
75-25	14	Yes
75-50	2	No
75-100	1	No
100-0	38	Yes
100-25	13	Yes
100-50	1	No
50-0	37	Yes
50-25	25	Yes
25-0	25	Yes

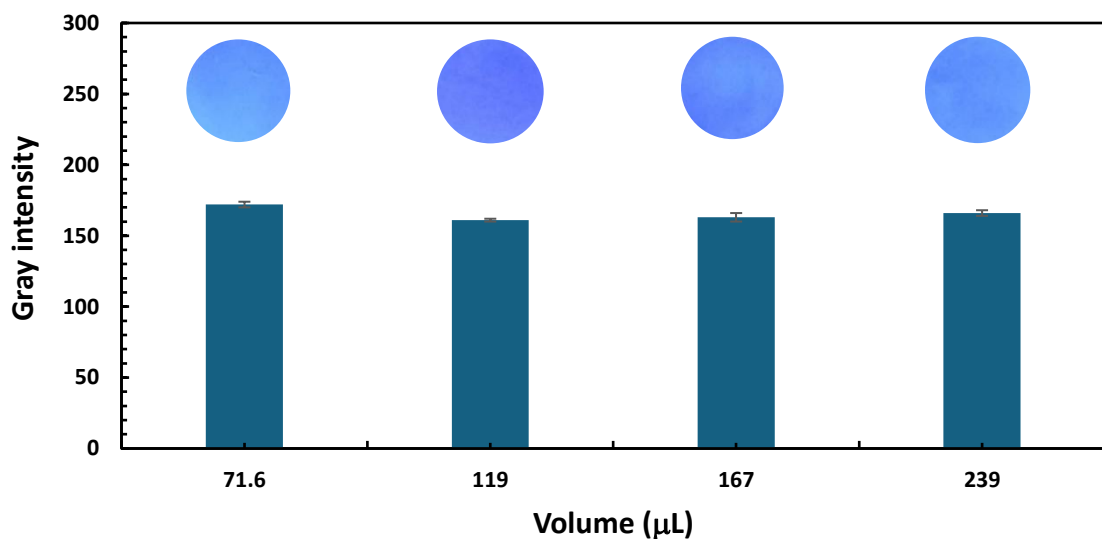


Fig. S13 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP/2,4-D membrane at varying volume of APTES.

Table S7 One way ANOVA test for optimization of APTES

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
71.6	3	517	172.3333	2.333333
119	3	482	160.6667	0.333333
167	3	482	160.6667	0.333333
239	3	498	166	4

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	276.9166667	3	92.30556	52.74603	1.29E-05	4.066181
Within Groups	14	8	1.75			
Total	290.9166667	11				

P-value ≤ 0.05

k = 4, df = 8, q = 4.53 and HSD = 3.46 ($\alpha = 0.05$)

Table S8 Comparison of the mean differences with Post-hoc Tukey HSD test for APTES

Volume of APTES (μL)	Mean differences	Significant if Mean difference > HSD (3.46)
119-71.6	11	Yes
119-167	0	No
119-239	5	Yes
167-71.6	11	Yes
167-239	5	Yes
239-71.6	6	Yes

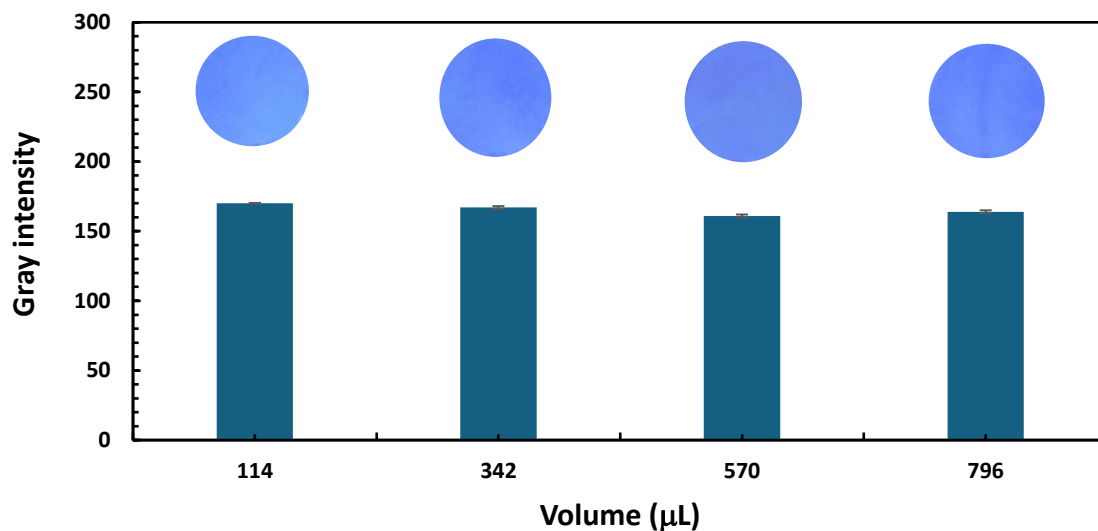


Fig. S14 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP/2,4-D membrane at varying volume of TEOS.

Table S9 One way ANOVA test for optimization of TEOS

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
114	3	510	170	0
342	3	501	167	3
570	3	482	160.6667	0.333333
796	3	490	163.3333	1.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	150.9166667	3	50.30556	43.11905	2.76E-05	4.066181
Within Groups	9.333333333	8	1.166667			
Total	160.25	11				

P-value ≤ 0.05

k = 4, df = 8, q = 4.53 and HSD = 2.83 ($\alpha = 0.05$)

Table S10 Comparison of the mean differences with Post-hoc Tukey HSD test for TEOS

Volume of TEOS (μL)	Mean differences	Significant if Mean difference > HSD (2.83)
570-114	9	Yes
570-342	6	Yes
570-796	2	No
796-114	7	Yes
796-342	4	Yes
342-114	3	Yes

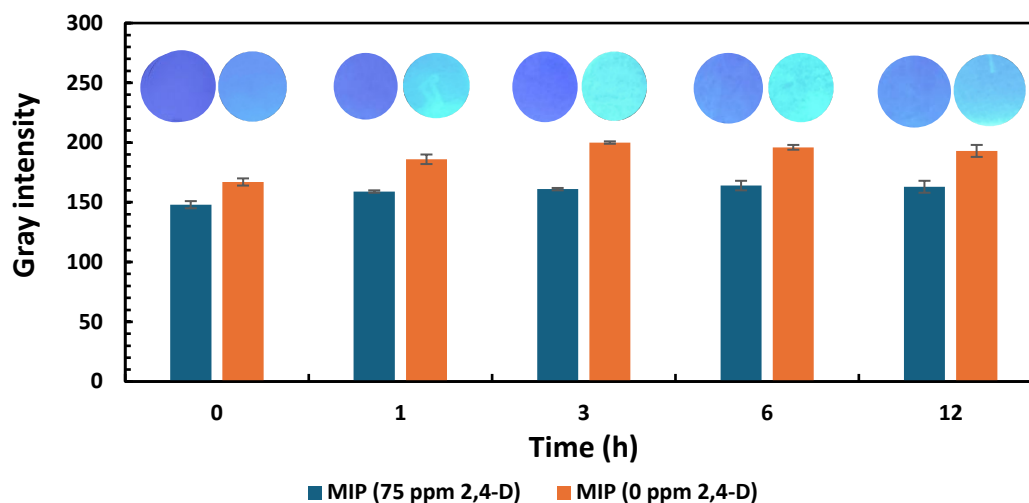


Fig. S15 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP/2,4-D membrane at different polymerization times.

Table S11 One way ANOVA of time optimization for MIP (75 mg/L 2,4-D)-modified membrane

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
0	3	442	147.3333	5.333333
1	3	475	158.3333	1.333333
3	3	482	160.6667	0.333333
6	3	492	164	12
12	3	490	163.3333	25.33333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	548.2667	4	137.0667	15.45865	0.000277	3.47805
Within Groups	88.66667	10	8.866667			
Total	636.9333	14				

P-value ≤ 0.05

k = 5, df = 10, q = 4.65 and HSD = 8.0 ($\alpha = 0.05$)

Table S12 One way ANOVA of time optimization for MIP (0 mg/L 2,4-D)-modified membrane

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
0	3	501	167	7
1	3	559	186.3333	16.33333
3	3	599	199.6667	2.333333
6	3	589	196.3333	4.333333
12	3	580	193.3333	26.33333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2029.066667	4	507.2667	45.02367	2.31E-06	3.47805
Within Groups	112.6666667	10	11.26667			
Total	2141.733333	14				

P-value ≤ 0.05 ;k = 5, df = 10, q = 4.65 and HSD = 9.01 ($\alpha = 0.05$)

Table S13 Comparison mean differences with Post-hoc Tukey HSD test for polymerization time

PVDF-APTES-GA@N-CDs-MIP (75 mg/L 2,4-D)			PVDF-APTES-GA@N-CDs-MIP (0 mg/L 2,4-D)		
Time	Mean difference	Significant if Mean difference >HSD (8.0)	Time	Mean difference	Significant if Mean difference >HSD (9.01)
3h-0h	14	Yes	3h-0h	33	Yes
3h-1h	3	No	3h-1h	14	Yes
3h-6h	3	No	3h-6h	4	No
3h-12h	2	No	3h-12h	7	No
0h-1h	11	Yes	6h-0h	29	Yes
0h-6h	17	Yes	6h-1h	10	Yes
0h-12h	16	Yes	6h-12h	3	No
1h-6h	6	No	12h-0h	26	Yes
1h-12h	5	No	12h-1h	7	No
12h-6h	1	No	1h-0h	19	Yes

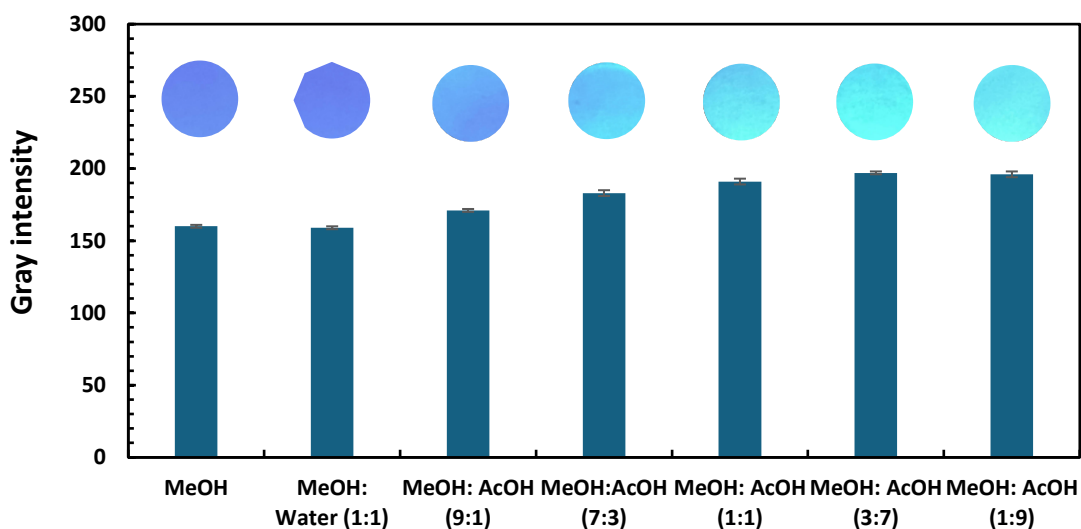


Fig. S16 Comparison of gray intensity of PVDF-APTES-GA@N-CDs-MIP membrane after washing with different extraction solvents.

Table S14 One way ANOVA of optimization for extraction 2,4-D from MIP-modified membrane

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
100% MeOH	3	479	159.6667	1.333333
50%MeOH/50% H2O	3	475	158.3333	1.333333
90%MeOH/10%AcOH	3	515	171.6667	2.333333
70%MeOH/30%AcOH	3	549	183	4
50%MeOH/50%AcOH	3	574	191.3333	4.333333
30%MeOH/70%AcOH	3	591	197	1
10%MeOH/90%AcOH	3	589	196.3333	4.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	4933.619	6	822.2698	308.3512	4.79E-14	2.847726
Within Groups	37.33333	14	2.666667			
Total	4970.952	20				

P-value ≤ 0.05 ; k = 7, df = 14, q = 4.83 and HSD = 4.56 ($\alpha = 0.05$)

Table S15 Comparison mean differences with Post-hoc Tukey HSD test for extraction 2,4-D

Solvent	Mean differences	Significant if Mean difference > HSD (4.56)
F-A	37	Yes
F-B	39	Yes
F-C	25	Yes
F-D	14	Yes
F-E	6	Yes
F-G	1	No
G-A	36	Yes
G-B	38	Yes
G-C	24	Yes
G-D	13	Yes
G-E	5	Yes
E-A	31	Yes
E-B	33	Yes
E-C	19	Yes
E-D	8	Yes
D-A	23	Yes
D-B	25	Yes
D-C	11	Yes
C-A	12	Yes
C-B	14	Yes
A-B	2	No

Note: A) 100% MeOH, B) 50%MeOH/50% H₂O, C) 90%MeOH/10%AcOH, D) 70%MeOH/30%AcOH, E) 50%MeOH/50%AcOH, F) 30%MeOH/70%AcOH, G) 10%MeOH/90%AcOH

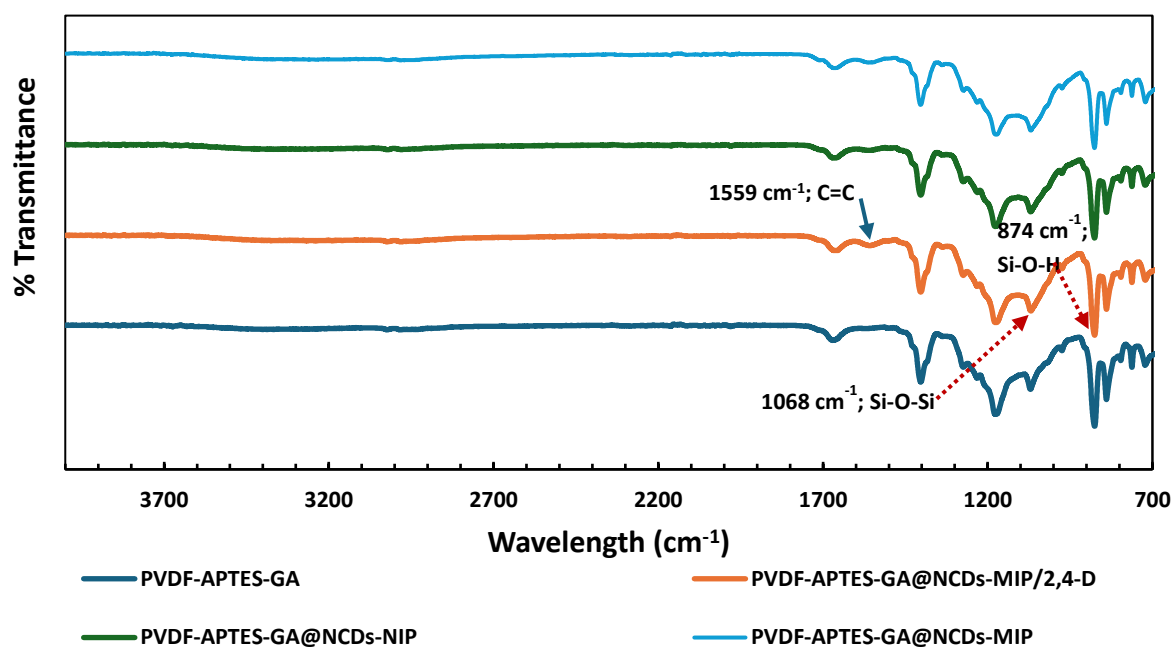


Fig. S17 ATR-FTIR spectra of PVDF membrane at different functional stages: PVDF-APTES-GA, PVDF-APTES-GA@N-CDs-MIP/2,4-D and PVDF-APTES-GA@N-CDs-NIP

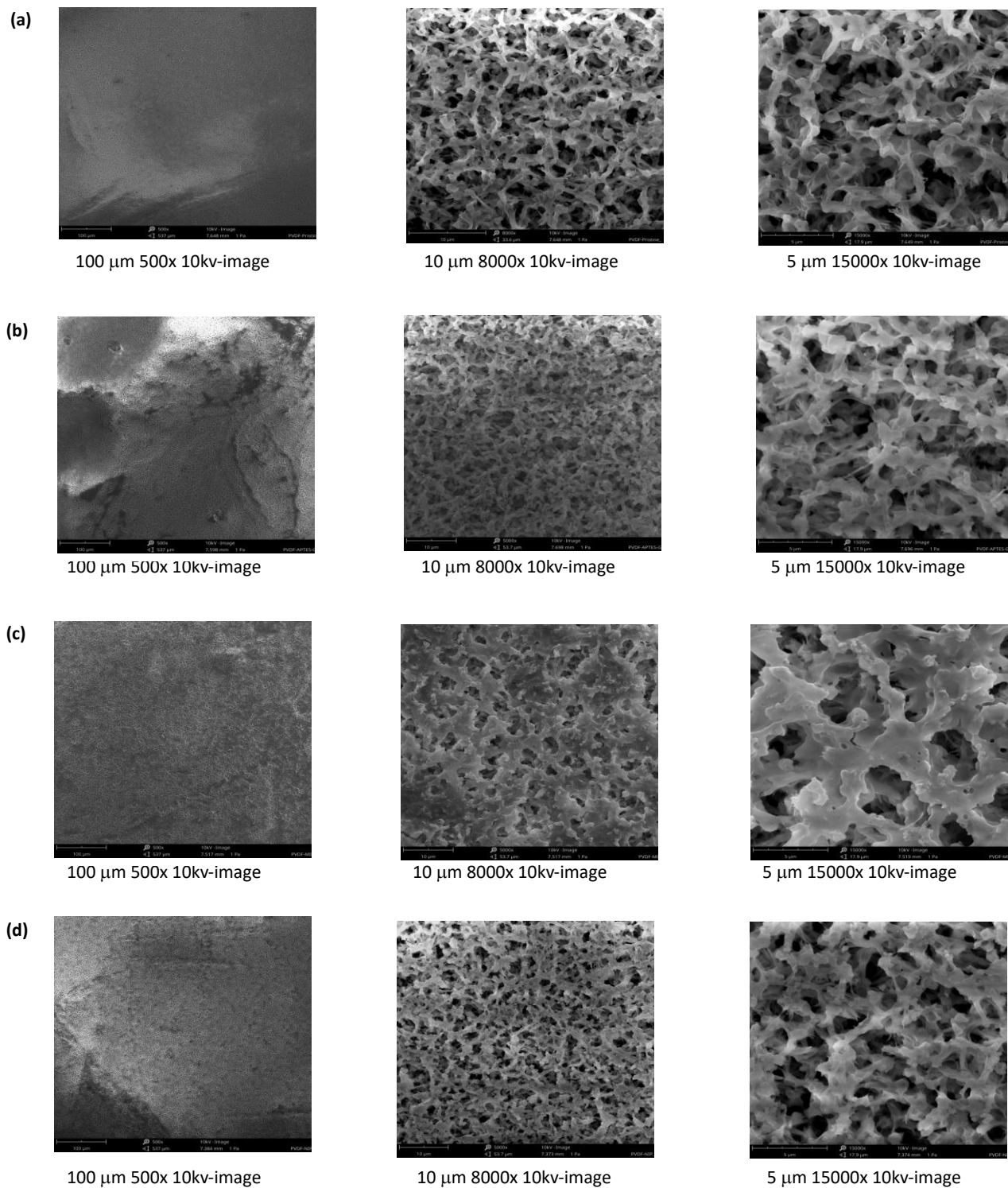


Fig. S18 SEM images of (a) Pristine PVDF, (b) PVDF-APTES-GA, (c) PVDF-APTES-GA@N-CDs-MIP, and (d) PVDF-APTES-GA@N-CDs-NIP at magnification of 500x (100 μ m), 8000x (10 μ m), and 15000x (5 μ m), respectively.

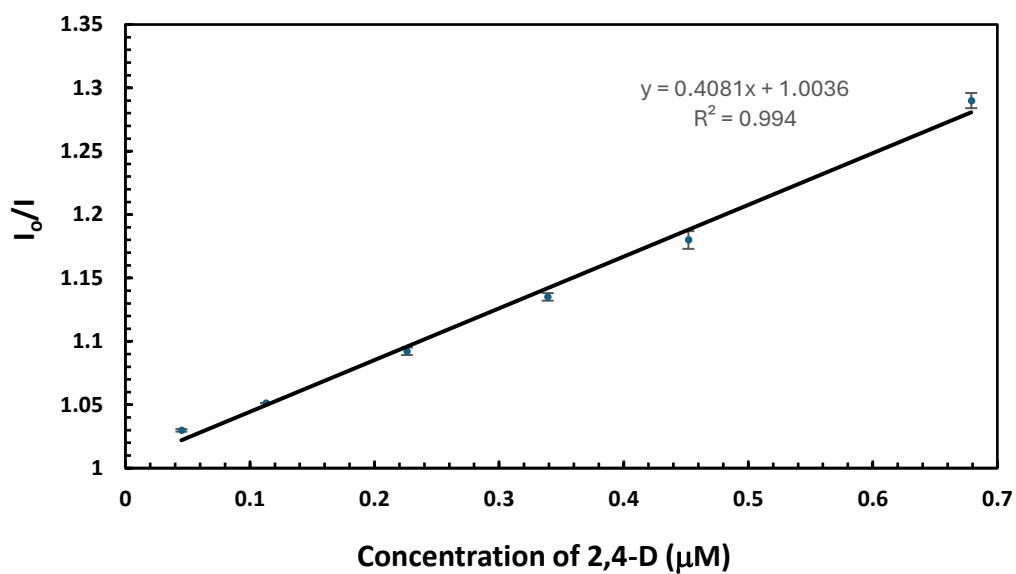


Fig. S19 Stern-Volmer plot of the quenching of the PVDF-APTES-GA@N-CDs-MIP sensor toward 2,4-D.