SUPRAMOLECULAR-ASSISTED EUTECTIC SYNTHESIS OF NICKEL-INCORPORATED CARBON NITRIDE FRAMEWORKS FOR PHOTON-ASSISTED CATALYTIC CO_2 REDUCTION

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Synthesis of Melamine Cyanurate (CAM) Precursor

1. Eutectic synthesis using melamine cyanurate precursor:
   1. Preparation of a 1:1 mixture of melamine and cyanuric acid using Millipore water.
   2. Reflux and stirring of the mixture at 90 °C for 6 h.
   3. Cooling of the mixture followed by filtration to obtain melamine cyanurate crystals.
   4. Washing of the crystals with water and drying at 110 °C in a vacuum furnace overnight under 10^{-5} torr pressure.
2. Recrystallization of melamine cyanurate from an ethanol solution:
   1. Weighing of 0.5 g of melamine cyanurate powder and transferring it to a beaker.
   2. Addition of 50 mL of ethanol to the beaker and heating the solution on a hot plate until the melamine cyanurate dissolved.
   3. Constant stirring of the solution as it cooled.
   4. Filtration of the cooled solution through a piece of filter paper and transfer of the crystals to a Petri dish.
   5. Complete drying of the crystals.
3. Resulting product:
   1. Grounding of the crystals into a powder using a mortar and pestle.
   2. Storage of the powder in a 25 mL amber bottle labeled as CAM.

Synthesis of CAM-gCN

1. Recrystallization and sample preparation:
    1. Collection of recrystallized precursors.
    2. Grinding of the precursors in a mortar.
    3. Transfer of the ground precursors into an alumina boat with a lid using a spatula.
    4. Placement of the alumina crucible in a SIGMA Laboratory tubular furnace under N_2 atmosphere
    5. Heating for 4 h with a ramping rate of 2 °C min^{-1} and a terminal temperature of 450 °C.
2. Post-heating process and storage:
    1. Transfer of the resulting fine yellow block of graphitic carbon nitride into a mortar.
    2. Grinding of the block well using a pestle.
    3. Transfer of the delicate yellow powder into a 25 mL storage amber glass vial with an airtight cap.
    4. Labeling of the vial as CAM-gCN.

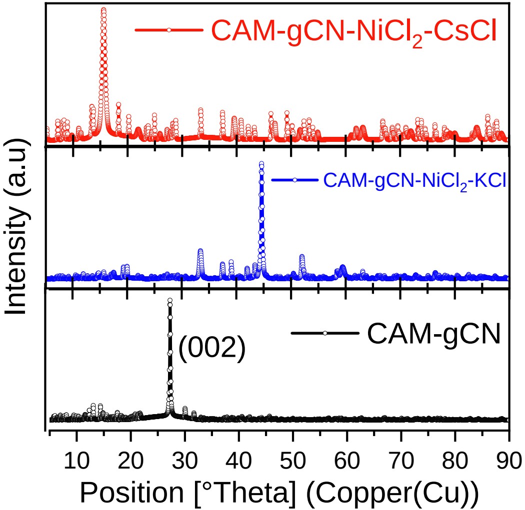
Synthesis of CAM-gCN-$NiCl_2$-KCl

1. Experimental procedure for synthesis:
   1. Grinding of 2 g of recrystallized melamine cyanurate ($C_6H_9N_9O_3$) with 10 g of a nickel chloride and potassium chloride eutectic mixture (39.4:60.6 wt%) in a glove box under an inert atmosphere.
   2. Transfer of the resulting mixture into a Quarts boat with a lid.
   3. Introduction of the reaction mixture into a tubular furnace under a nitrogen atmosphere.
   4. Heating of the mixture at a ramping rate of $2\,^{\circ}C\,min^{-1}$ for 4 h until reaching a terminal temperature of $450\,^{\circ}C$.
   5. Removal of the salt block from the reaction mixture through boiling distilled water washing and centrifugation at 10 000 rpm for 15 min.
   6. Drying of the obtained material in a vacuum oven at $110\,^{\circ}C$ overnight under a pressure of 10^{-5} torr.
2. Storage and labeling:
   1. Transfer of the resulting powder into a 25 mL amber bottle.
   2. Labeling of the bottle as CAM-gCN-$NiCl_2$-KCl.

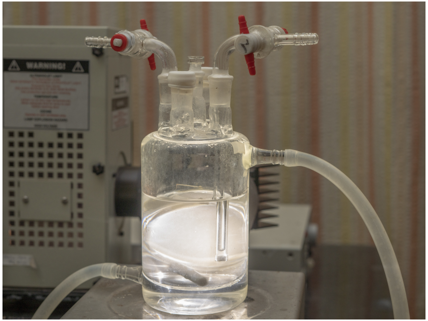
Synthesis of CAM-gCN-$NiCl_2$-CsCl

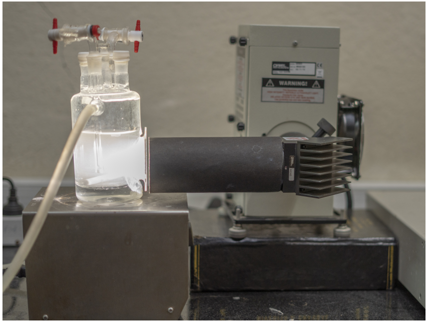
1. Experimental procedure for synthesis:
   1. Grinding of 2 g of melamine cyanurate ($C_6H_9N_9O_3$), recrystallized from methanol, along with 10 g of a nickel chloride and caesium chloride eutectic mixture (50:50 wt
   2. Transfer of the resulting mixture into a Quarts boat with a lid.
   3. Introduction of the reaction mixture into a tubular furnace under a nitrogen atmosphere.
   4. Heating of the mixture at a ramping rate of 2 °C min^{-1} for 4 h until reaching a terminal temperature of 450 °C.
   5. Removal of the salt block from the reaction mixture through washing with boiling distilled water and centrifugation at 10 000 rpm for 15 min.
   6. Drying of the obtained material in a vacuum oven at 110 °C overnight under a pressure of 10^{-5} torr.
2. Storage and labeling:
   1. Transfer of the resulting powder into a 25 mL amber bottle.
   2. Labeling of the bottle as CAM-gCN-$NiCl_2$-CsCl.

X-ray Diffraction Analysis



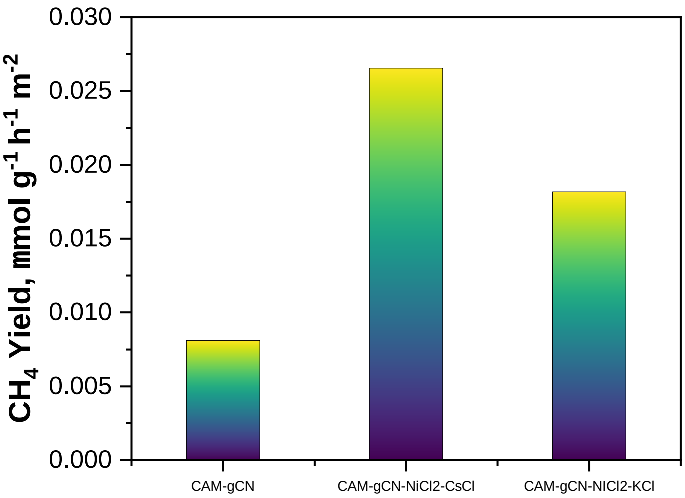
Experimental



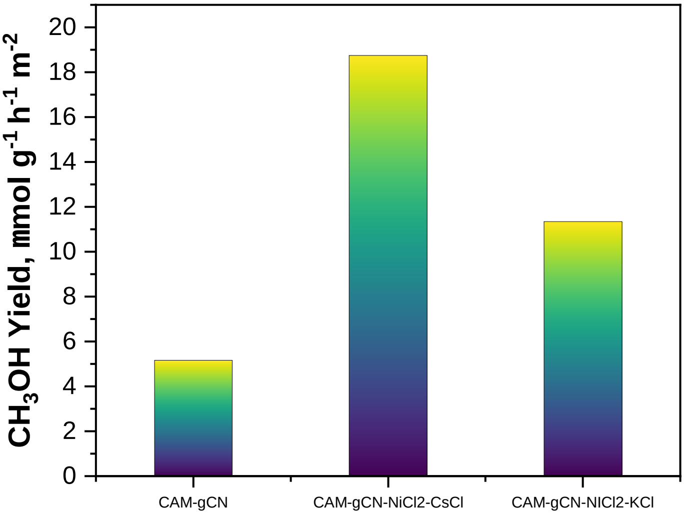


Conditions: 0.1g/L (Catalyst Loading) in 0.2N NaOH ; 300W Xe Lamp: AM 1.5 Filter

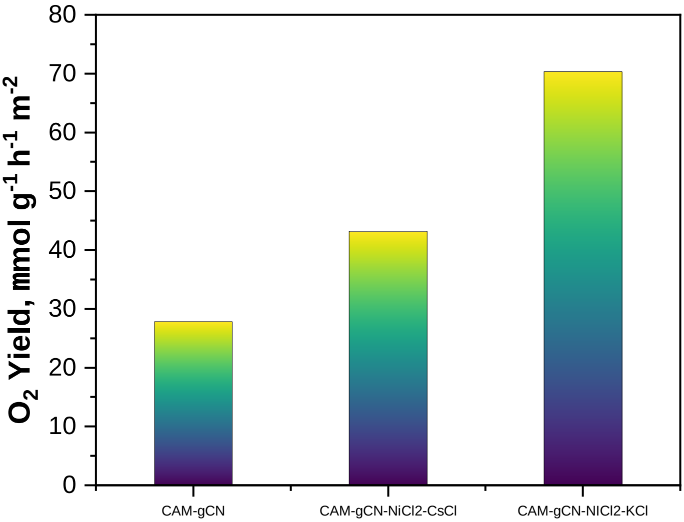
Surface Areas versus CH_4 Yield



Surface Areas versus CH_3OH Yield



Surface Areas versus O_2 Yield



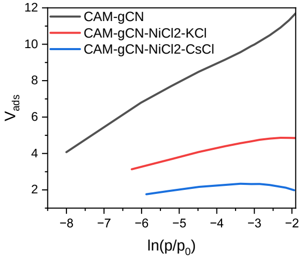
The B.E.T Surface Area

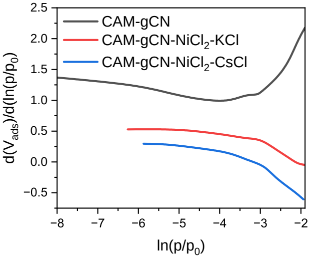
	B.E.T S.A	**C**
CAM-gCN	42.35	-623.69
CAM-gCN-$NiCl_2$-CsCl	2.17	-10.10
CAM-gCN-$NiCl_2$-KCl	12.83	-26.44

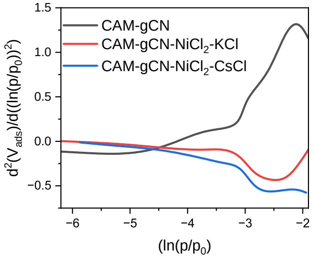
Surface Area Analysis: BETSI vs. SESAMI Method

	Surface Area, m^2/g						
	B.E.T	**BETSI**	**SESAMI**	**C, SESAMI**	**qm, mol/kg**	**Pore Size, nm**	**t-plot M.A**
CAM-gCN	42.35	44	43.5	377.8	0.45	21.59	9.56
CAM-gCN-$NiCl_2$-CsCl	2.17	10	10.1	1002	0.10	104.76	18.85
CAM-gCN-$NiCl_2$-KCl	12.83	20	19.8	777.8	0.20	43.91	17.71

Derivative Isotherm Summation







Energy-Dispersive X-ray Analysis (EDAX)

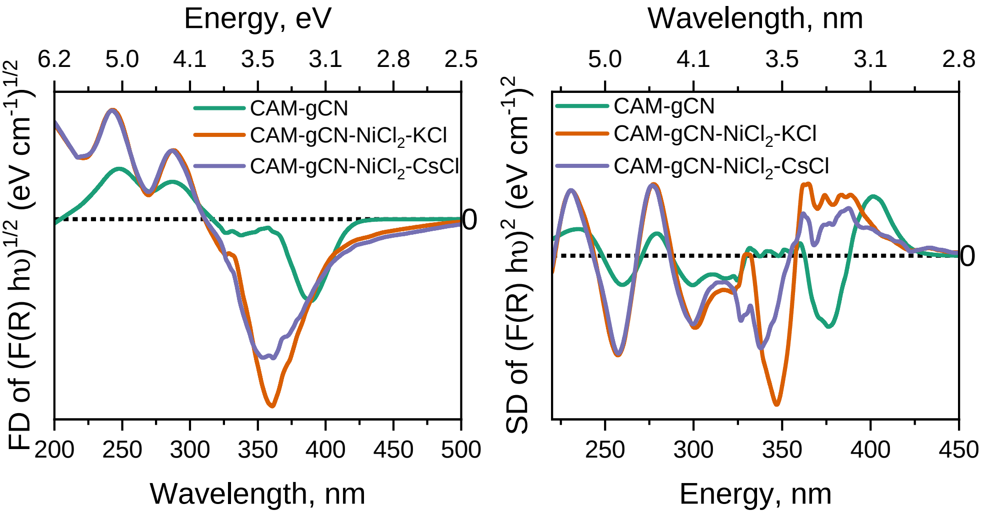
	Element	Weight %	MDL	Atomic %	Net Int.	Error %
gCN-NiK	C K	31.6	1.73	43.0	55.9	13.9
	N K	27.9	1.81	32.6	40.2	14.5
	O K	15.9	0.72	16.3	55.0	13.6
	Cl K	7.1	0.12	3.3	374.8	4.0
	K K	0.1	0.14	0.0	2.7	62.6
	Ni K	17.5	0.39	4.9	250.3	3.6
gCN-NiCs	C K	25.9	2.05	37.9	40.5	14.7
	N K	24.9	1.66	31.3	40.8	14.5
	O K	17.6	0.65	19.4	71.7	13.2
	Cl K	10.0	0.12	4.9	565.8	3.8
	Ni K	21.4	0.39	6.4	333.7	3.3
	Cs L	0.3	0.48	0.0	3.8	56.9

UV-Visible Diffuse Spectroscopy Analysis

Sample	Band Gap, eV						U.E	R.I
	Tauc Plot			K-M Plot			meV	
	L.R	F.D	S.D	L.R	F.D	S.D	L.R	
CAM-gCN	2.96	3.14	3.03	3.06	3.19	3.08	229	2.3555
CAM-gCN-$NiCl_2$-KCl	2.82	3.42	3.19	3.43	3.12	3.4	1001	2.2564
CAM-gCN-$NiCl_2$-CsCl	2.66	3.42	3.2	2.98	3.43	3.2	1166	2.3163

L.R = Linear Regression; F.D = First Derivative; S.D = Second Derivative;
U.E= Urbach Energy; R.I= Refractive Index

Derivative Kubelka-Monk Plots



Derivative Diffuse Reflectance Spectroscopic Analysis

	Min	Intensity	Max	Intensity	D Parameter	S.A	Slope	D.P /S.A
CAM-gCN	376	-0.05251	401	0.04348	0.09599	43.5	377.8	0.0022
CAM-gCN-$NiCl_2$-KCl	338	-0.06827	365	0.03192	0.12139	19.8	777.8	0.0061
CAM-gCN-$NiCl_2$-CsCl	347	-0.11024	388	0.05312	0.14529	10.1	1002	0.0143

Note: D.P = D parameter, difference between the maxima and minima, S.A= surface area, slope= B.E.T Slope from SESAMI Analysis

Surface Functional Groups in Ni-based Carbon Nitrides

	(C)-N-H_x	N-(C)=N	C=(N)-C	N-(NH)-C	C-(N)-H_x	OH
gCN	1.38	**35.34**	**35.36**	7.65	6.26	0.24
gCN-NiCs	3.32	19.78	6.26	6.9	**7.56**	**11.27**
gCN-NiK	**3.68**	20.61	15.26	**8.27**	5.23	7.23

Atomic Percentage (%)

$$\text{Normalized Surface Concentration, NSC\%} = \left(\frac{\text{XPS At\%}}{\text{SESAMI Surface Area}}\right)$$

	(C)-N-H_x	N-(C)=N	C=(N)-C	N-(NH)-C	C-(N)-H_x	OH
gCN	0.0317	0.8124	**0.8129**	0.1759	0.1439	0.0055
gCN-NiCs	**0.3287**	**1.9584**	0.6198	**0.6832**	**0.7485**	**1.1158**
gCN-NiK	0.1859	1.0409	0.7707	0.4177	0.2641	0.3652

Normalized Surface Concentration (NSC%)

Bold values indicate highest in each column

Comparison of Ni 2p and Cl 2p in Ni-based Carbon Nitrides

	Ni $2p_{3/2}$	Ni $2p_{3/2}$	Ni $2p_{1/2}$	Ni $2p_{1/2}$	Cl 2p	Cl 2p	Cl 2p
gCN-NiCs	**1.72**	0.91	**0.53**	0.42	**7.70**	**4.22**	-
gCN-NiK	1.37	**0.96**	0.43	**0.44**	4.95	3.86	1.44

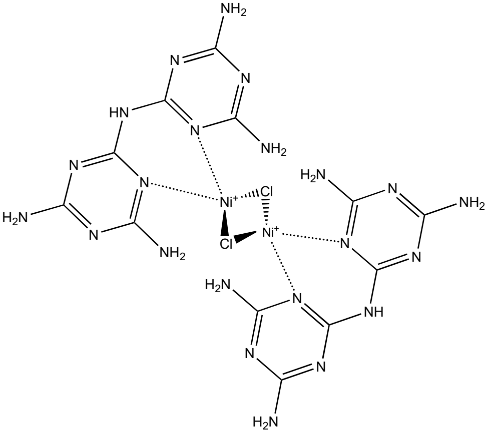
Atomic Percentage (%) of Ni 2p and Cl 2p

	Ni $2p_{3/2}$	Ni $2p_{3/2}$	Ni $2p_{1/2}$	Ni $2p_{1/2}$	Cl 2p	Cl 2p	Cl 2p
gCN-NiCs	**0.1703**	**0.0901**	**0.0525**	**0.0416**	**0.7624**	**0.4178**	-
gCN-NiK	0.0692	0.0485	0.0217	0.0222	0.2500	0.1949	**0.9846**

Normalized Surface Concentration (NSC%) of Ni 2p and Cl 2p

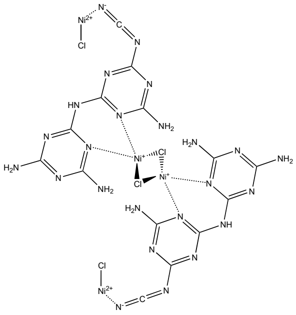
Bold values indicate higher concentration between the two samples

Possible Structure

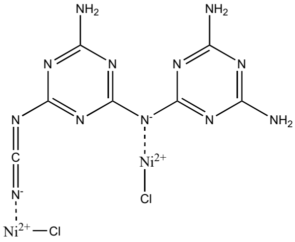


Potential coordination environment of a nickel cation with melam as bidentate ligand. Nickel is sharing two chloride ligands, thus formally exhibiting the oxidation state +1.

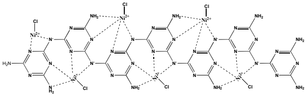
Possible Structures



(a)



(b)



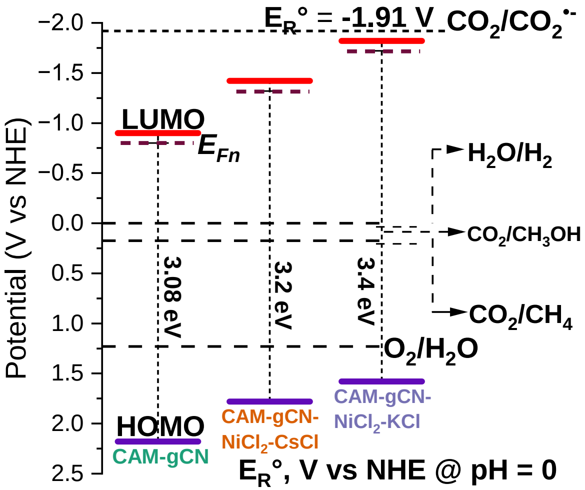
(c)

Hypothetical structures of Ni-CNx, assuming a molecular (a-b) and an oligomeric (c) arrangement of subunits. The melam units in (a) feature a coordinative and ionic bond towards nickel with oxidation states of +1 and +2, respectively. In (b) the melam is negatively charged featuring only ionic bonds and ox. state +2. (c) In the oligomeric form only ionic bonds persist; with nickel in ox. state +2.

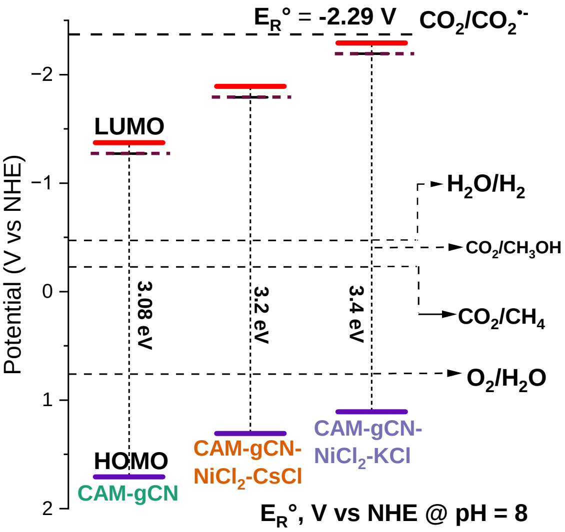
Valence Band XPS Analysis

Sample	Highest Occupied Molecular Orbital (HOMO), eV				
	SD	Curve Fitting			
		Position	Original Value	FWHM	STD
CAM-gCN	2.18	2.28	2.2832	1.53	1.368
CAM-gCN-$NiCl_2$-CsCl	1.78	1.74	1.7359	1.74	1.35
CAM-gCN-$NiCl_2$-KCl	1.58	1.57	1.5701	1.67	1.818

Energy Band Diagram Elucidation



Energy Band Diagram Elucidation: pH Correction



Methane Formation Mechanism on gCN-$NiCl_2$

Direct CO_2 Reduction

1. Light absorption:

$$gCN\text{-}NiCl_2 + h\nu \rightarrow gCN\text{-}NiCl_2^* + e^- + h^+$$

2. CO_2 activation:

$$CO_2 + gCN\text{-}NiCl_2^* \rightarrow CO_2^* + gCN\text{-}NiCl_2$$

3. PCET steps:

$$CO_2^* + e^- + H^+ \rightarrow CO^* + HCOOH^*$$
$$CO^* + H^+ + e^- \rightarrow HCHO^*$$
$$HCHO^* + H^+ + e^- \rightarrow CH_3OH^*$$
$$CH_3OH^* + H^+ + e^- \rightarrow CH_4^*$$

Indirect Pathway via CO

1. Light absorption
2. CO_2 activation and CO formation:

$$CO_2 + gCN\text{-}NiCl_2^* \rightarrow CO_2^* + gCN\text{-}NiCl_2$$
$$CO_2^* + e^- \rightarrow CO^* + O^-$$

3. CO hydrogenation:

$$CO^* + H^+ + e^- \rightarrow CH_2^* + OH^-$$
$$CH_2^* + H^+ + e^- \rightarrow CH_3^* + H_2O$$
$$CH_3^* + H^+ + e^- \rightarrow CH_4^*$$

4. Water oxidation:

$$h^+ + H_2O \rightarrow \frac{1}{2}O_2 + H^+ + e^-$$

Methanol Formation Mechanism on gCN-$NiCl_2$

CO_2 Radical Anion Reactions

1. Dimerization:

$$2CO_2^{\bullet} \rightarrow C_2O_4^{2-}$$
$$C_2O_4^{2-} + 2H^+ + 2e^- \rightarrow HCOOH + H_2O$$

2. Protonation:

$$CO_2^{\bullet} + H^+ \rightarrow HCOO^{\bullet}$$
$$HCOO^{\bullet} + 2H^+ + 2e^- \rightarrow HCHO + H_2O$$

Pathways to Methanol

1. Formate Pathway:

$$HCOO^- + H^+ + e^- \rightarrow HCHO + H_2O$$
$$HCHO + H^+ + e^- \rightarrow CH_2OH$$

2. Methoxy Pathway:

$$CO_2^{\bullet} + 2H^+ + 2e^- \rightarrow CHO^{\bullet}$$
$$CHO^{\bullet} + H^+ + e^- \rightarrow CH_2O^{\bullet}$$
$$CH_2O^{\bullet} + H^+ + e^- \rightarrow CH_3O^{\bullet}$$
$$CH_3O^{\bullet} + H^+ + e^- \rightarrow CH_3OH$$

Water Oxidation

$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$$

Conclusion

Advantages

- Promising for solar fuel applications
- In-situ synthesis of metal-incorporated structures
  - Frameworks and hybrids (e.g., gCN-Ni)
  - Many structures remain unknown
- Precursor engineering via supramolecular chemistry
- Incorporation of functionalities at precursor stage

Challenges and Future Directions

- Complexity in catalyst design
  - Numerous interconnected factors
  - Design changes based on reaction requirements
- Future research:
  - Explore unknown structures
  - Optimize precursor engineering
  - Develop predictive models
- Key goal: Balance complexity and functionality

Key Takeaway: A key strength of this research lies in its multifaceted analytical approach. By employing a wide array of advanced characterization techniques and introducing novel parameters such as **normalized surface concentration (NSC%)** and **light absorption efficiency per unit surface area (DP/SA)**, this work provides unprecedented insights into the structure-property-performance relationships of g-C_3N_4 materials.

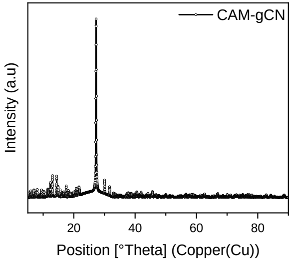
Appreciation

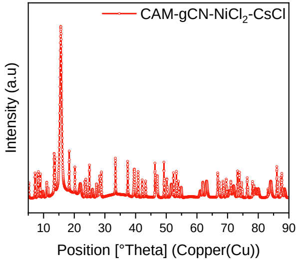
Thank you for your attention! Any questions?

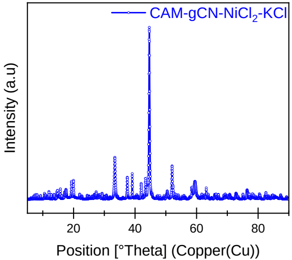
The presentation, as well as the dataset, will be available on the Catalysis Database at http://catalysis.eprints.iitm.ac.in/.

Additional Slides

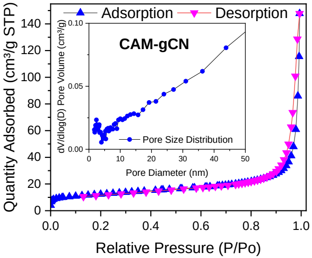
X-ray Diffraction Analysis

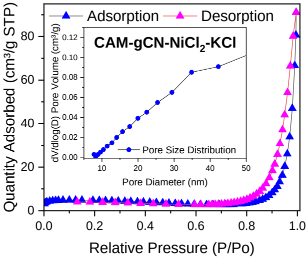


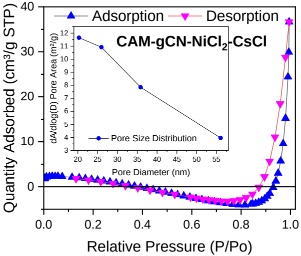




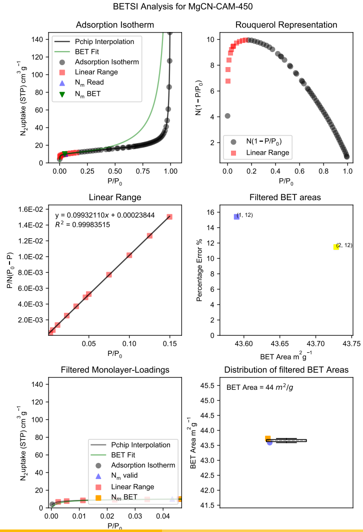
Physical Adsorption Characterization

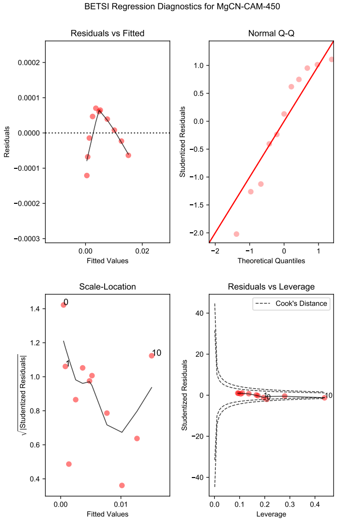




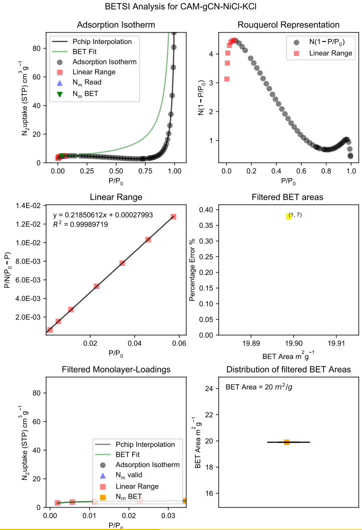


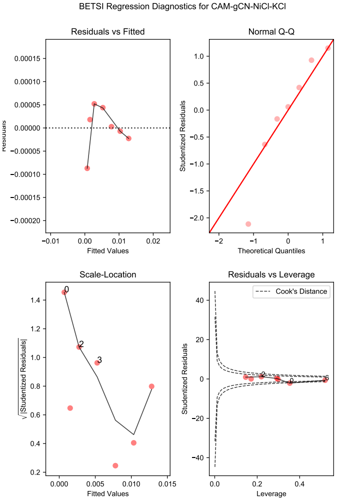
BET Surface Identification (BETSI) Analysis of CAM-gCN



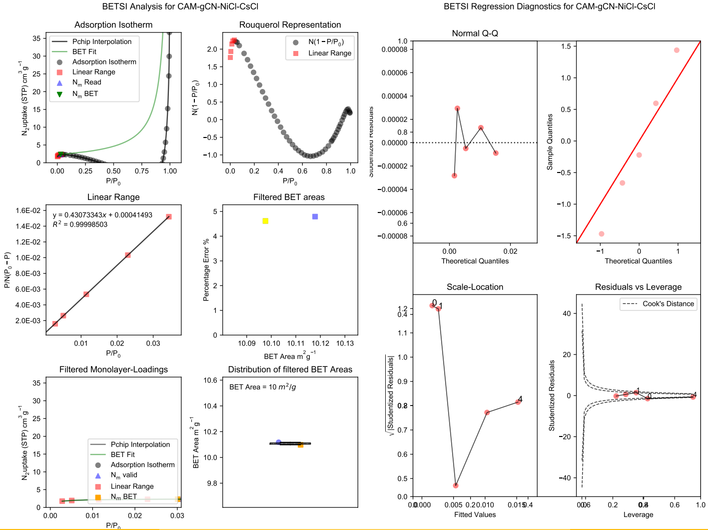


BET Surface Identification (BETSI) Analysis of CAM-gCN-$NiCl_2$-KCl

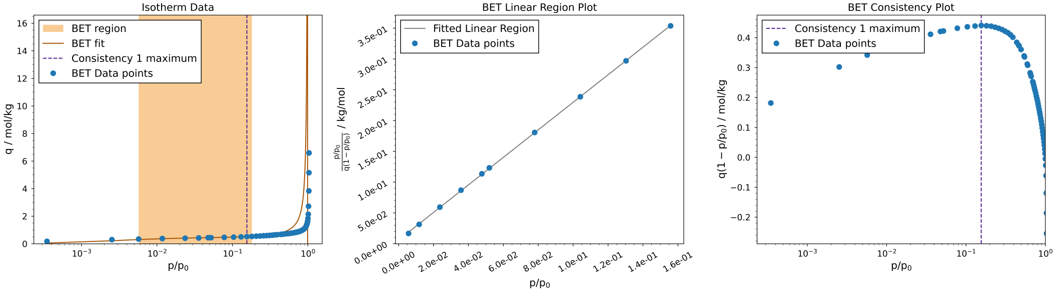




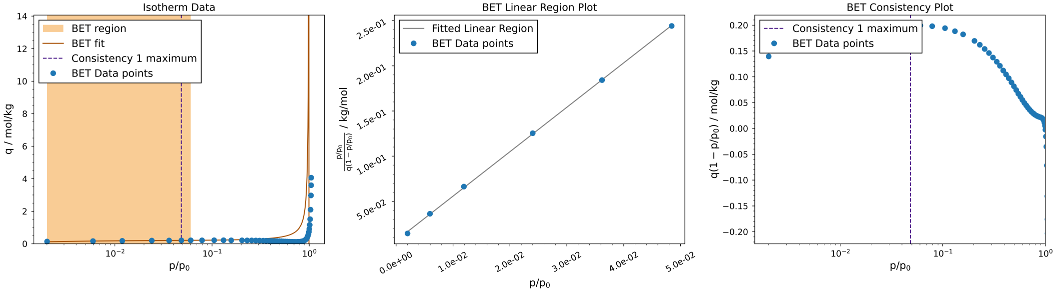
BET Surface Identification (BETSI) Analysis of CAM-gCN-$NiCl_2$-CsCl



SESAMI Analysis of CAM-gCN



SESAMI Analysis of CAM-gCN-$NiCl_2$-KCl



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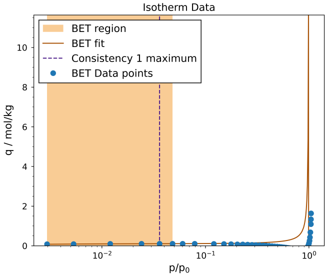
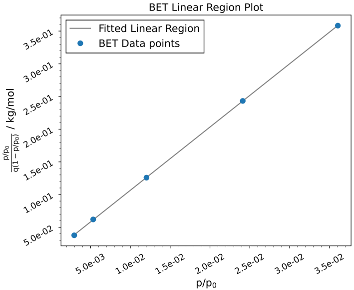
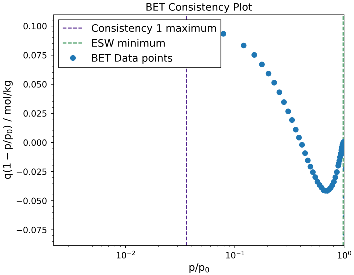
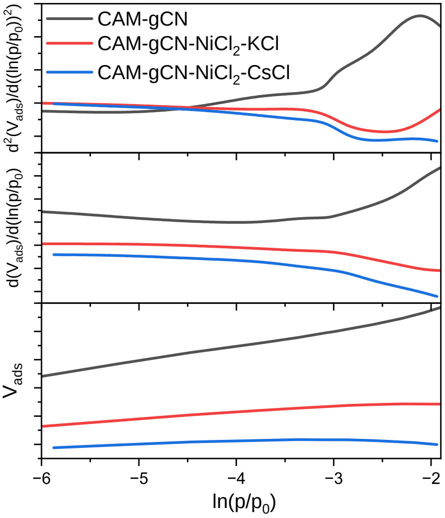


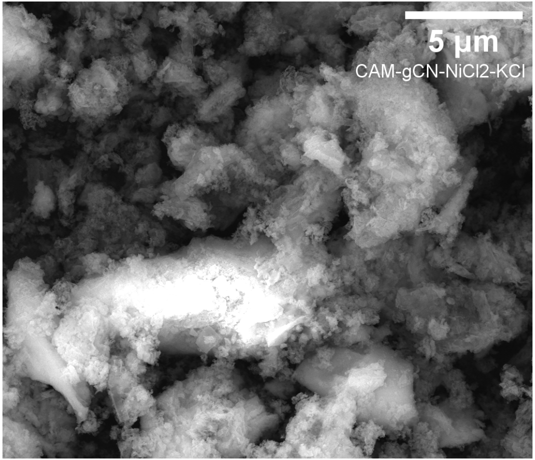


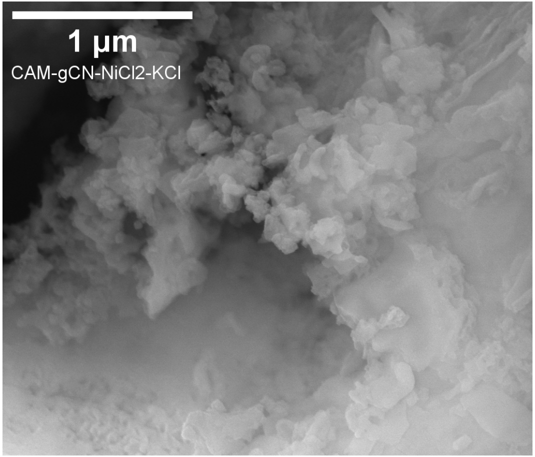


Derivative Isotherm Summation

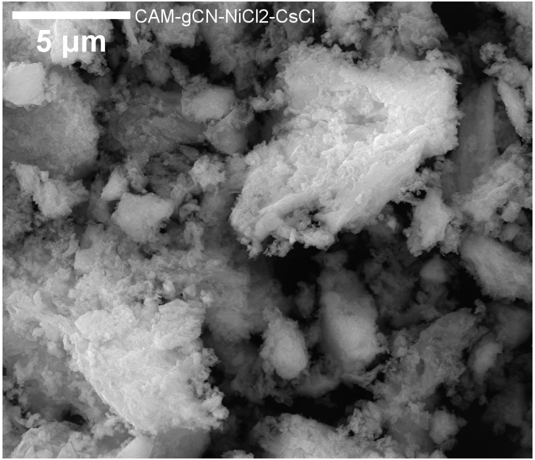


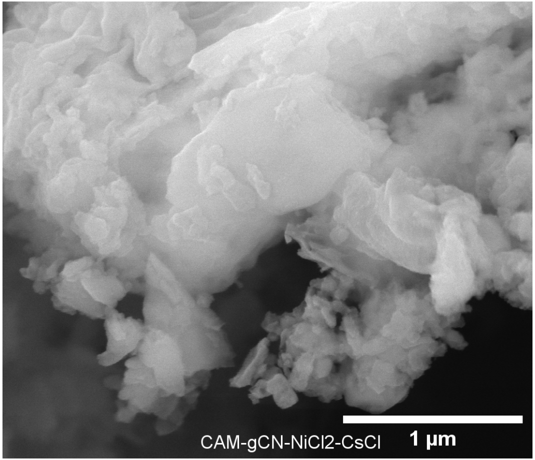
Field Emission Scanning Electron Microscopy (FESEM)



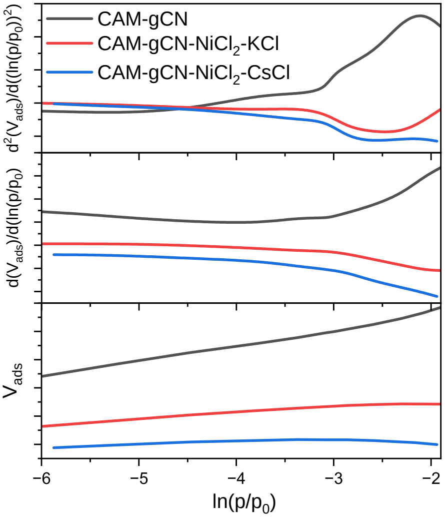


Field Emission Scanning Electron Microscopy (FESEM)

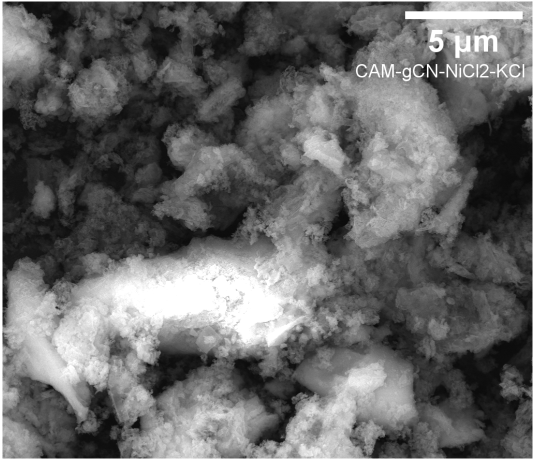


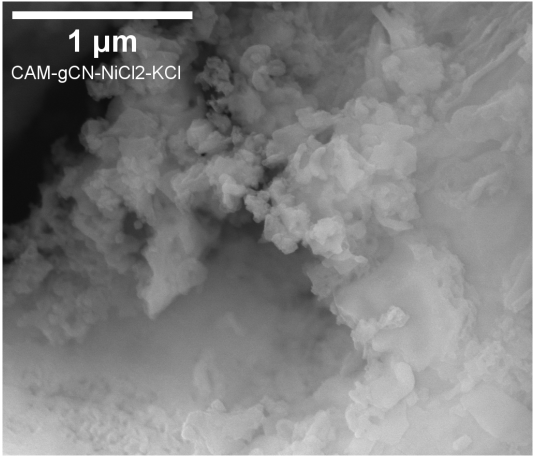


Derivative Isotherm Summation

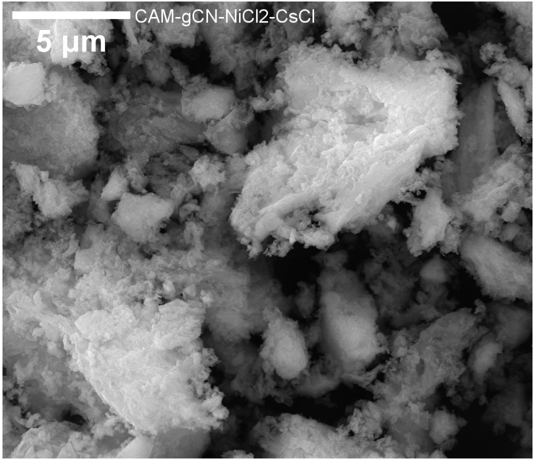


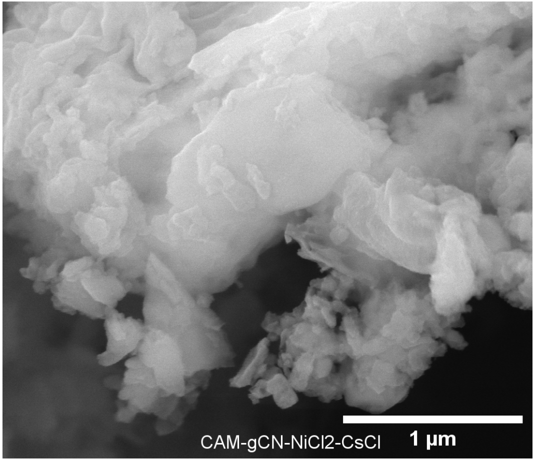
Field Emission Scanning Electron Microscopy (FESEM)



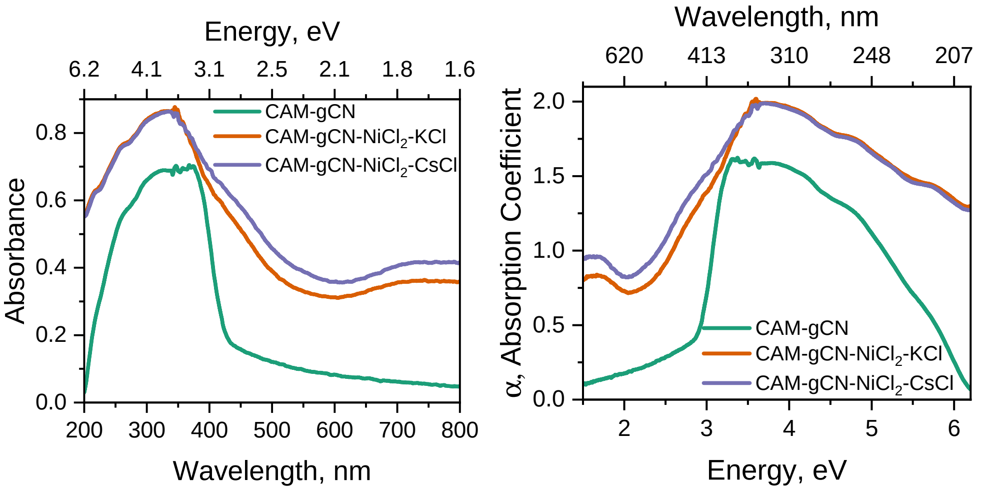


Field Emission Scanning Electron Microscopy (FESEM)

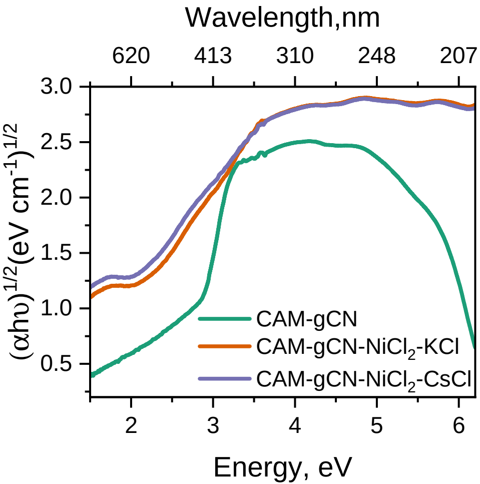


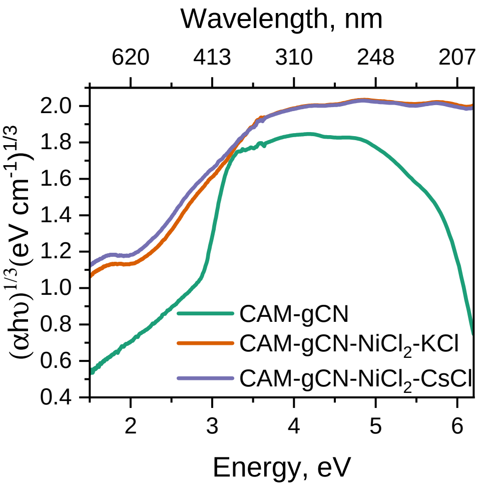


Solid UV-Visible Spectroscopy

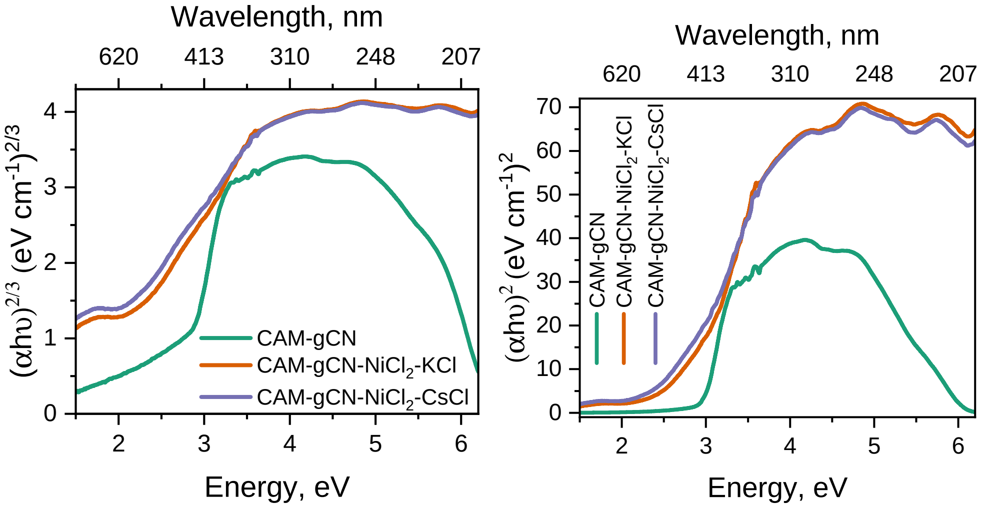


Tauc Plot Validation

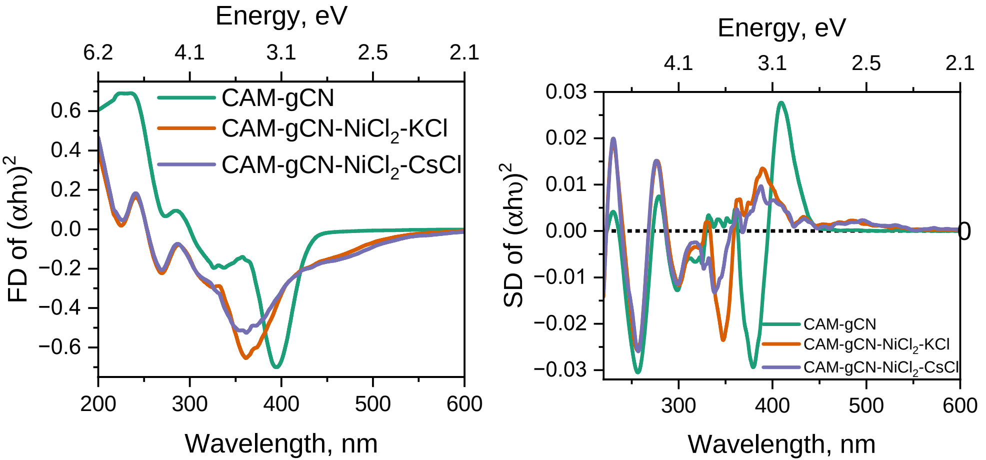




Tauc Plot Validation



Derivative Tauc Plot

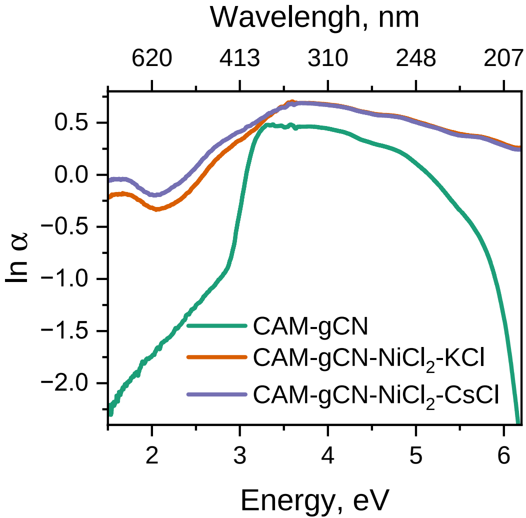


Derivative Tauc Plot Analysis

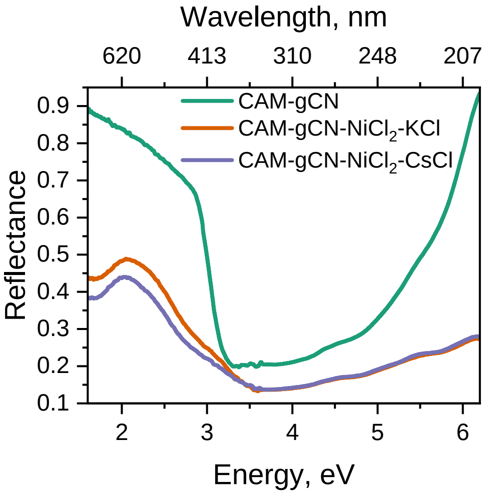
	Min	Intensity	Max	Intensity	D Parameter	S.A	Slope	D.P / S.A
CAM-gCN	379	-0.02948	409	0.02775	0.05723	43.5	377.8	0.001315632
CAM-gCN-$NiCl_2$-KCl	347	-0.02373	389	0.01358	0.03731	19.8	777.8	0.001884343
CAM-gCN-$NiCl_2$-CsCl	338	-1.33E-02	388	0.00978	0.02312	10.1	1002	0.002289109

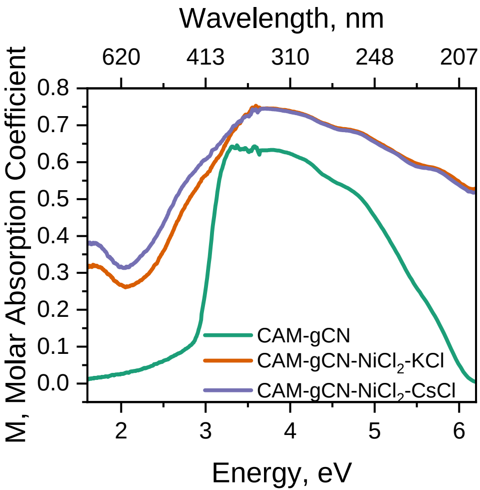
Note: D.P = D parameter, difference between the maxima and minima, S.A= surface area, slope= B.E.T Slope from SESAMI Analysis

Urbach Plot

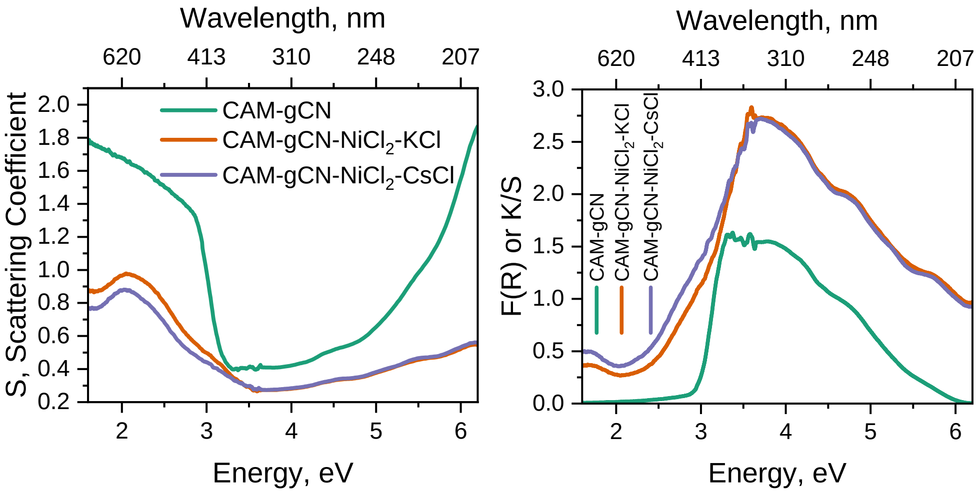

Wavelengh, nm
620
413
310
248
207
0.5
0.0
−0.5
−1.0
−1.5
−2.0
ln α
CAM-gCN
CAM-gCN-NiCl2-KCl
CAM-gCN-NiCl2-CsCl
2
3
4
5
6
Energy, eV

Diffuse Reflectance Spectroscopy

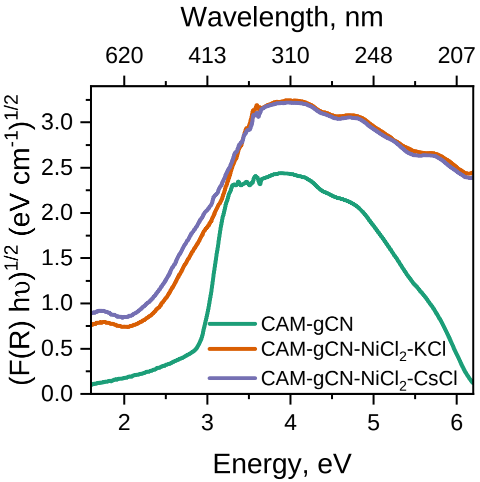


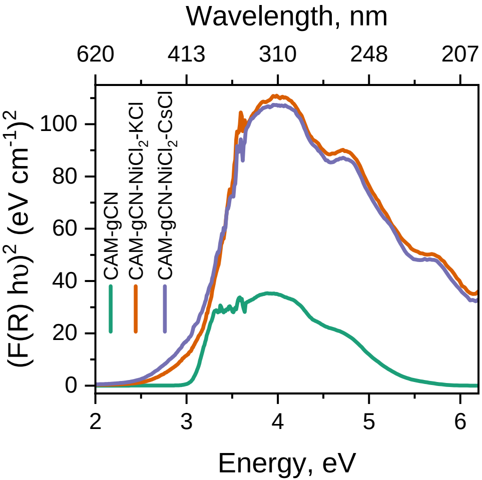


Diffuse Reflectance Spectroscopy

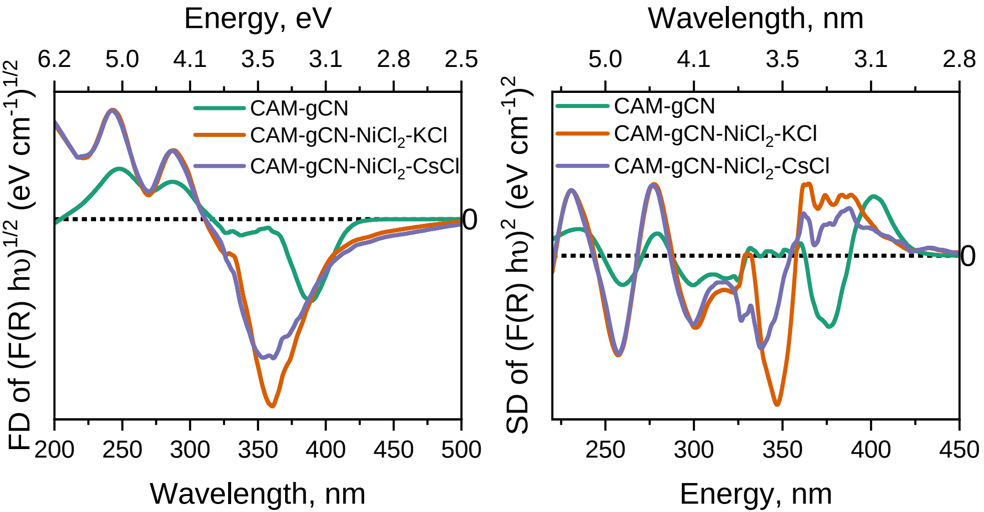


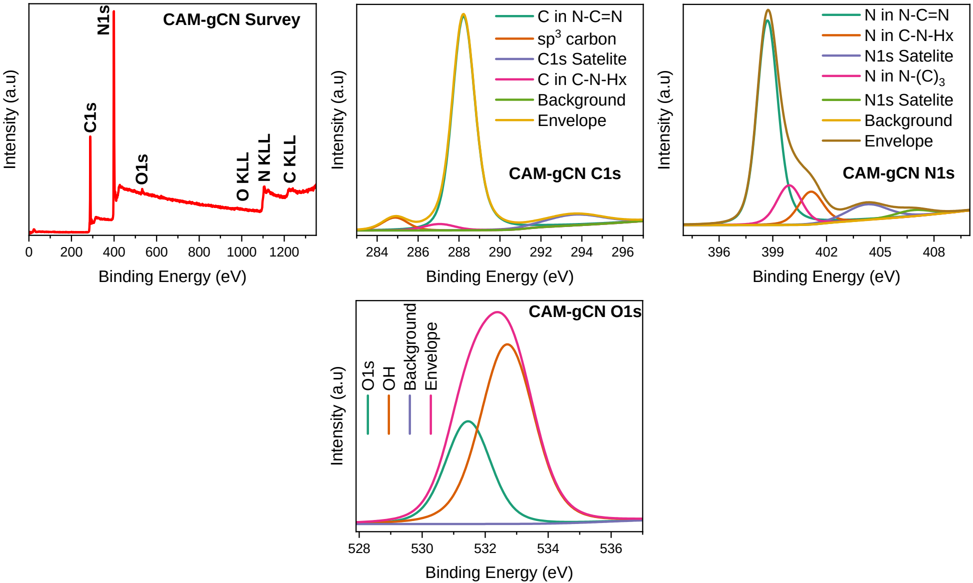
Kubelka-Monk Plots





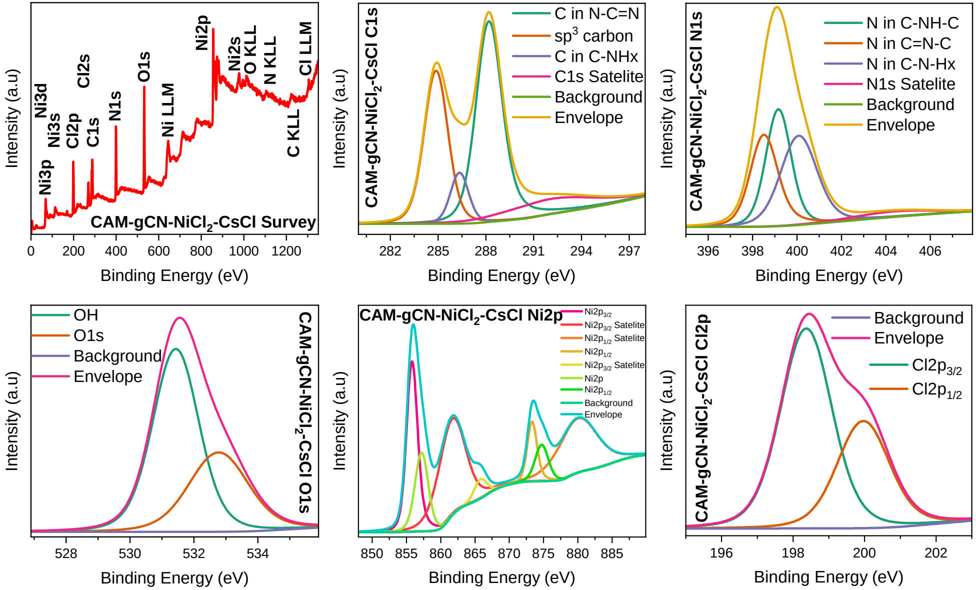
Derivative Kubelka-Monk Plots




CAM-gCN Survey
N1s
C1s
O1s
O KLL
N KLL
C KLL
Intensity (a.u)
Binding Energy (eV)
C in N-C=N
sp3 carbon
C1s Satelite
C in C-N-Hx
Background
Envelope
CAM-gCN C1s
N in N-C=N
N in C-N-Hx
N1s Satelite
N in N-(C)3
N1s Satelite
Background
Envelope
CAM-gCN N1s
CAM-gCN O1s
O1s
OH
Background
Envelope

Peak Assignment	Pos.	FWHM	L.Sh	Area	At%	Total%	STD
sp^3	284.88	1.45	LA(1.3, 243)	8946.39	2.26		
C in C−N−Hx	287.05	1.78	LA(1.3, 243)	5446.39	1.38		
C in N−C=N	288.19	1.28	LA(1.03, 1.24, 243)	139748.92	35.34	35.34	1.183
C1s Satelite 1	293.64	3.33	LA(1.3, 243)	17036.86	4.31		
N in C=N−C	398.67	1.36	LA(1.03, 1.24, 243)	251677.86	35.36	49.27	1.096
N in N−(C_3)	399.92	1.63	LA(1.3, 243)	54474.7	7.65		
N in C−N−Hx	401.13	1.61	LA(1.3, 243)	44595.35	6.26		
N1s Satelite 1	404.26	2.73	LA(1.3, 243)	35832.03	5.03		
N1s Satelite 2	406.84	2.31	LA(1.3, 243)	11858.5	1.67		
OH	531.46	1.69	LA(1.3, 243)	2802.28	0.24	0.24	0.8794
O1s	532.7	2	LA(1.3, 243)	5802.05	0.5		

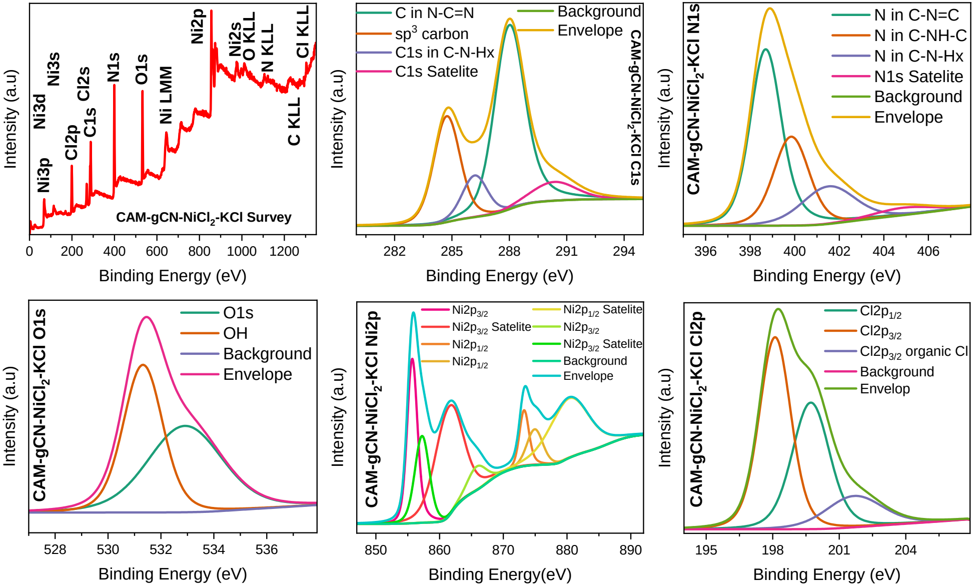
Table 1: Spectral Features of CAM-gCN



CAM-gCN-NiCl2-CsCl Survey
Ni3p
Ni3d
Ni3s
Cl2p
Cl2s
C1s
N1s
O1s
Ni LLM
Ni2p
Ni2s
O KLL
N KLL
C KLL
Cl LLM
CAM-gCN-NiCl2-CsCl C1s
C in N-C=N
sp3 carbon
C in C-NHx
C1s Satelite
Background
Envelope
CAM-gCN-NiCl2-CsCl N1s
N in C-NH-C
N in C=N-C
N in C-N-Hx
N1s Satelite
Background
Envelope
OH
O1s
Background
Envelope
CAM-gCN-NiCl2-CsCl O1s
CAM-gCN-NiCl2-CsCl Ni2p
Ni2p3/2
Ni2p3/2 Satelite
Ni2p1/2 Satelite
Ni2p1/2
Ni2p3/2 Satelite
Ni2p
Ni2p1/2
Background
Envelope
CAM-gCN-NiCl2-CsCl Cl2p
Background
Envelope
Cl2p3/2
Cl2p1/2
Intensity (a.u)
Binding Energy (eV)

Peak Assignment	Pos.	FWHM	L.Sh	Area	At%	Total%	STD
sp^3	284.87	1.77	LA(1.3, 243)	26175.63	13.05		
C in C−N−Hx	286.35	1.35	LA(1.3, 243)	6665.81	3.32		
C in N−C=N	288.15	1.91	LA(1.03, 1.24, 243)	39659.82	19.78	19.78	0.9326
C1s Satelite 1	292.07		LA(1.3, 243)	9559.53	4.77		
N in C=N−C	398.48	1.45	LA(1.03, 1.24, 243)	22605.93	6.26	20.72	0.918
N in C−NH−C	399.16	1.34	LA(1.3, 243)	24898.56	6.9		
N1s in C−N−Hx	400.08	1.93	LA(1.3, 243)	27305.05	7.56		
N1s Satelite	404.33	4.28	LA(1.3, 243)	3729.92	1.03		
Ni 2p 3/2	855.78	1.88	LA(1.03, 1.24, 243)	76375.89	1.72	3.58	0.9357
Ni 2p 3/2	857.21	2.3	LA(1.3, 243)	40287.69	0.91		
Ni 2p 3/2 Satelite	861.62	4.66	LA(1.3, 243)	100169.43	2.25		
Ni 2p 3/2 Satelite	865.79	2.2	LA(1.3, 243)	9442.57	0.21		
Ni 2p 1/2	873.3	1.66	LA(1.03, 1.24, 243)	23676.55	0.53		
Ni 2p 1/2	874.73	2.29	LA(1.3, 243)	18521.18	0.42		
Ni 2p 1/2 Satelite	880.03	6.68	LA(1.3, 243)	80807.16	1.82		
OH	531.43	1.7	LA(1.3, 243)	66218.8	11.27	11.27	1.152
O1s	532.77	2.19	LA(1.3, 243)	36937.88	6.29		
Cl 2p	198.37	1.69	LA(1.3, 243)	35288.42	7.7	11.92	1.023
Cl 2p	199.97	1.73	LA(1.3, 243)	19333.42	4.22		

Table 2: Spectral Features of CAM-gCN-$NiCl_2$-CsCl



Intensity (a.u)
Binding Energy (eV)
Ni3p
Ni3d
Ni3s
Cl2p
C1s
Cl2s
N1s
O1s
Ni LMM
Ni2p
Ni2s
O KLL
N KLL
C KLL
Cl KLL
CAM-gCN-NiCl2-KCl Survey
0
200
400
600
800
1000
1200
C in N-C=N
sp3 carbon
C1s in C-N-Hx
C1s Satelite
Background
Envelope
CAM-gCN-NiCl2-KCl C1s
282
285
288
291
294
N in C-N=C
N in C-NH-C
N in C-N-Hx
N1s Satelite
Background
Envelope
CAM-gCN-NiCl2-KCl N1s
396
398
400
402
404
406
O1s
OH
Background
Envelope
CAM-gCN-NiCl2-KCl O1s
528
530
532
534
536
Ni2p3/2
Ni2p3/2 Satelite
Ni2p1/2
Ni2p1/2
Ni2p1/2 Satelite
Ni2p3/2
Ni2p3/2 Satelite
Background
Envelope
CAM-gCN-NiCl2-KCl Ni2p
850
860
870
880
890
Binding Energy(eV)
Cl2p1/2
Cl2p3/2
Cl2p3/2 organic Cl
Background
Envelop
CAM-gCN-NiCl2-KCl Cl2p
195
198
201
204

Peak Assignment	Pos.	FWHM	L.Sh	Area	At%	Total%	STD
sp^3	284.73	1.62	LA(1.3, 243)	22193.62	9.77		
C in C-N-Hx	286.19	1.56	LA(1.3, 243)	8360.15	3.68		
C in N-C=N	287.97	1.84	LA(1.03, 1.24, 243)	46787.5	20.61	20.61	0.9505
C1s Satelite 1	290.34	2.72	LA(1.3, 243)	6605.52	2.91		
N in C=N-C	398.67	1.63	LA(1.03, 1.24, 243)	62371.5	15.26	28.76	0.9694
N in C-NH-C	399.85	1.87	LA(1.3, 243)	33797.03	8.27		
N1s in C-N-Hx	401.52	2.8	LA(1.3, 243)	21389.26	5.23		
N1s Satelite 2	404.86	3.14	LA(1.3, 243)	4748.98	1.16		
Ni 2p 3/2	855.67	1.87	LA(1.03, 1.24, 243)	68766.7	1.37	3.2	0.9221
Ni 2p 3/2	857.25	2.69	LA(1.3, 243)	48578.09	0.96		
Ni 2p 3/2 Satelite	861.47	5.11	LA(1.3, 243)	116346.18	2.31		
Ni 2p 3/2 Satelite	865.84	3.5	LA(1.3, 243)	17305.37	0.34		
Ni 2p 1/2	873.23	1.74	LA(1.03, 1.24, 243)	21755.92	0.43		
Ni 2p 1/2	874.94	2.95	LA(1.3, 243)	21996.04	0.44		
Ni 2p 1/2 Satelite	880.29	7.29	LA(1.3, 243)	90494.99	1.8		
OH	531.32	1.76	LA(1.3, 243)	48099.66	7.23	7.23	0.9721
O1s	532.91	3.32	LA(1.3, 243)	53016.83	7.97		
Cl 2p	198.11	1.68	LA(1.3, 243)	25696.39	4.95	8.81	0.9985
Cl 2p	199.72	1.99	LA(1.3, 243)	20016.17	3.86		
Cl 2p	201.68	3	LA(1.3, 243)	7464.45	1.44		

Table 3: Spectral Features of CAM-gCN-$NiCl_2$-KCl

Comparison of Surface Functional Groups in Ni-based Carbon Nitrides

	(C)-N-H_x	N-(C)=N	C=(N)-C	N-(NH)-C	C-(N)-H_x	OH
gCN	1.38	**35.34**	**35.36**	7.65	6.26	0.24
gCN-NiCs	3.32	19.78	6.26	6.9	**7.56**	**11.27**
gCN-NiK	**3.68**	20.61	15.26	**8.27**	5.23	7.23

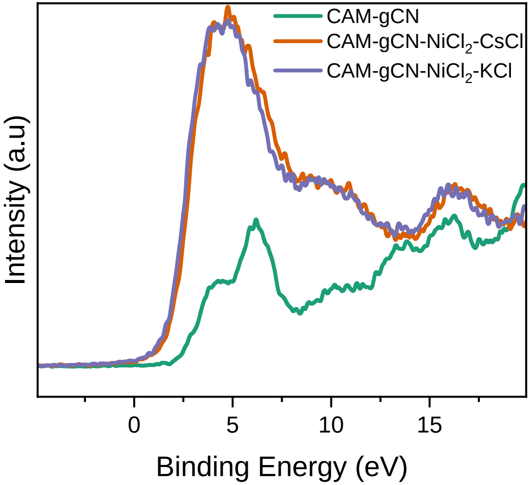
Atomic Percentage (%)

Bold values indicate highest in each column

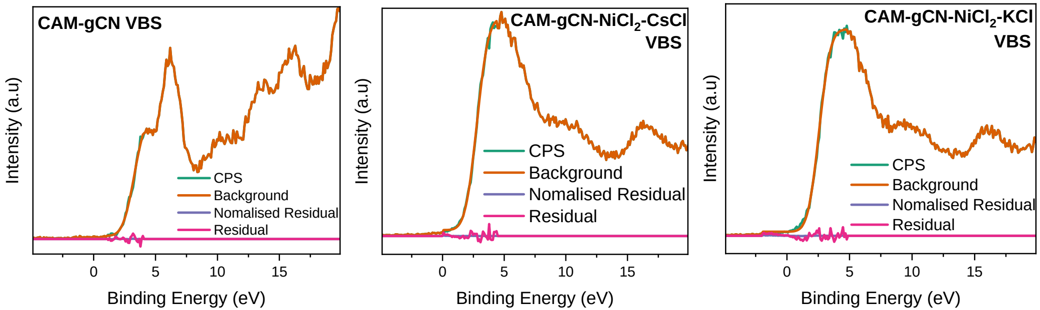
	(C)-N-H_x	N-(C)=N	C=(N)-C	N-(NH)-C	C-(N)-H_x	OH
gCN	3.17	81.24	**81.29**	17.59	14.39	0.55
gCN-NiCs	**32.87**	**195.84**	61.98	**68.32**	**74.85**	**111.58**
gCN-NiK	18.59	104.09	77.07	41.77	26.41	36.52

Normalized Surface Concentration (NSC%)

Valence Band XPS Analysis



Valence Band XPS Analysis



Derivative Valence Band XPS Analysis