Electronic Supplementary Material (ESI) for RSC Advances.


Supporting Information for

# A Comparison Study of Sodium ion and Potassium ion Modified Graphitic Carbon Nitride for Photocatalytic Hydrogen Evolution

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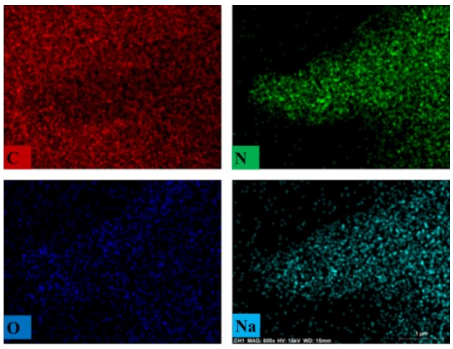


Fig. S1: Element mapping images of GCN-Na-5.

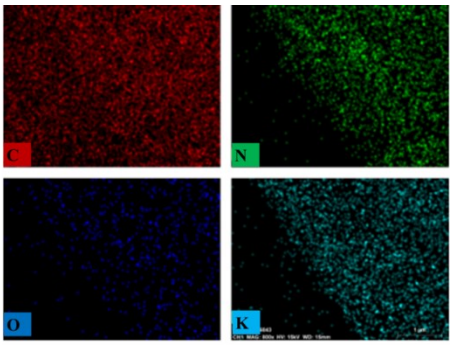


Fig. S2: Element mapping images of GCN-K-5.

Table S1: BET surface area, average pore diameter and pore volume for each sample.

| Sample | $S_{BET}$($m^2$/g) | Average pore diameter(nm) | Pore volume($cm^2$/g) |
|---|---|---|---|
| GCN | 10.40 | 20.78 | 0.054 |
| GCN-Na-0.5 | 6.81 | 16.75 | 0.029 |
| GCN-Na-5 | 10.30 | 13.74 | 0.035 |
| GCN-K-0.5 | 6.30 | 14.03 | 0.023 |
| GCN-K-5 | 7.02 | 11.63 | 0.020 |

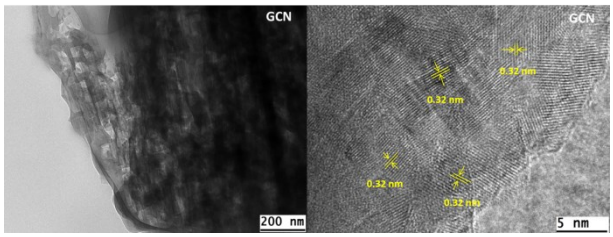


Fig. S3: TEM and high resolution TEM images of GCN.

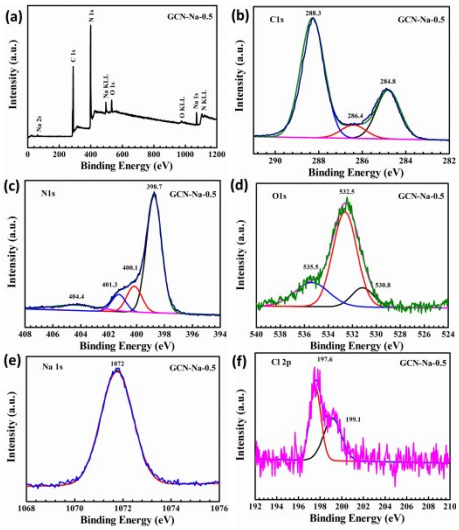


Fig. S4: XPS spectrum of GCN-Na-0.5 (a). High resolution XPS spectra of C1s (b), N 1s (c), O 1s (d), Na 1s (e) and Cl 1s (f) for GCN-Na-0.5.

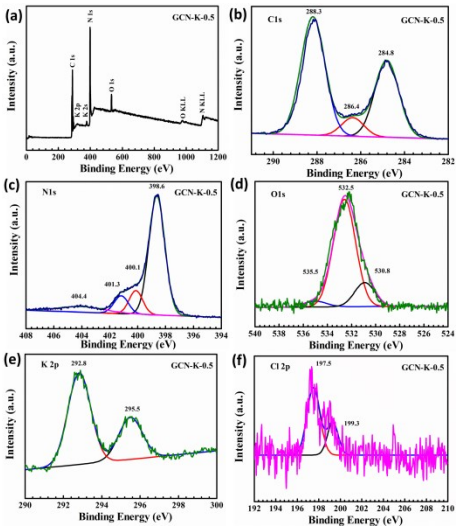


Fig. S5: XPS spectrum of GCN-K-0.5 (a). High resolution XPS spectra of C1s (b), N1s (c), O1s (d), K 2p (e) and Cl 1s (f) for GCN-K-0.5.

Table S2: Elemental composition according to EDS measurements.

| Sample | C/N(at.) | Na(at.%) | K(at.%) | O(at.%) |
|---|---|---|---|---|
| GCN | 0.659 | -- | -- | 2.85 |
| GCN-Na-0.5 | 0.670 | 2.46 | -- | 3.97 |
| GCN-Na-5 | 0.687 | 2.49 | -- | 5.75 |
| GCN-K-0.5 | 0.682 | -- | 2.47 | 4.58 |
| GCN-K-5 | 0.706 | -- | 3.01 | 5.76 |

Table S3: XPS elemental composition analysis.

| Sample | C 1s (at.%) | N 1s (at.%) | O 1s (at.%) | K 2p (at.%) | Na 1s (at.%) | Cl 2p (at.%) |
|---|---|---|---|---|---|---|
| GCN | 43.74 | 54.64 | 1.62 | -- | -- | -- |
| GCN-Na-0.5 | 49.65 | 45.69 | 2.86 | -- | 1.64 | 0.15 |
| GCN-Na-5 | 45.09 | 51 | 1.73 | -- | 2.08 | 0.1 |
| GCN-K-0.5 | 51.57 | 41.07 | 4.77 | 2.35 | -- | 0.1 |
| GCN-K-5 | 46.07 | 48.11 | 2.85 | 2.91 | -- | 0.06 |

Table S4: Elmental analysis data for each sample.

| Sample | C (wt.%) | N (wt.%) | H (wt.%) | C/N (mol ratio) | Average(mol ratio) |
|---|---|---|---|---|---|
| GCN | 34.45 | 60.92 | 1.85 | 0.653 | 0.657±0.005 |
| | 34.45 | 60.86 | 1.81 | 0.660 | |
| GCN-Na-0.5 | 31.91 | 55.38 | 1.62 | 0.672 | 0.673±0.001 |
| | 31.91 | 55.29 | 1.65 | 0.673 | |
| GCN-Na-5 | 30.13 | 51.52 | 1.90 | 0.683 | 0.683±0.000 |
| | 30.13 | 51.53 | 1.92 | 0.683 | |
| GCN-K-0.5 | 29.88 | 50.87 | 1.52 | 0.674 | 0.680±0.008 |
| | 29.86 | 50.79 | 1.45 | 0.686 | |
| GCN-K-5 | 28.70 | 48.18 | 1.66 | 0.695 | 0.695±0.000 |
| | 28.74 | 48.25 | 1.51 | 0.695 | |

Table S5: ICP-AES data for each sample.

| Sample | Number of Experiments | | | Na(wt.%) | K(wt.%) |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | | |
| GCN | | | | -- | -- |
| GCN-Na-0.5 | 4.48 | 4.54 | 3.62 | 4.21±0.515 | -- |
| GCN-Na-5 | 5.20 | 5.32 | 5.68 | 5.40±0.250 | -- |
| GCN-K-0.5 | 10.36 | 10.26 | 10.53 | | 10.38±0.137 |
| GCN-K-5 | 11.06 | 11.19 | 11.62 | | 11.29±0.293 |

Table S6: The derived band gap data for each sample.

| Sample | Bandgap(eV) | Average(eV) |
|---|---|---|
| GCN | 2.80<br>2.81<br>2.80 | 2.80±0 .007 |
| GCN-Na-0.5 | 2.75<br>2.77<br>2.75 | 2.76±0.012 |
| GCN-Na-5 | 2.79<br>2.82<br>2.80 | 2.80±0.016 |
| GCN-K-0.5 | 2.76<br>2.75<br>2.75 | 2.75±0.07 |
| GCN-K-5 | 2.78<br>2.77<br>2.78 | 2.78±0.07 |

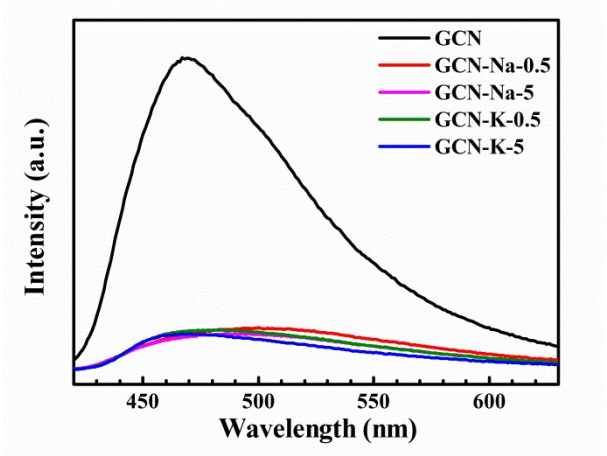


Fig. S6: Florescence spectra of GCN, GCN-Na-0.5, GCN-Na-5, GCN-K-0.5 and GCN-K-5. The excitation wavelength is 370 nm.

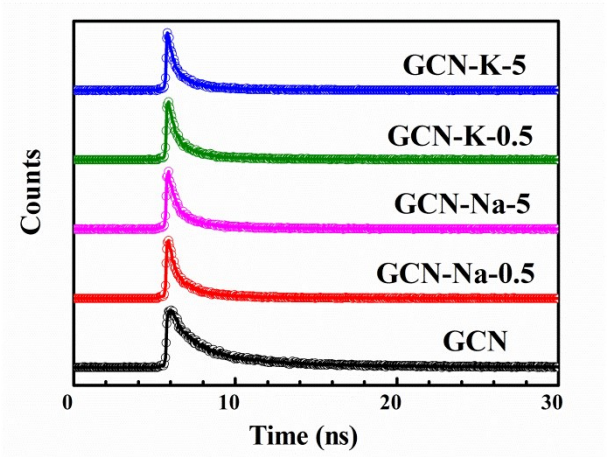


Fig. S7: Fluorescence decays of GCN, GCN-Na-0.5, GCN-Na-5 GCN-K-0.5 and GCN-K-5. Excitation wavelength, 375 nm; detection wavelength, 470 nm.

Table S7: The fitting parameters of fluorescence decay with bi-exponential function.

| $\lambda_{ex}$ (nm) | Sample | $a_1$ | $\tau_1$ (ns) | $a_2$ | $\tau_2$ (ns) | $<\tau>$ (ns) |
|---|---|---|---|---|---|---|
| 375 | GCN | 0.4485 | 1.5375 | 0.5515 | 6.6826 | 4.375 |
| | GCN-Na-0.5 | 0.5669 | 0.7653 | 0.4331 | 4.206 | 2.256 |
| | GCN-Na-5 | 0.5625 | 0.6929 | 0.4375 | 3.807 | 2.055 |
| | GCN-K-0.5 | 0.5565 | 0.6628 | 0.4435 | 3.504 | 1.923 |
| | GCN-K-5 | 0.5855 | 0.6345 | 0.4145 | 3.515 | 1.828 |

Table S8: Photocatalytic $H_2$ evolution rate for different samples.

| Sample | $H_2$ evolution $\lambda$>420 nm ($\mu molh^{-1}$) | Average $\lambda$ >420 nm($\mu molh^{-1}$) |
|---|---|---|
| GCN | 4.78<br>4.79<br>4.72 | 4.76±0.038 |
| GCN-Na-0.5 | 3.28<br>4.03<br>3.75 | 3.69±0.379 |
| GCN-Na-5 | 7.32<br>7.22<br>7.32 | 7.29±0.058 |
| GCN-K-0.5 | 10.6<br>9.75<br>10.3 | 10.2±0.432 |
| GCN-K-5 | 32.2<br>30.4<br>28.2 | 30.3±2.004 |