Nitrogen-mediated Wet-chemical Formation of Carbon Nitride/ZnO Heterojunctions for Enhanced Field-emission

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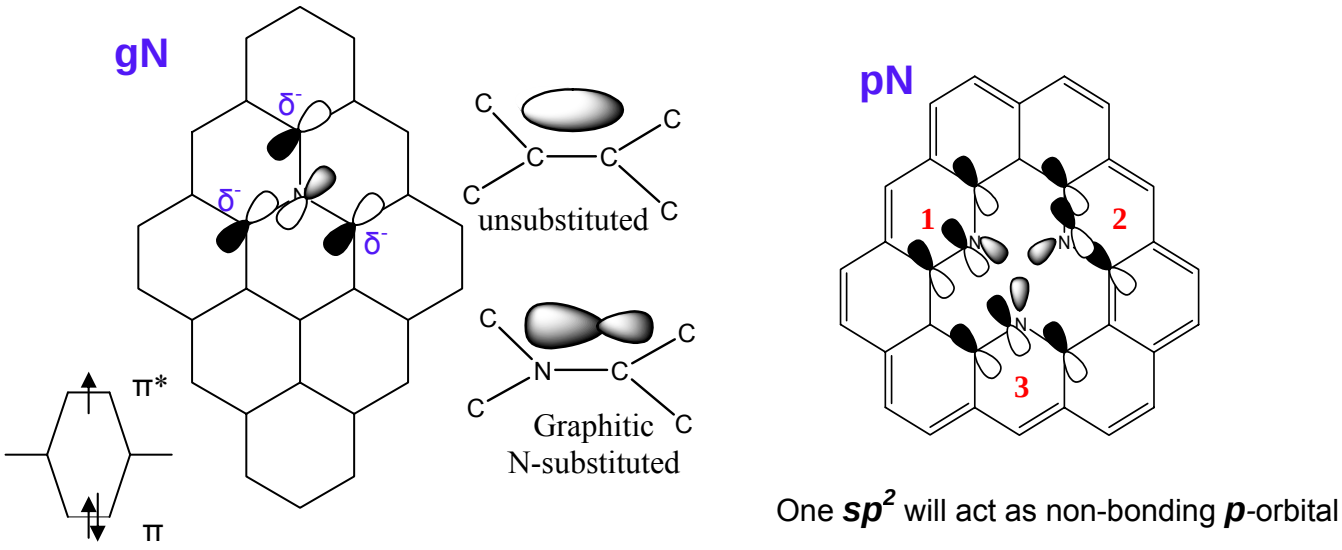
Supporting information



Bond order= ½ (N) +½ (C) - ½ (N) = ½

Figure S1. Pictorial representation of N-substituted graphitic (gN) and pyridinic (pN) functionalities present on the CNx surface. The polarized π-electron density towards more electronegative nitrogen atom of gN units and the non-bonding *p*-orbitals of pN units are prone to undergo strong *d-p* mixing with metal ions. Thus gN and pN behave as nucleation centers for the secondary metal oxide growth. It is believed that the pN substitution would give higher stability to the metal nanoparticle nucleation via chilate-complex formation.

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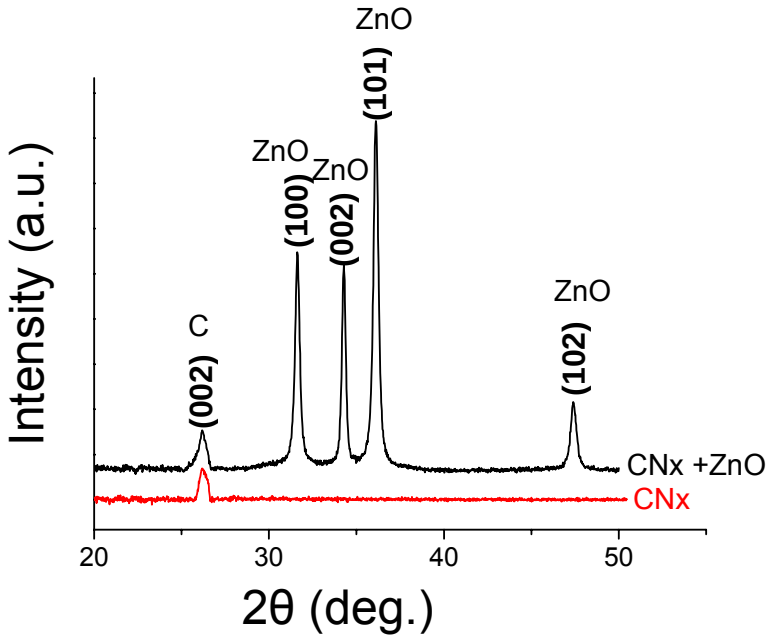

Figure S2. XRD spectra of bare CNx and CNx-ZnO hybrid.

The main intense peaks observed at $2\theta = 31.62^{\circ}$, 34.28° and 36.12° corrospond to the reflections from (100), (002) and (101) planes of ZnO. The lattice parameters were calculated to be $a_1 = 3.2647$ Å and $c_1 = 5.2276$ Å which are close to that of wurtzite ZnO (JCPDS, 36-1451). Almost same intensities of (100) and (002) planes, and slightly higher contribution from (101) plane suggest to the random orientation of ZnO crystals on the CNx surface. Moreover, we observed a distinct reflection at 26.18^{o} for both pristine CNx as well as CNx-ZnO hybrid, which refers to the reflection from wraped graphene planes (002) of CNx. As per Debye-Scherrer equation, avarage crystal size of ZnO was estimated to be 29 to 42 nm which is much smaller than what is seen in Figure 1e. So we believe that the XRD reflections are coming from individual ZnO petals rather than the whole flower.

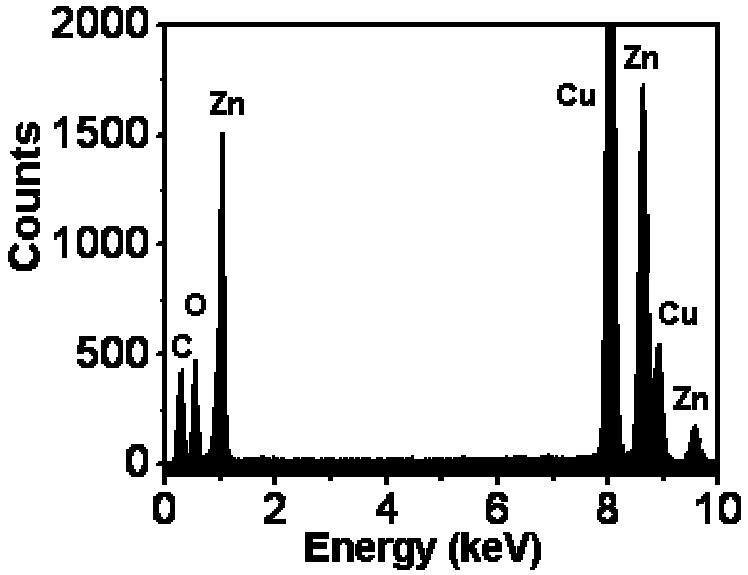

Figure S3. EDX spectrum of CNx-ZnO nanohybrid.

It is worth mentioning that EDX analysis of our sample with the electron beam focused at one of the CNx-ZnO heterojunction revealed nearly 45% atomic contribution of ZnO with respect to carbon. Moreover, the O/Zn ratio was calculated to be 0.85 which accounts for the oxygen vacancies in ZnO structure, and hence assigning an n-type character to ZnO.

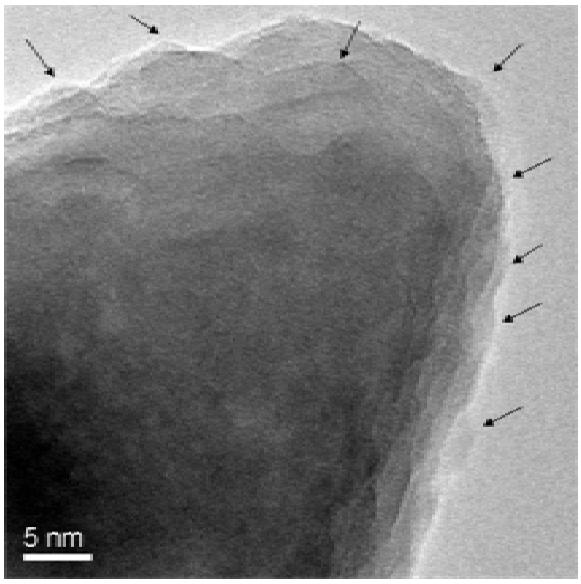

Figure S4. TEM image of the tip of a ZnO petal showing many pointed protrusions which act as effective emitters. Thus the emitter site density is quite high.

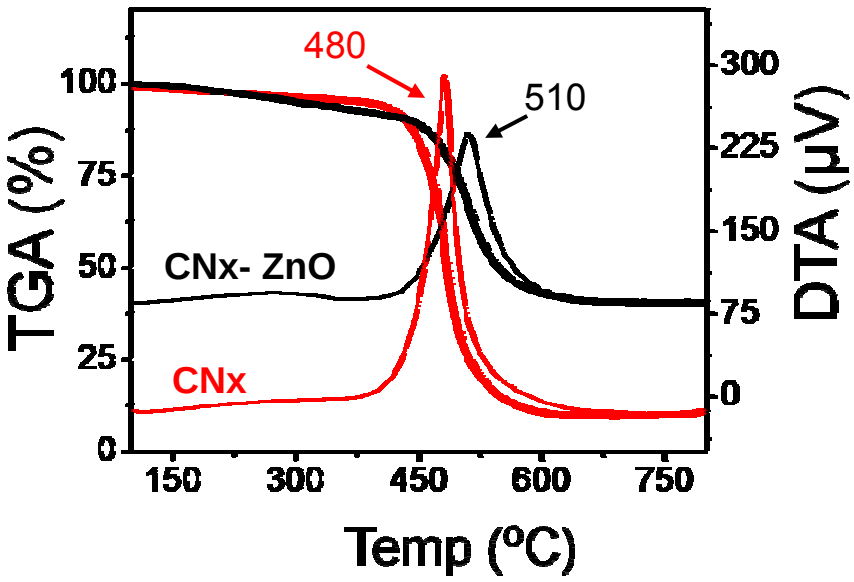

Figure S5. TG-DTA plots of bare CNx and CNx-ZnO heterostructure shows that ZnO nanohybrids improve the thermal stability of CNx matrix against arial oxidation.

The thermal stability of CNx and CNx-ZnO hybrid was tested by TGA. The oxidation of bare CNx starts at 480°C whereas that for the hybrid is 510°C, suggesting that the latter is thermally more stable. It is well known that the N-substituents on the CNTs matrix make it more susceptible towards arial oxidation [1-3]. This relevant possibility is modulated via such heterojunction formation, which implies that the ZnO readily protect the CNx defective sides from oxygen attack via direct chemical bonding with gN and pN functionalities [4-6]. The TGA plot (thick line) suggests an existence of ~40% ZnO in the hybrid system.

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