

Supplementary Information

Formation of reusable Au-acetonitrile polymers and N-doped graphene catalyst under UV light via submerged liquid plasma process

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Formation of NPs under submerged liquid plasma condition

In the beginning of the experiment, the tungsten needle and Si electrode distance was adjusted to get the maximum plasma width. When the tungsten needle touched the silicon electrode, there was no plasma observed in the solution. The plasma torch width of 77, 141 and 213 μm were observed for the distances of 32, 78 and 100 μm , respectively. Beyond 100 μm , there was no plasma formed in the solution and this may be due to the poor conductivity of pure acetonitrile. Hence, ~ 100 μm electrode distance was maintained for all the experiments. The colorless acetonitrile solution turns pale yellow and then become light brown at the end of the reaction. The plasma submerged in acetonitrile initiates hydrogen detachment in the first step and forms highly reactive free radical monomer ($\cdot\text{CH}_2\text{—C}\equiv\text{N}$) due to the low bond energy of C—H (413 kJ/mol) compared to C \equiv N (891 kJ/mol). Compound containing nitrile group are stable towards electron attack due to high stability of C—CN bond and are in favor of plasma polymerization rather than fragmentation.

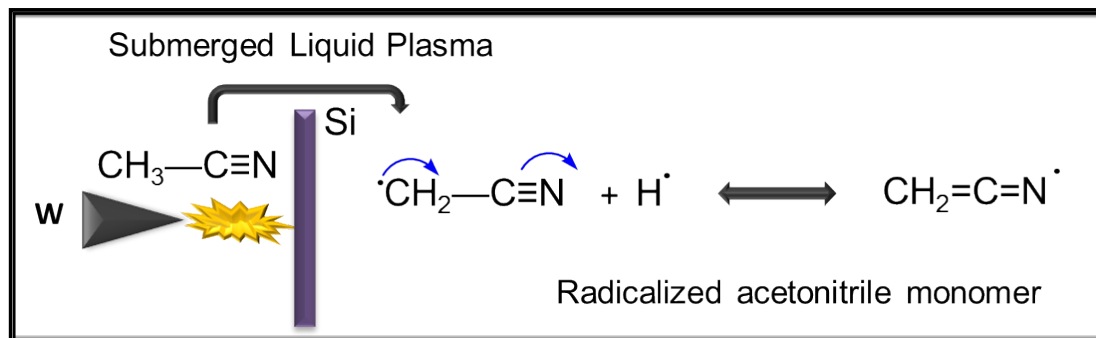


Figure 1: Formation of radical monomer under submerged liquid plasma condition

Formation NFG under submerged liquid plasma condition

When a high potential difference is applied across the graphite and platinum electrodes in acetonitrile solution, micro-plasma discharge occurs at the interface and leads to the flow of electrons between the electrodes. The micro-plasma discharge forms radicalized graphene sheets, which are exfoliated in the acetonitrile solvent instantly. The non-polar acetonitrile has no affinity towards radicalized carbon and prevents agglomeration, forming stable dispersion. The free electrons generated during micro-plasma discharge collide with acetonitrile and initiate hydrogen detachment, which results in highly reactive free radical monomers ($\cdot\text{H}$ and $\cdot\text{CH}_2\text{-C}\equiv\text{N}$). The nitrile group resists electron attack due to the high stability of $\text{-C}\equiv\text{N}$ (891 kJ/mol) bond. The C-H (413 kJ/mol) bond present in acetonitrile is more vulnerable to electron attack due to its lower bond energy compared to that of $\text{-C}\equiv\text{N}$. Highly reactive nascent $\cdot\text{H}$ effectively reacts with radicalized graphene and partially restores the sp^2 network. Similarly, the $\cdot\text{CH}_2\text{-C}\equiv\text{N}$ radical reacts with the radicalized graphene layer and forms pyridinic and pyrrolic nitrogen. The pyridinic (-N=CH-) and pyrrolic (-NH) nitrogen act as intermittent terminal groups and cause marginal disorderness in the sp^2 carbon network.

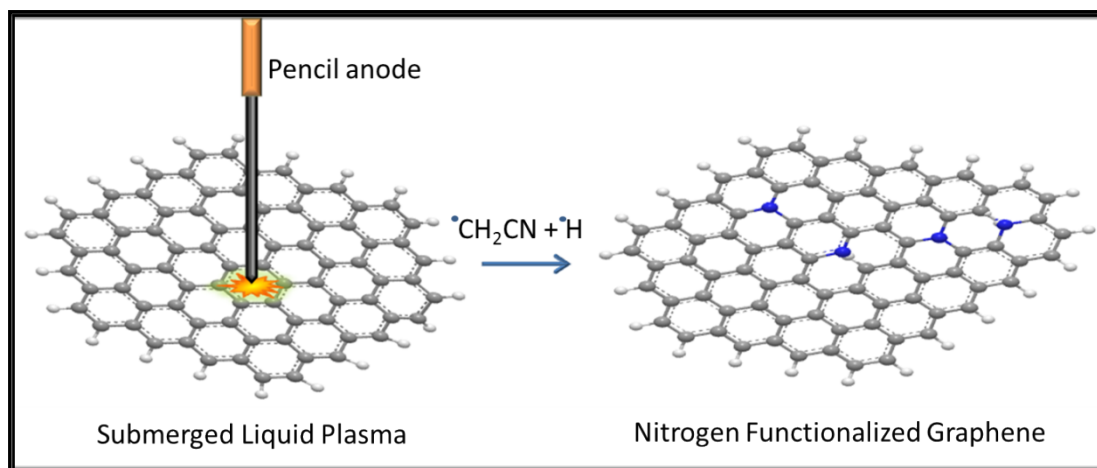


Figure 2: Formation of nitrogen functionalized graphene under submerged liquid plasma condition

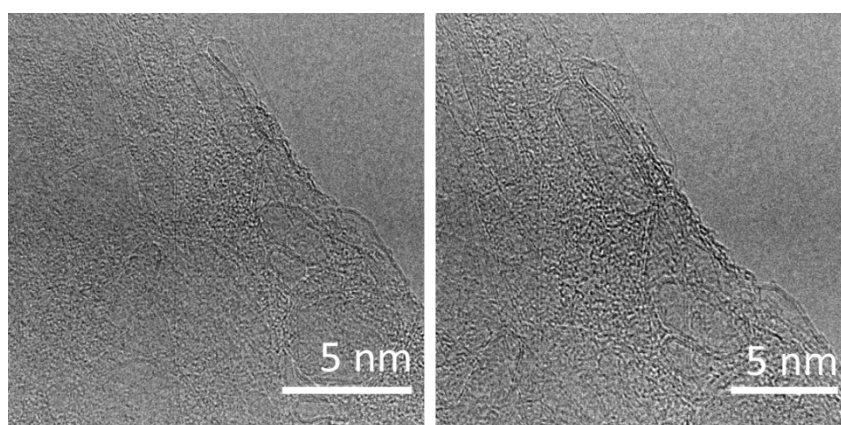


Figure 3: HR-TEM image of nitrogen functionalized graphene

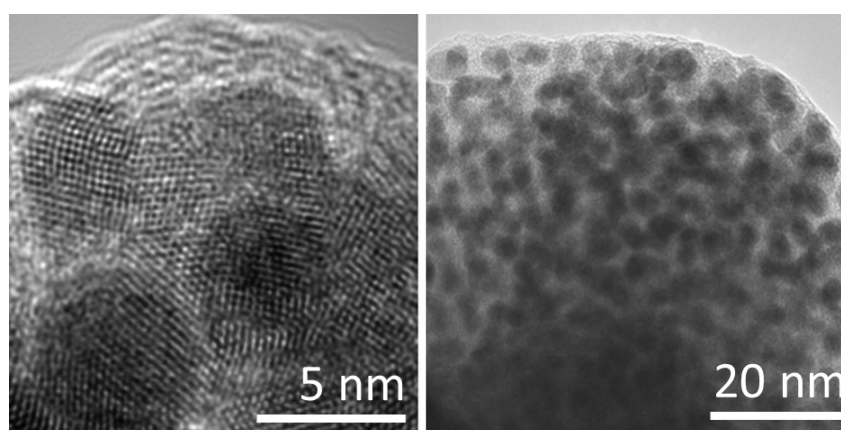


Figure 4: HR-TEM image of Au-NPs-NFG

Table 1: Daughter peaks are identified in LC/MS/MS analysis

| S. No | LC/MS/MS ANPs | Molecular mass $m/z(m+1)$ | Daughter peaks $m/z(m+1)$ |
|--------------|--|---|---|
| 1 | 1,4,7,9,13-Pentaaza-11-carbonitrile anthracene | 211 | 172, 162, 145, 122, 104, 81, 65 |
| 2 | 1,4,7,9,13-Pentaaza-anthracene | 186 | 172, 162, 145, 122, 104, 81, 65 |
| 3 | Pyrazine-2-carbonitrile | 106 | 80, 68, 56, 42 |
| 4 | 2,4-Dihydro-pyrazine | 83 | 68, 56, 42 |
| 5 | Pyrazine | 81 | 66, 54, 41 |