

Poly(n-vinylpyrrolidone-co-acrylonitrile-co-methacrylic acid)-graphene quantum dot conjugate: Synthesis, structural and electrical characterization for sensing ammonia vapour

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ELECTRONIC SUPPLEMENTARY INFORMATION

S1. UV-Visible spectroscopy of Graphene Oxide and Reduced Graphene Oxide

Graphene oxide (GO) shows a distinct absorption peak at 228 nm, which corresponds to π to π^* transition. After the complete reduction of GO by the ethanolic extract of *Elaeocarpus serratus*, a peak is observed at 265 nm. The redshift indicates the complete reduction of GO forming the reduced graphene oxide (rGO) and restoration of the electronic conjugation of graphene sheets. The UV-visible spectra of GO and rGO is shown in figure S1.

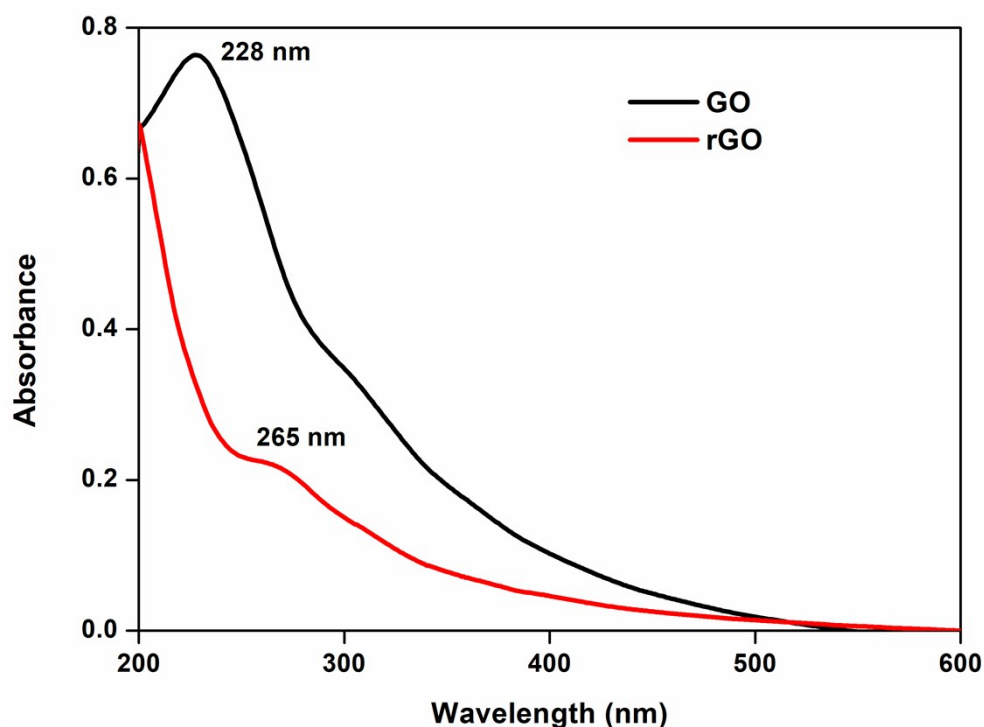


Figure S1. UV-Visible spectra of graphene oxide and reduced graphene oxide

S2. Zeta potential of Graphene Quantum dot

The DLS zeta potential of graphene quantum dot (GQD) was found to -5.8 mV, as shown in figure S2. The negative surface of GQD can be predicted due to the presence of electron-rich oxygen-containing moieties and the overfall electronic conjugation of the graphene fragments.

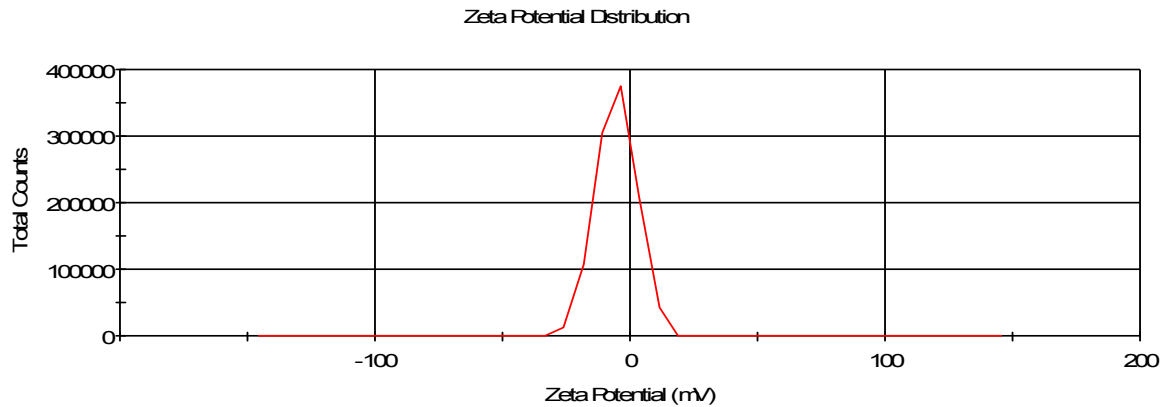


Figure S2. Zeta potential measurement of GQD

S3. Effect of humidity

The impedance (Z) values of the sensor with respect to time was observed at varying humidity conditions, ranging from 20 % to 80 % humidity, as shown in figure S3. It was observed that at different humidity conditions, the $\log Z$ values of the sensor did not change, thus making it a suitable sensing material.

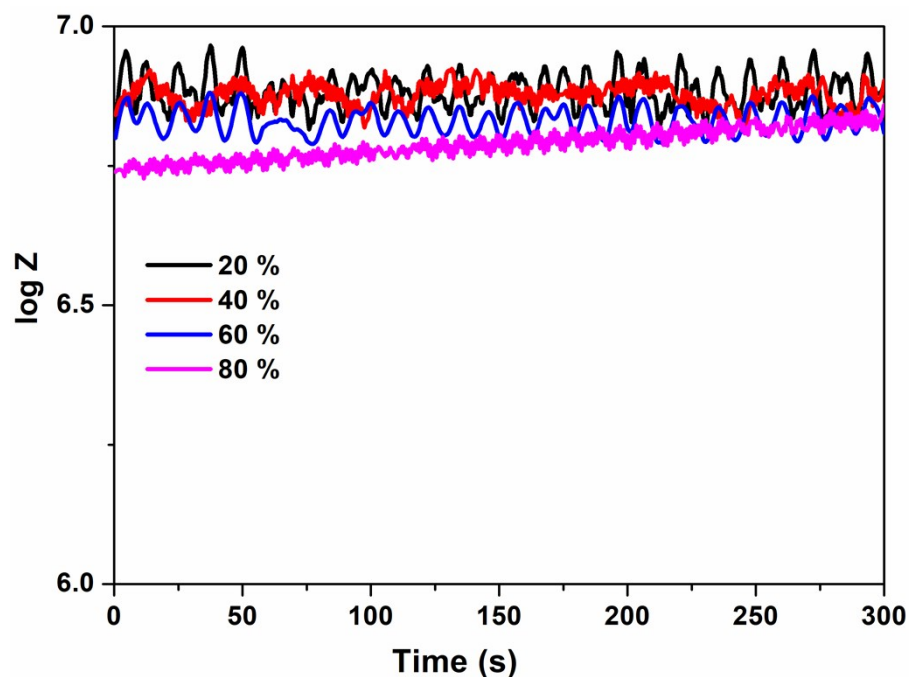


Figure S3. Effect of humidity on the impedance response of the sensor

S4. Reversibility cycles of the sensor

The sensor, P(VP-Acn-MA)-GQD was found to be reversible in nature, which enables multiple and repeated use of our sensor system. The logZ values of the sensor was found to be restored immediately after the removal of its contact with the ammonia vapours. The reversibility of the same detector was investigated in five different cycles, and it was observed that the sensor is reversible in nature and could be used in repeated sensing experiments. In addition to the reversibility plot presented in figure 7(B) for cycle 1, four more reversibility plots were taken, as presented in figure S4 (cycle 2-5).

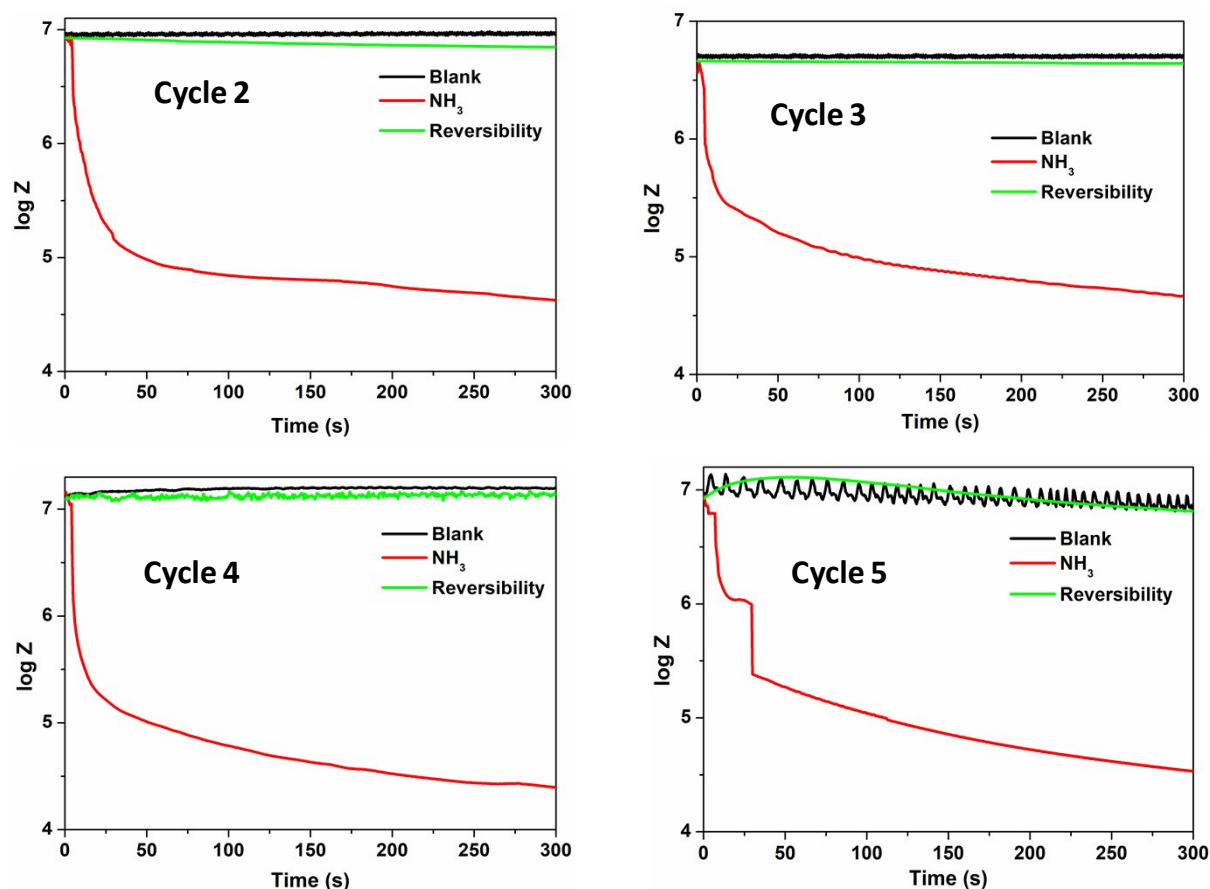


Figure S4. Reversibility plots of the sensor in different cycles

S5. Behaviour P(VP-Acn-MA)-GQD towards the vapours of other amines

The logZ value of the sensor, P(VP-Acn-MA)-GQD was observed in presence of other derivatives of ammonia, such as methylamine, ethylene diamine (EDA) and triethyl amine (TEA) as shown in figure S5. A very small decrease in the logZ values of methylamine and EDA was observed, which is negligible when compared to the value obtained in case of

ammonia vapour. No change in the logZ value of P(VP-Acn-MA)-GQD was observed in presence of the tertiary amine, TEA.

The electronegativity differences of the N and H leads to the polar nature of the N-H bond in amines, which results in the formation of H-bonds with other H-bonding systems. H-bonding in amines depends on the number of hydrogens attached to the nitrogen atom. Ammonia, primary amines and secondary amines (up to a certain extent) form intermolecular H-bonding. Tertiary amines do not show intermolecular H-bonding, due to the unavailability of H atoms attached to the central N atom¹. Moreover, with increase in the +I effect on N atom, the basic character predominates, which in turn leads to the lesser availability of protons for intermolecular H-bonding.

The intermolecular H-bonding of P(VP-Acn-MA)-GQD with ammonia is maximum, followed by methylamine, and EDA. The tertiary amine, TEA shows no intermolecular H-bonding with the P(VP-Acn-MA)-GQD. The H-bonding with P(VP-Acn-MA)-GQD causes the selective and reversible detection of ammonia vapour. The result is in agreement with the electrical measurements, where the maximum decrease in logZ values was observed for ammonia vapour only.

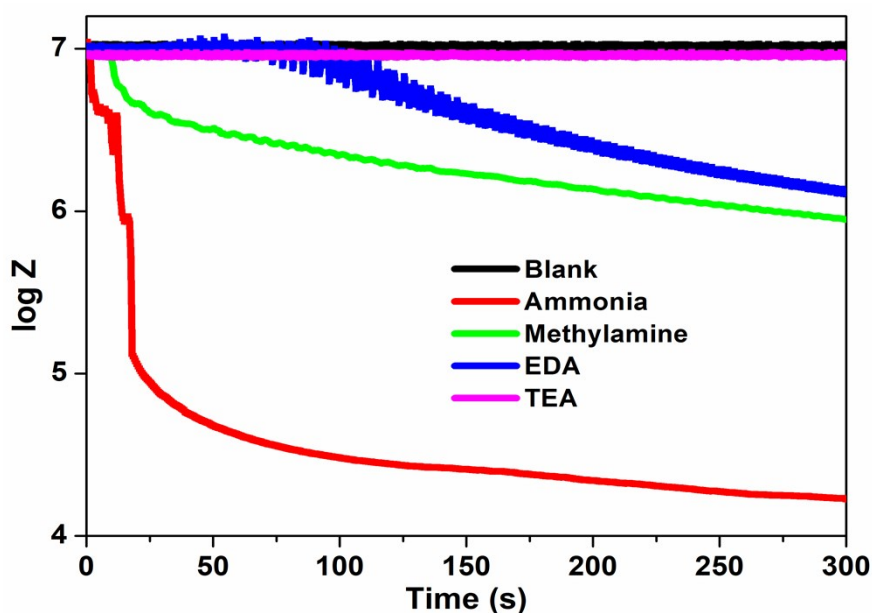


Figure S5. logZ vs time values of P(VP-Acn-MA)-GQD in presence of different ammonia derivatives

S6. FT-IR spectra of polymer composite before and after sensing ammonia vapour

The FT-IR spectra of the polymer conjugate, P(VP-Acn-MA)-GQD were recorded before and after sensing of ammonia vapour, as shown in figure S6. No significant change in the FT-IR

spectra of P(VP-Acn-MA)-GQD was observed after sensing. This suggests that the interaction between the polymer conjugate and the ammonia vapour is of reversible physisorption.

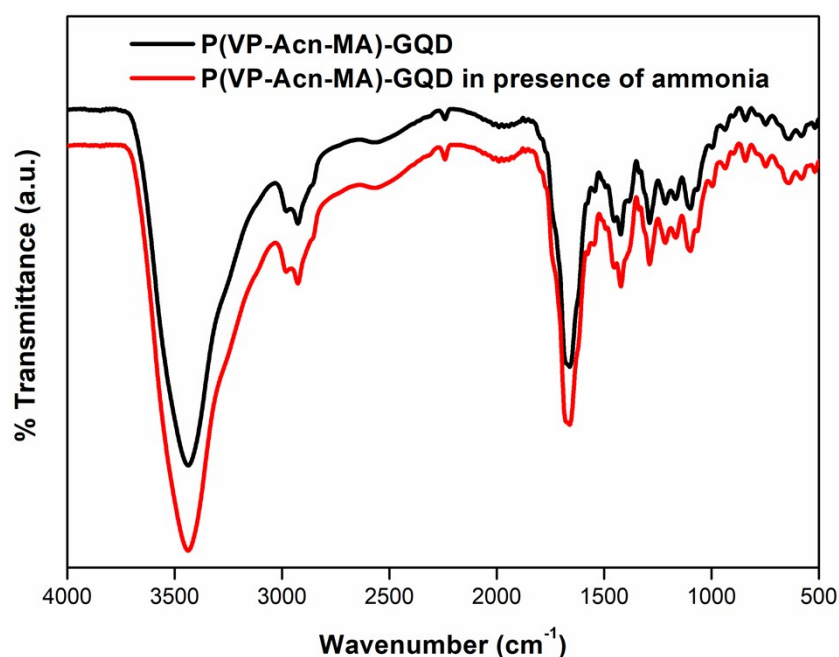


Figure S6. FT-IR spectra of P(VP-Acn-MA)-GQD before and after sensing ammonia vapour

S7. FESEM analysis of P(VP-Acn-MA)-GQD before and after sensing ammonia

The FESEM images of the polymer composite were obtained before and after contact with ammonia vapour, as depicted in figure S7. No significant change in the surface morphology was observed after contact with ammonia, thus confirming the reversible physisorption of ammonia on the surface of the P(VP-Acn-MA)-GQD.

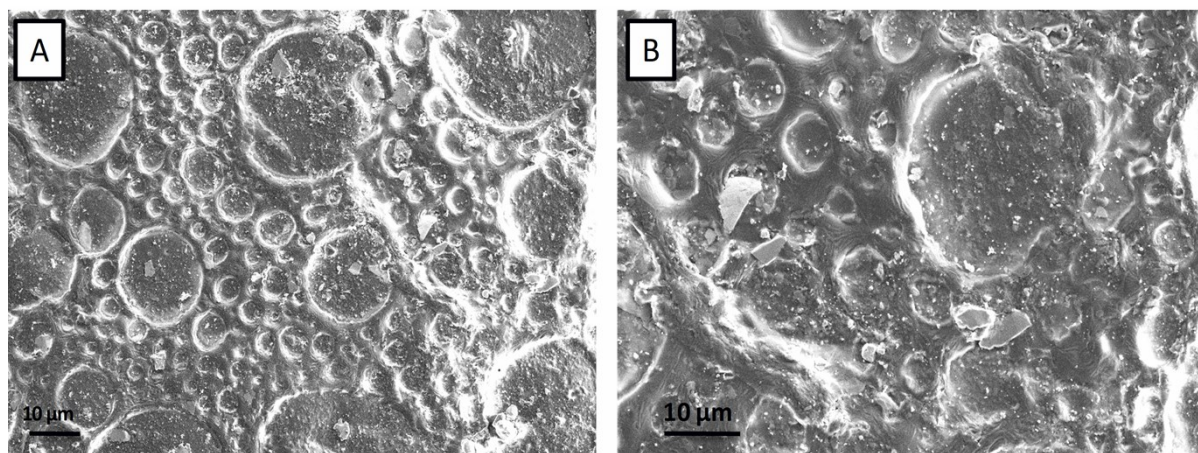


Figure S7. FESEM images of P(VP-Acn-MA)-GQD before (A) and after (B) sensing ammonia

S8. Transport number of P(VP-Acn-MA)-GQD before and after sensing ammonia

The current vs. time plot of the P(VP-Acn-MA)-GQD was obtained before and after sensing ammonia vapour, as shown in figure S8. The percentage of ionic characteristics of P(VP-Acn-MA)-GQD was found to be intact and was not changed on interaction with the ammonia vapour. The study signifies that no chemical interaction of ammonia takes place with P(VP-Acn-MA)-GQD, thus causing no change in the ionic characteristics. This study further confirms the weak reversible physisorption between the sensor and the ammonia vapour, as suggested by FT-IR and FESEM.

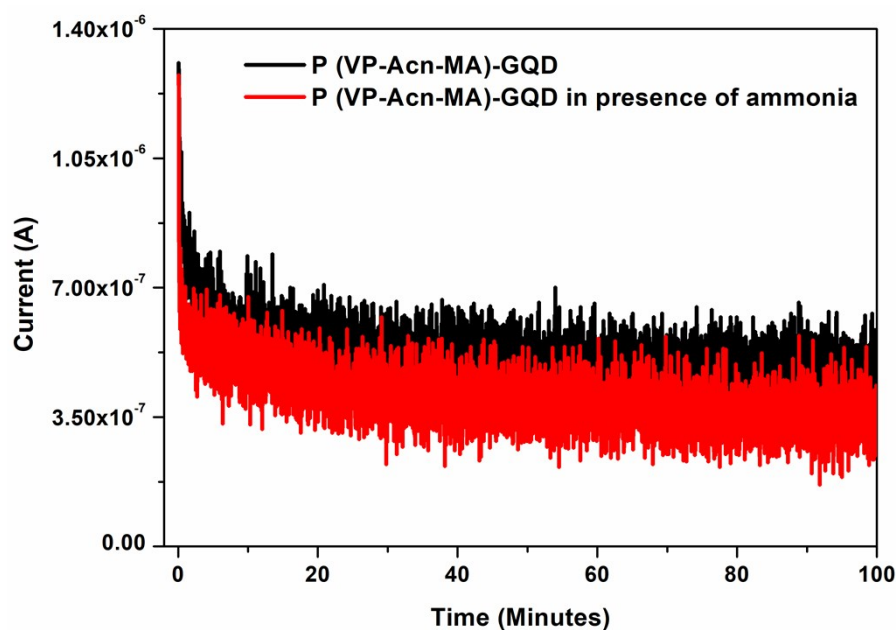


Figure S8. The current versus time plot of P(VP-Acn-MA)-GQD before and after sensing ammonia

References

1. R. J. Ouellette and J. D. Rawn, *Organic chemistry: structure, mechanism, and synthesis*: Elsevier, Chapter-23, 1, 2014, 803-842.