Electronic Supplementary Information (ESI)

Solar-Powered CO_2 Marvel: Ultrahigh Graphene Quantum Dots Covalently Coupled PhS Unleash Photocatalytic Magic for Valuable Chemical Transformation

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1. Chronoamperometry

The photocurrent generate by the GQDCCPhS photocatalyst is 18μA whereas of GQDs is 16 μA. Thus, this shows the higher current carrying of the GQDCCPhS photocatalyst as compare to the GQDs as shown in figure S3.

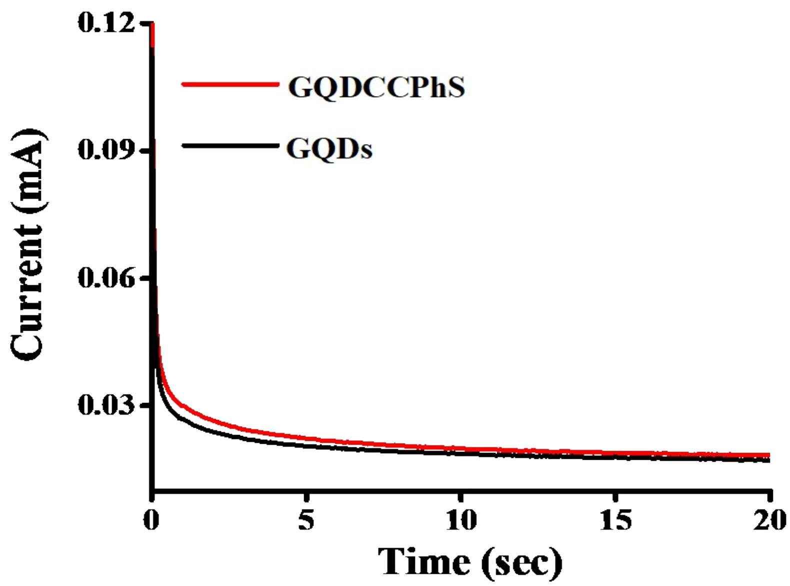


Figure S3: Chronoamperometry of GQDCCPhS and GQDs.

2. Zeta potential

The value of zeta potential of GQDs and GQDCCPhS were calculated to be -9.72mV and -13.2 mV respectively, which shown in figure S4 (a) and S4 (b) respectively. In comparison between GQDs and GQDCCPhS photocatalyst, more negative zeta potential value is shown by GQDCCPhS photocatalyst which confirms the stability of GQDCCPhS photocatalyst. GQDs and PhS are covalently connected through amide bond. The greater chemical stability of the GQDCCPhS photocatalyst is due to the presence of amide bond[1].

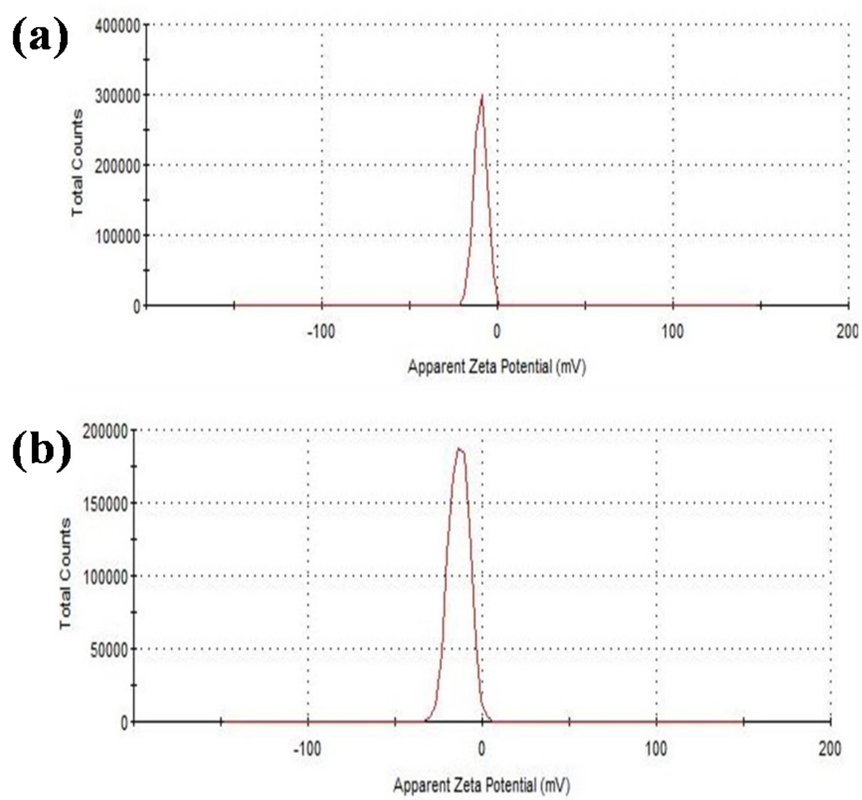


Figure S4: (a) Zeta potential of GQDs and **(b**) Zeta potential of GQDCCPhS.

3. Particle size

The analysis of particle size shows the excellent catalytic action of GQDCCPhS photocatalyst for 1,4-NADH regeneration and formic acid production as shown in figure S5 (a) and S5 (b). The particle size of GQDCCPhS photocatalyst is smaller is due to the formation of amide bond between GQDs and PhS[2]. Smaller the size of GQDCCPhS photocatalyst higher the charge transfer rate during 1,4-NADH regeneration and formic acid production[3].

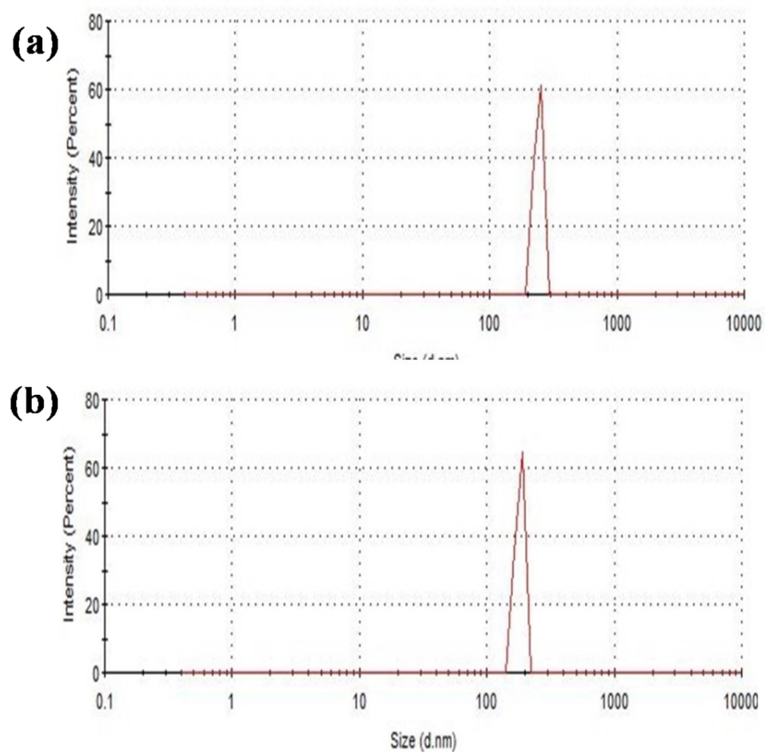


Figure S5: (a) Partical size of GQDs and **(b)** Particle size GQDCCPhS.

4. DSC Studies

Firstly, the exothermic peaks were showed in DSC at 90 to 110^{0}C temperature ranges. The one peak corresponding to adsorbed water physically near about at 100^{0}C in both cases (figure S6).Secondly, the exothermic peak showed a rapid weight loss may be at more than 350^{0}C reaching a maximum at 300^{0}C for GQDs photocatalyst and more than 350^{0}C for GQDCCPhS photocatalyst. It means, the second weight loss of GQDs photocatalyst sorbent took place at lesser temperature than the corresponding weight loss of GQDCCPhS photocatalyst exhibiting that of GQDs photocatalyst has poor stability than GQDCCPhS photocatalyst due to the formation of new amide bond in between GQD and PhS.[4]

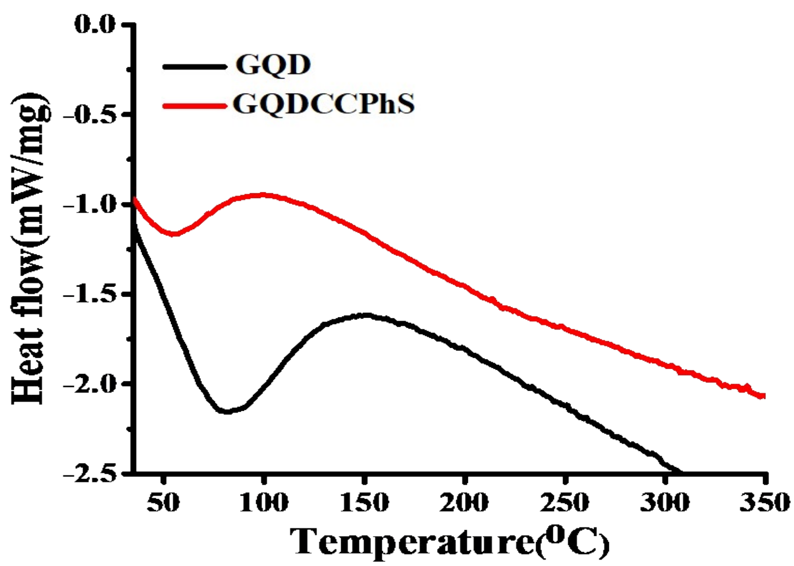


Figure S6: Differential scanning calorimetry (DSC) of the GQDs and GQDCCPhS.

5. Cyclic Voltammetry

The oxidation and reduction potential of the GQDCCPhS photocatalyst are estimated by cyclic voltammetry (FigureS7a). However, the reduction and oxidation potential of the GQDCCPhS photocatalyst are -0.86 V and +1.16 V respectively. The band gap of GQDCCPhS photocatalyst is calculated by using obtained redox potential via Latimer diagram i.e. 2.02 eV in Figure S7 (b).

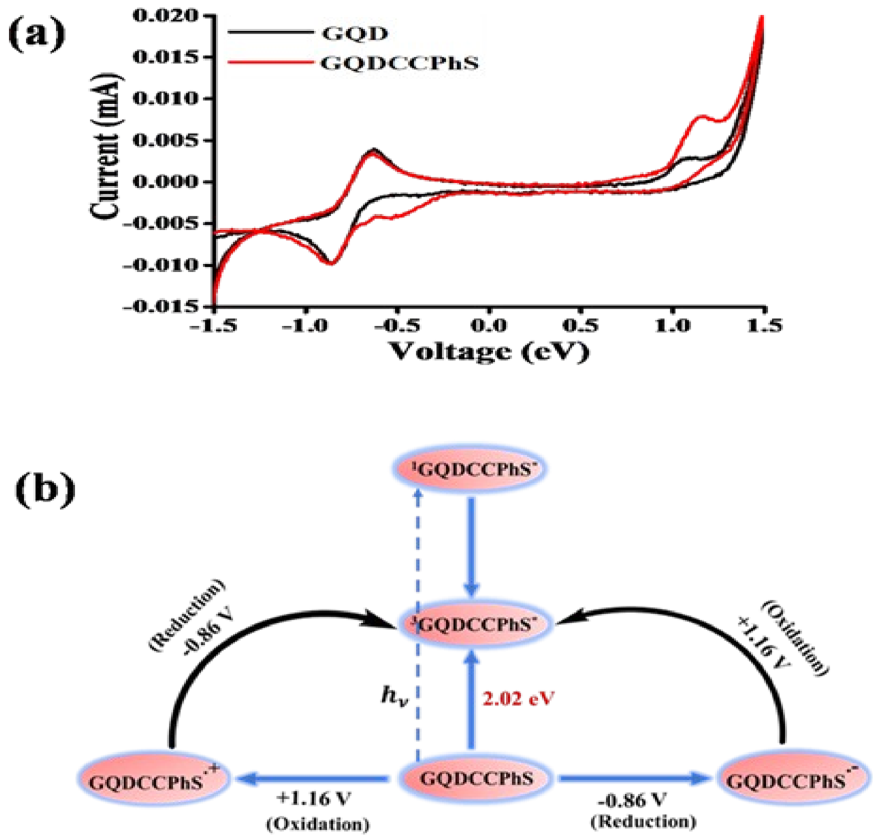


Figure S7: (a) Cyclic Voltammetry of GQD and GQDCCPhS photocatalyst (b) Latimer diagram of GQDCCPhS photocatalyst.

6. High Resolution Transmission Electron Microscopy (HR-TEM)

The high resolution transmission electron microscopy (HR-TEM) image of GQDCCPhS photocatalyst is shown in the figure S8. The size of the quantum dots exhibited size of 4.34nm while the HR-TEM of GQDCCPhS photocatalyst shows the increment of size to 50nm. However, the size of the quantum dots (GQD) remain as it is and shows the hazy appearance which implies that phenosafranine dye are stack over GQD shows the bonding of the dye with GQD resulting in the formation of GQDCCPhS photocatalyst i.e. the surface morphology of GQD changes after phenosafranine stacking.[5]

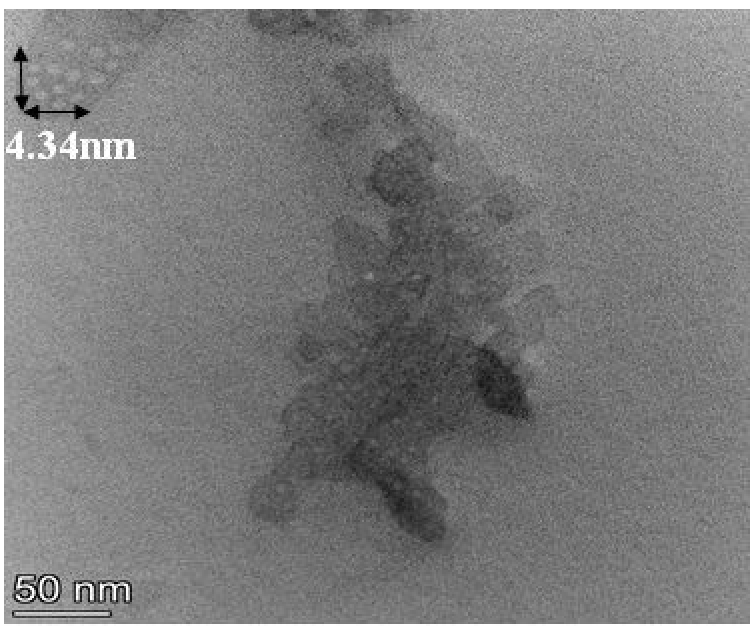
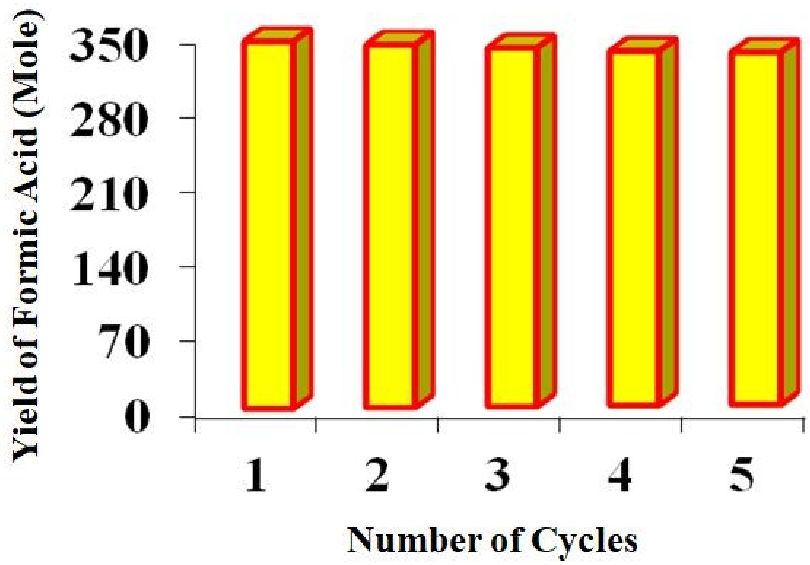


Figure S8: High Resolution Transmission Electron Microscopy (HR-TEM) of GQDCCPhS photocatalyst.

7. Cyclic Reusability Experiments

Different cyclic reusability experiments are performed for regeneration of NADH and production of formic acid. (Figure S9)



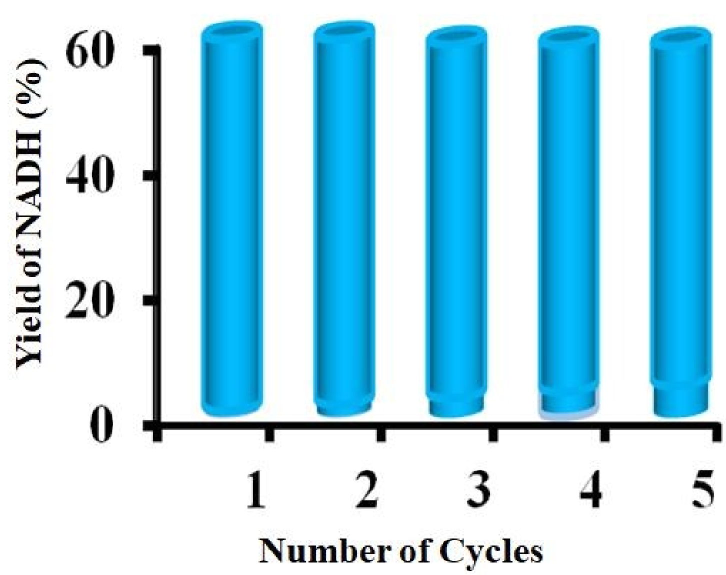


Figure S9: Cyclic experiments via GQDCCPhS photocatalyst.

References

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