

# Effect of nitrogen doping on hydrogen storage capacity of palladium decorated graphene

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## SUPPORTING INFORMATION

### 1. Raman spectra of graphite and Pd-HEG

The Figure S1 shows Raman spectrum of graphite powder (Gr) and Pd-HEG mechanically mixed mixture. The positions of D-band around  $1350\text{ cm}^{-1}$  and G-band around  $1576\text{ cm}^{-1}$  have been indicated.

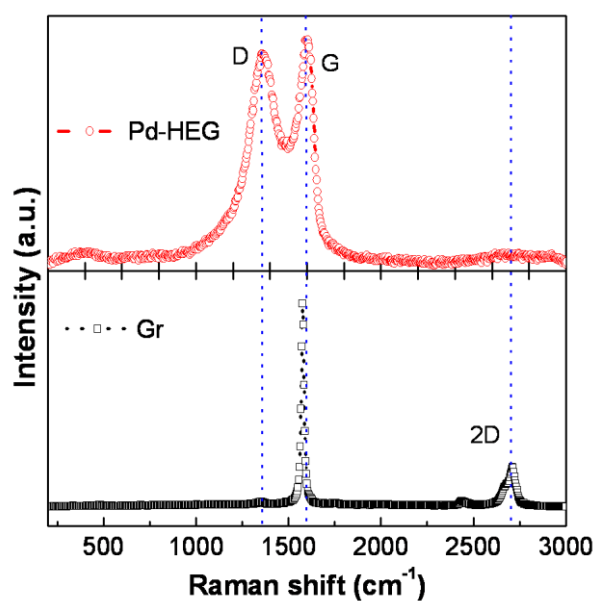


Figure S1(a). Raman spectra of graphite and Pd-HEG mixture.

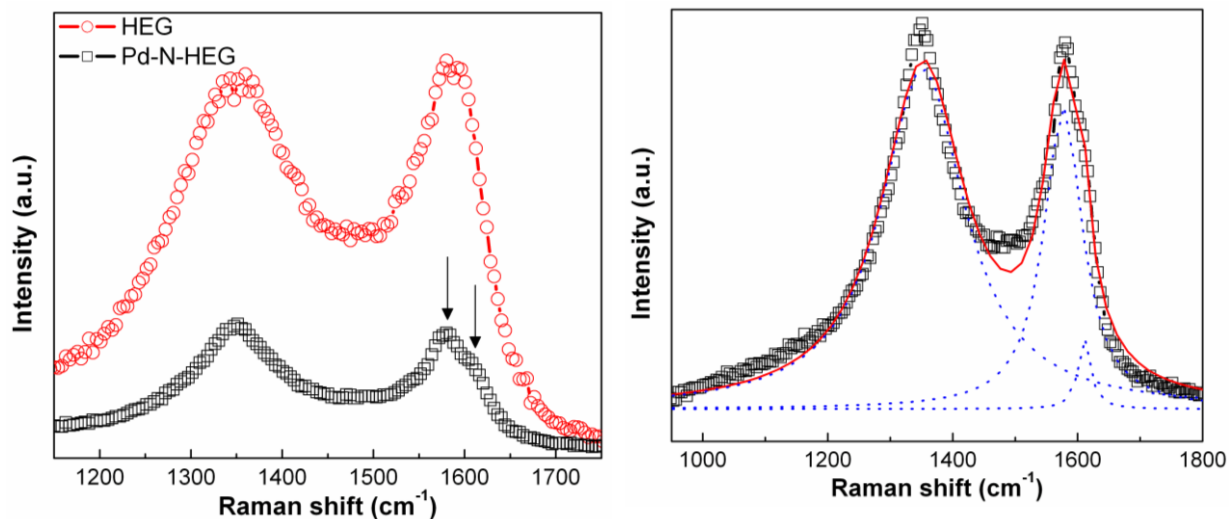


Figure S1(b): The magnified view of the Raman spectra of Pd-N-HEG sample.

## 2. XRD diffractogram of Pd-HEG

Figure S2 shows the X-ray diffractogram of Pd-HEG sample which indicates the fcc structure of the Pd particles. The crystallite size as estimated from Scherrer's formula was determined to be about 8.2 nm.

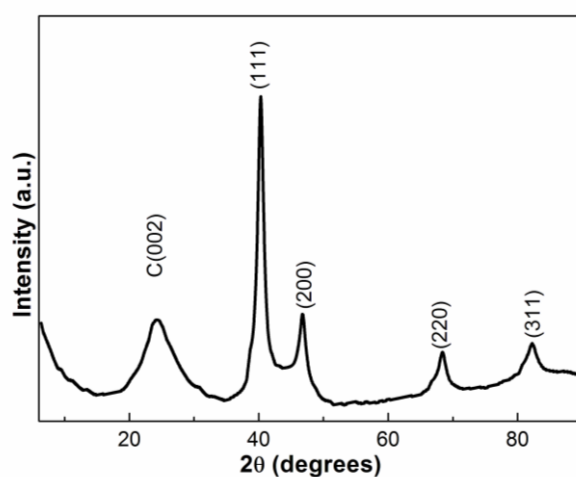


Figure S2. X-Ray diffractogram of Pd-HEG sample shows the Pd peaks along with the graphitic (002) plane originating from graphene.

### 3. TEM micrographs of HEG and Pd-HEG

Figure S3 shows the transmission electron micrographs of (a) HEG and (b) Pd-HEG mixture. The graphene sheets with a wrinkled morphology can be seen clearly post-exfoliation process. In case of Pd-HEG mixture the agglomerated Pd nanoparticles dispersed on graphene sheets can be seen. The dispersion of the agglomerates is also not uniform.

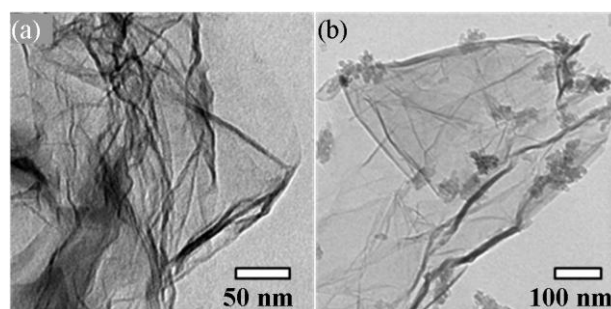


Figure S3. Transmission electron micrographs of (a) HEG and (b) Pd-HEG showing Pd particles agglomerated on graphene sheets.

### 4. EDX spectrum of Pd-N-HEG

The presence of Pd nanoparticles was also confirmed by energy dispersive X-ray analysis as shown in Figure S4 below.

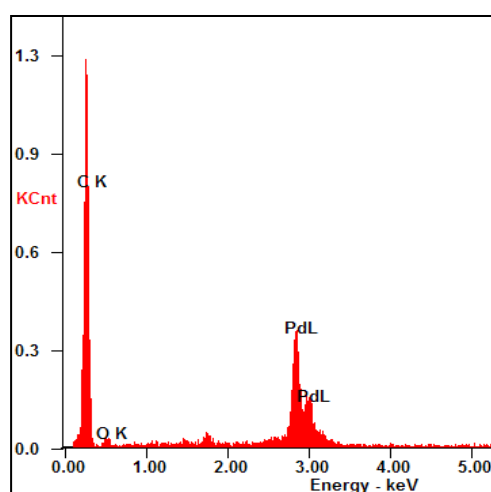


Figure S4. Energy dispersive X-ray spectrum of Pd-N-HEG sample acquired during SEM investigation.

## 5. Pressure-composition isotherms of HEG and Pd-HEG acquired in a high pressure Sievert's apparatus

The pressure-composition isotherms for HEG and Pd-HEG samples are shown in Figure S5.

A systematic increase in the hydrogen uptake capacity can be attained.

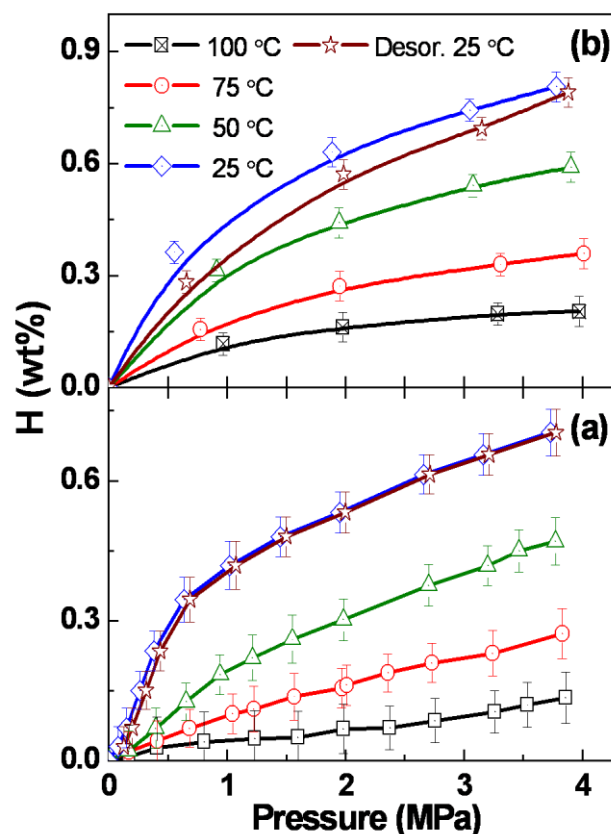


Figure S5. Pressure-composition isotherms of (a) HEG and (b) Pd-HEG nanocomposite in the 25-100 °C temperature range and 0.1-4 MPa pressure range.

Table S1. The weight percentage of hydrogen stored by different specimens at 25 °C temperature and 2 MPa, 4 MPa pressures.

Specimen	Hydrogen uptake capacity (%) at 25 °C	
	2 MPa	4 MPa
HEG	0.53	0.70
Pd-HEG Mixture	0.63	0.81
N-HEG	0.88	1.47
Pd-functionalized graphene <sup>S1</sup>	1.76	2.99
Pd-N-HEG	1.97	4.40

## 6. Interaction of hydrogen on graphene and nitrogen doped graphene with Pd

This paragraph briefly discusses the results of density functional theory calculations performed by Corral et al., which is pertinent to the present work and helps in better understanding the interactions during hydrogenation of Pd-graphene system by theoretical calculations.<sup>S2</sup> First, the interaction between Pd-graphene is discussed. It was reported that when Pd is decorated on graphene, the neighboring carbon atoms experience a decrease in the electron occupation of  $2p_z$  orbital while an increase was registered for C  $2s$  orbital. Thus, the C  $2p_z$  participate more in the Pd-graphene interaction. In the presence of atomic hydrogen, a strong Pd-H bond forms where the occupation of Pd  $5s$ ,  $5p$ , and  $4d_{z^2}$  increases indicating the interaction of these orbitals with the H  $1s$  orbital. In the presence of nitrogen-doped graphene investigated in the present work, the interaction between the Pd-C is anticipated to be stronger due to the higher  $\pi$ -electron density donated by nitrogen atoms. Also, the formation of N-H bonds during hydrogenation aid in increasing the hydrogen uptake capacity by the Pd-N-HEG as discussed in light of other theoretical studies in the main paper.

## REFERENCES

- S1. Vinayan, B. P.; Nagar, R.; Sethupathi, K.; Ramaprabhu, S., *J. Phys. Chem. C* **2011**, *115*, 15679-15685.
- S2. López-Corral, I.; Germán, E.; Juan, A.; Volpe, M. A.; Brizuela, G. P., *J. Phys. Chem. C* **2011**, *115*, 4315-4323.