

Supporting information

Morphology Controlled Graphene-Alloy Nanoparticles Hybrids with Tunable carbon monoxide conversion to carbon dioxide

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1. *Elemental and Compositional Analysis*

The elemental mapping of the G-PdPt (No PVP) and G-PdPt (with PVP) hybrid nanoparticles, having nanoflower and urchin morphologies, was carried out and shown in figure S1 (b and c) and figure S1 (e and f) respectively. In case of nanoflowers, Pt and Pd are uniformly distributed over the nanoflowers. On the other hand, Pt atoms are observed to be distributed over the peripheral region of each branch of urchin nanoparticles, whereas Pd atoms have been found to be predominantly present at the centre. Thus, the studies confirm the formation of two different types of nanoparticles decorated on the graphene surface.

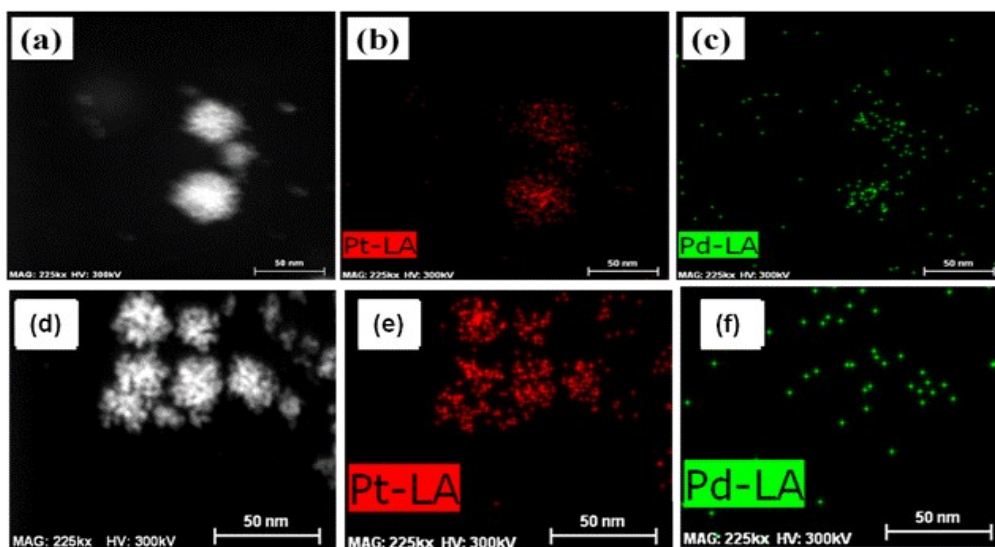
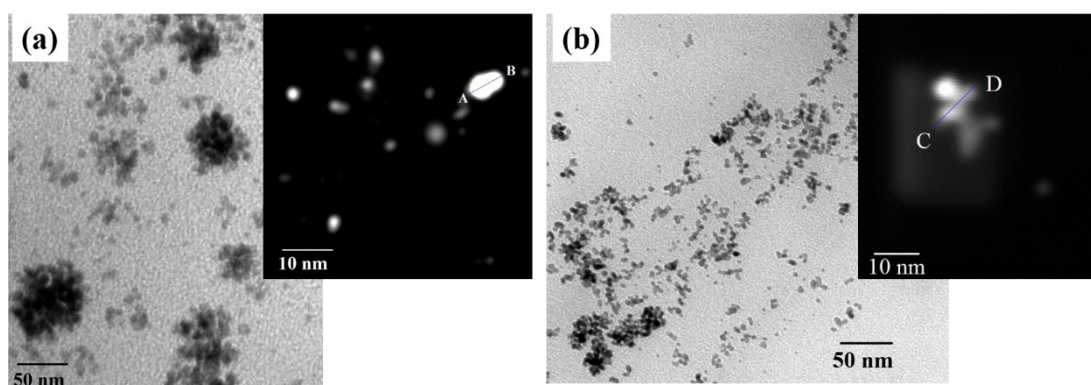


Figure S1: HAADF images and corresponding EDS mapping of nanoflowers G-PdPt (No PVP) (a-c) and urchin G-PdPt (with PVP) (d-f).

We have performed detailed compositional measurements using EDS detectors in TITAN. Both elemental mapping, as well as line profile have been obtained. The details are shown in figure S2. Figure S2(a) – (b) show bright field TEM images of the samples prepared without PVP and with PVP. The inset in each figure exhibit HAADF images showing typical morphologies, nanoflower (or nanodendritic) and urchin-like ones. The corresponding EDS line profiles along AB and CD are shown below, Figure S2 (c) – (d). The line profile along AB indicates that the nano-dendrites exhibit no change in composition along with the arms, whereas urchin-like morphology has Pd core with Pt at arms. In addition, Figure 4R, shown below presents EDS mapping of Pt and Pd for nanodendrite. It also indicates the similar features in which Pd centre with Pt dendritic arms are observed.



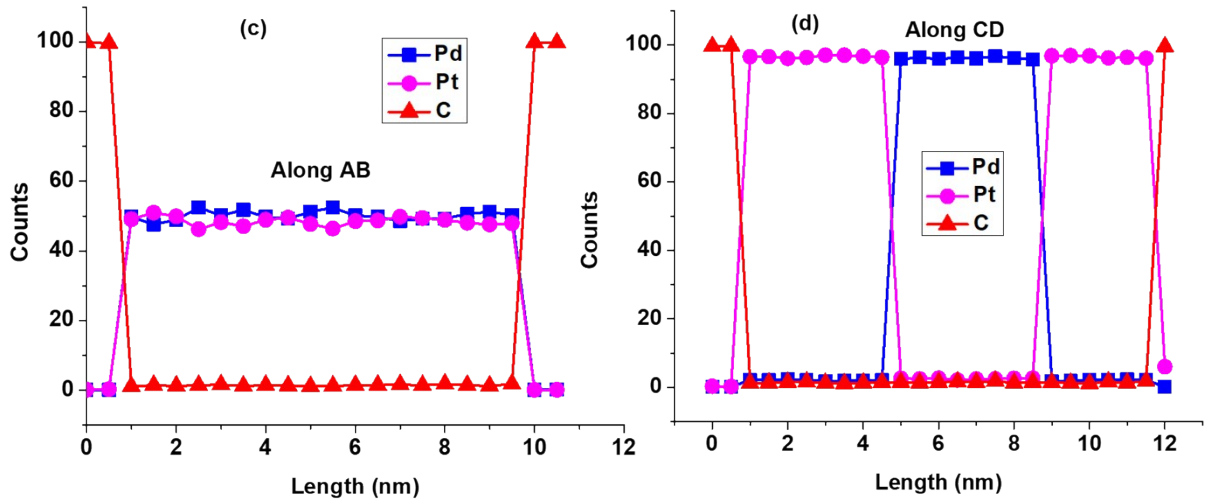


Figure S2: Bright field TEM images and EDS data of (a,c)G-PdPt (No PVP) and (b-d) urchin G-PdPt (with PVP). The inset of Figure 3R(a) and 3R(b) shows the HAADF images of G-PdPt (No PVP) and G-PdPt (with PVP), showing typical morphologies, nanoflower (or nanodendritic) and urchin-like.

2. X-Ray diffraction analysis

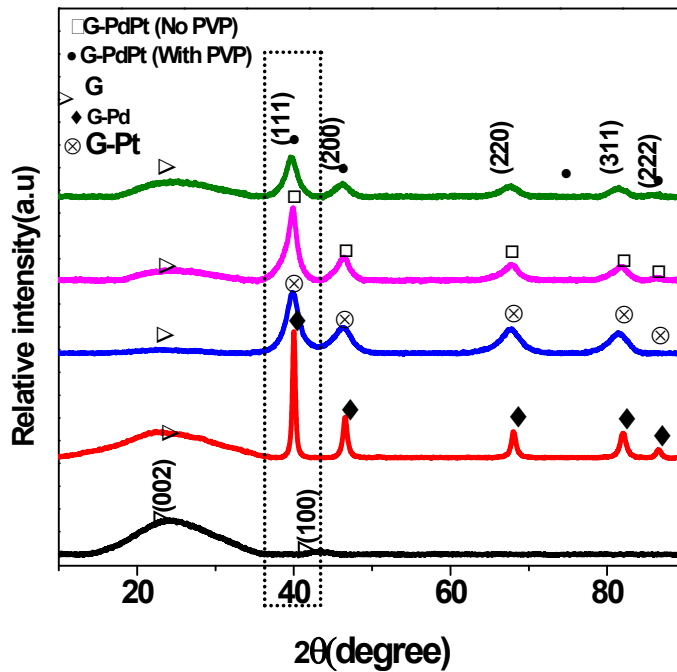


Figure S3: XRD patterns of G, G-Pd, G-Pt, G-PdPt (No PVP) and G-PdPt (with PVP).

3. Phase and Optical Analysis of graphene

The confirmation of formation of graphene from the graphene oxide can be obtained by using XRD and UV data. The disappearance of the sharp diffraction peak at 9.9° corresponding to (001) of graphene oxide in the XRD pattern of graphene and the presence of two distinct peaks at 24° and 44.8° corresponding to (002) and (100) reflections, indicate the formation of graphene [1, 2]. In the UV-visible spectra of graphene oxide, one can clearly see the two characteristic peaks are 230 and 302 nm, which corresponds to $\pi \rightarrow \pi^*$ transition of aromatic C-C bond and $n \rightarrow \pi^*$ transition of C=O bond, respectively. The shifting of adsorption from 203 to 266 and the disappearance of peak at 302 confirms the formation of graphene.

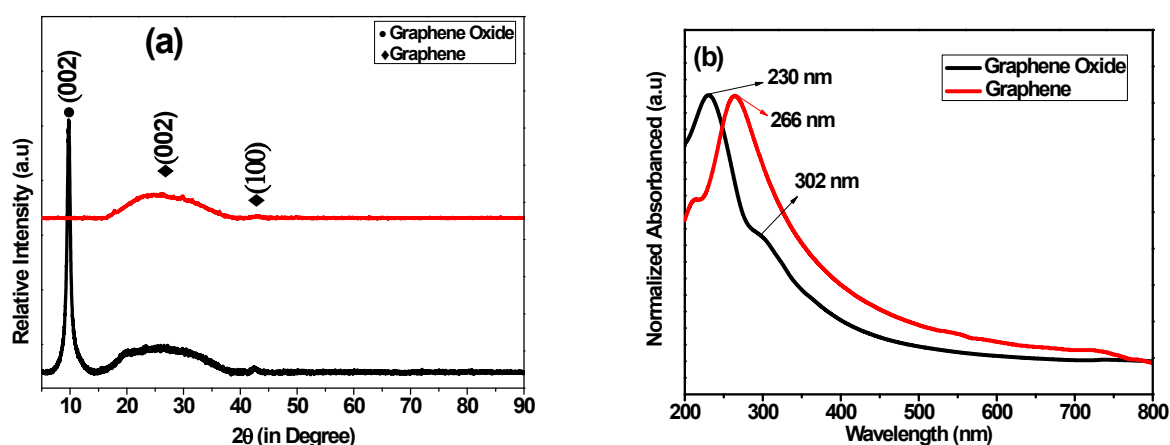


Figure S4: (a) XRD and (b) UV visible spectra of graphene oxide and graphene.

4. Probing the Formation of Metal Nanoparticles and Graphene-Metal Hybrids

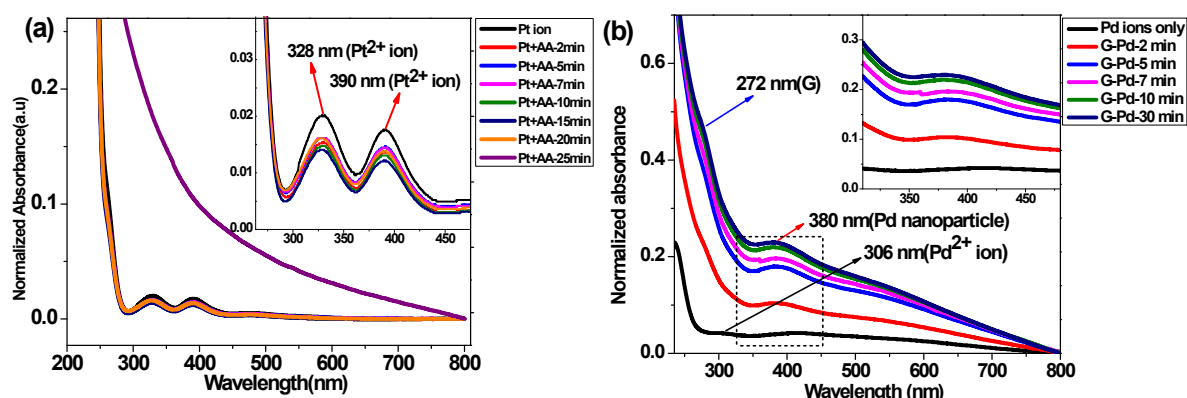
An extensive UV-Vis spectroscopic study was carried out to probe the formation of Pd and Pt nanoparticles and their decoration on the graphene surface. In the studies, UV-Vis spectra of the corresponding reaction solutions were obtained at definite time interval of 2 min, following the addition of respective reducing agents. It is to be noted that for reduction of Pd^{2+} and Pt^{2+} ions, sodium citrate and ascorbic acid were used respectively. Let us first discuss the UV-Vis spectra obtained from the *in situ* study for the formation of Pt nanoparticles, which is presented in **figure S5 (a)**. Here, it can clearly be observed that the Pt^{2+} ion exhibits two absorption bands at 328 and 390 nm. On careful observation, it is

evident that the intensity of these plasmonic absorption bands decrease as the reaction progresses, suggesting that the Pt^{2+} is converted into Pt atoms as reaction progresses. However, after 25 min of addition of the reducing agent, no characteristic absorption band is observed. To the best of the authors' knowledge, there is no report on the plasmonic peak position of Pt nanoparticles in the literature. Therefore, it can be inferred from the results that Pt ions are completely converted into Pt nanoparticles after 25 min of reaction. Similar study was carried out for the reduction of Pd^{2+} ions and it has been observed that Pd ions exhibits characteristic absorption band at 306 nm, whereas Pd nanoparticles at 384 nm, which is consistent with the reported literature [3, 4].

In the similar fashion, the *in situ* UV-Vis studies for G-Pt and G-Pd hybrids have also been carried out. Since the Pt nanoparticles do not show any plasmonic peak, G-Pt hybrids shows only a peak corresponding to graphene at 272 nm. On the other hand, the UV-Vis spectra obtained from the reaction solution of G-Pd hybrid, before adding reducing agent, shows plasmonic absorption band at 266 and 306 nm, corresponding to graphene and Pd ions (**figure S5 (b)**). However, after addition of reducing agent, the peak at 266 undergoes a red shift to 272 nm whereas the peak at 306 nm is shifted to 380 nm after 2 min of the addition of the reducing agent, indicating the formation of G-Pd hybrids.

From this study, it has been observed that Pt^{2+} ion exhibits two absorption bands at 328 and 390 nm, whereas Pt atoms or nanoparticles do not show any absorption band. On the other hand, Pd^{2+} ions and Pd nanoparticles exhibit plasmonic absorption bands at 306 nm and 380 nm, respectively, which is within the reported SPR wavelength range available in the literature. **Figure S5c** shows the UV-Vis spectra obtained from the *in-situ* study of G-Pd-Pt hybrid (without PVP). For comparison, the UV-Vis spectrum of the physically mixed reaction solution containing all the precursors; Pd^{2+} , Pt^{2+} ions and G were also obtained and presented in **Figure S5c**. From the **Figure S5c**, three characteristic plasmonic absorption

bands at 266, 314 and 386 nm can be observed, which may be attributed to graphene, Pd²⁺ (or overlapping peak of Pd²⁺ and Pt²⁺ ions) and Pt²⁺ ions, respectively. The absorption peak at 314 nm may be attributed to the absorption peak due to both Pd²⁺ and Pt²⁺ ions as their absorption bands are more or less overlapping. However, as soon as the reducing agent was added, the characteristic peaks corresponding to metal ions disappeared, indicating the formation of Pd-Pt structures. In addition, on careful observation, one can also observe that peak position of the graphene undergoes a red shift from 266 to 272 nm (shown in inset of **Figure S5c**). The detailed peak positions of all the relevant samples are also listed in Table T1. This shift would be possible because of the decoration of the nanoparticle on the graphene sheet. Therefore, the disappearance of the characteristic absorption bands of the metal ions and the shift of graphene absorption band suggest the formation of Pd-Pt alloys and its decoration on the graphene surface. Similar study has been carried out for G-Pd-Pt (with PVP), revealing a distinct absorption band at 380 nm, indicating the presence of Pd nanoparticles. However, no absorption band due to Pt has been observed, as discussed earlier.



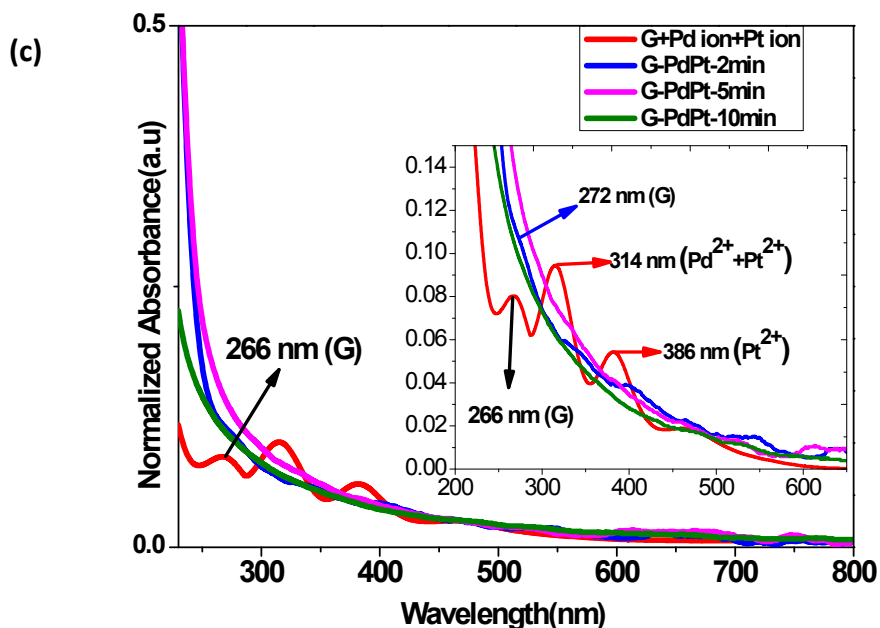


Figure S5: *In situ* UV-visible spectra; (a) Pt nanoparticles and (b) G-Pd nanoparticles hybrid. (c) *in situ* UV-visible spectra of G-PdPt (No PVP) nanoparticles hybrids.

TABLE T1: Comparison of UV-Visible peak positions of GO, G, Pd, Pt, Pt-Pd, G-Pd, G-Pt and G-Pt-Pd (No PVP) hybrids.

Material	Graphene Peak Position	Plasmon Peak Position
GO	230 nm ($\pi \rightarrow \pi^*$) and 303 nm ($n \rightarrow \pi^*$)	---
G	266 nm	---
Pd nanoparticles	---	384 nm
G-Pd hybrid	272 nm	380 nm
Pt nanoparticles	---	No SPR peak
G-Pt hybrid	272 nm	No SPR peak
Pd-Pt nanoparticles	---	No SPR peak
G-Pd-Pt (No PVP)	272 nm	No SPR peak

References

1. S. R. Sahu, M. M. Devi, P. Mukherjee, P. Sen, K. Biswas, *J. Nanomater.*, 2013, 2013, 1–9.
2. Y. Li, Y. Yu, J. G. Wang, J. Song, Q. Li, M. Dong, C. J. Liu, *Appl. Catal. B: Environ.* 2012, 125, 189–196.
3. Devi, M. M.; Sahu, S. R.; Mukherjee, P.; Sen, P.; Biswas, K. Graphene: A self-

- reducing template for synthesis of nanoparticles. *RSC Adv.*, 2015, 5, 62284-62289.
4. Xiong, Y.; Chen, J.; Wiley, B.; Xia, Y.; Yin, Y.; Li, Z.Y. Size-dependence of surface plasmon resonance and oxidation for Pd nanocubes synthesized *via* a seed etching process. *Nano Lett.*, 2005, 5, 1237-1242.