

Supporting Information

S1. Reaction parameters influencing the size of nanoparticle in hybrids

Factors responsible for controlling the particle size are:

- a. The concentration of the metal salts should be less ($\leq 0.001\text{M}$) so that agglomeration of metal nanoparticle can be avoided.
- b. The reduction should be carried out in an optimum reaction time and temperature (15 min at 90°C) because higher temperature and longer reaction time lead to growth of the particles.
- c. Heating and cooling rate should be sufficiently fast during reaction ($\geq 10^\circ\text{C}$ per min). Because the reduced metal nanoparticles will not get sufficient time to grow during heating or cooling.
- d. Kinetics also plays a strong role in controlling particle size. So, the reactants (metal salt solution and graphene solution) should be mixed very slowly so that rate of reaction should not be fast.

S2. Evidences for the formation of hybrid between graphene and metal nanoparticles

In order to get ascertained the formation of hybrids between the graphene and metal nanoparticles rather than a physical mixture, metal (Ag, Au, Cu and Pd) nanoparticles were separately prepared and SPR peak positions were identified using UV-Vis spectroscopy. The SPR peak position of Ag, Au, Cu and Pd nanoparticles has been found to be at 431, 522, 518 and 384 nm respectively (see figure below S1(a)). One can clearly be observed that the SPR peak position of metal nanoparticles get shifted after incorporation these nanoparticles with graphene due to charge transfer between nanoparticles and graphene [1], suggesting the formation of graphene-metal nanoparticles hybrids (see figure below S1 (b)).

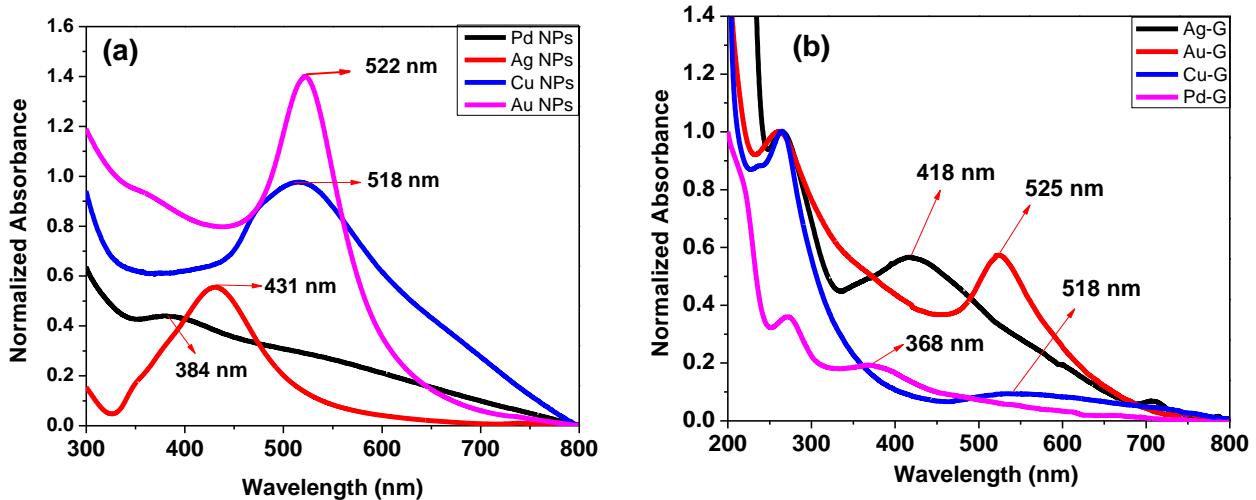


Figure S1: UV-Visible spectra of (a) pure metal nanoparticles and (b) hybrids.

S3. Evidences for the stability of graphene-metal nanoparticles hybrids

In order to elucidate the stability of hybrids as a function of time and temperature, reactions were carried out as a function of time (0, 5, 15, 30, 45 and 60 min) and temperature (30, 50, 70, and 90°C) at fixed temperature (90°C) and time (15 minutes) respectively. Only the representative results are presented here. The average particle sizes of Pd nanoparticles in hybrids have been observed to be 8 ± 2 and 22 ± 3 nm, which were prepared at 90°C for 15 and 60 min respectively (see figure S2(a) and S2(b)), suggesting good stability of hybrid because the particle size are not increased significantly with time. In addition, the UV-Visible spectra of Pd-G as a function of temperature also clearly shows that at lower temperature ($\leq 70^\circ\text{C}$), the SPR peaks corresponding to Pd nanoparticle does not appear to be prominent (Figure S2 (b)). At 90°C, the SPR peak become prominent and shifted from 364 to 368 nm. This can be attributed to complete reduction of Pd ions to Pd nanoparticles and slightly growing in particle size. In addition, high revolution TEM micrographs are also provided in Figure S2 (c), showing that nanoparticles are atomically bonded with graphene network, implying the formation of stable graphene-metal nanoparticles

hybrids. Moreover, it has been reported that the transition metals; Fe, Co, Ni etc. which are highly prone to form carbides with carbonaceous materials can be uniformly decorated on graphene sheet without forming any carbide, indicating a very high stability of graphene [2-4]. Thus, Ag, Au, Cu, Pt and Pd do not likely to react with graphene as they are noble metals. Hence, these graphene-metal hybrids in the present investigation are highly stable.

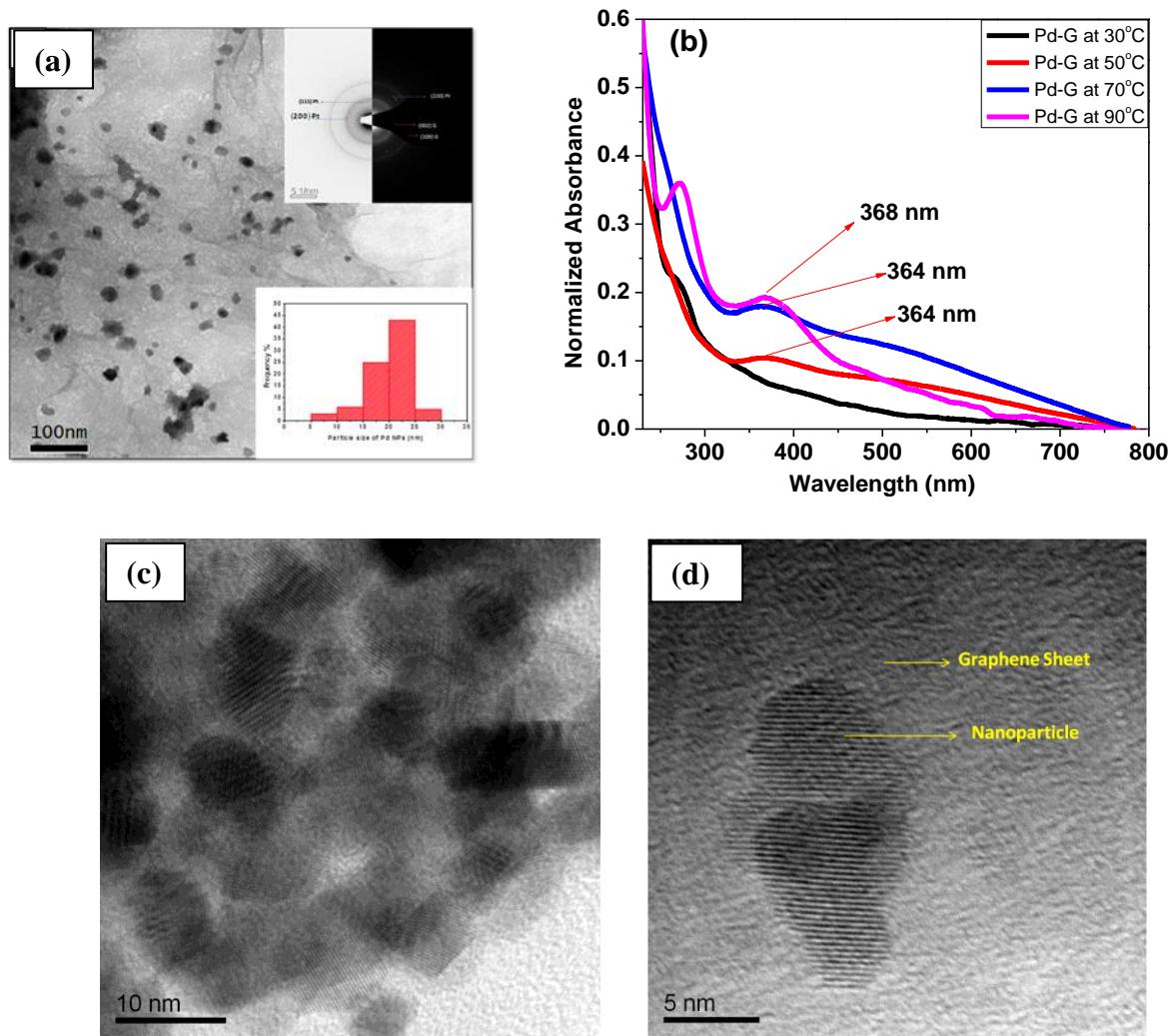


Figure S2: (a) TEM image of Pd-G and corresponding SAD pattern (upper inset) and particle size distribution (lower inset) and (b) UV-Visible spectra of Pd-G as a function of temperature. (c) and (d) High revolution TEM micrographs of graphene-metal nanoparticle hybrids.

S4. *In-situ* detection of Hydrazine Hydrate in the graphene stock solution

To confirm the complete removal of hydrazine hydrate from the graphene stock solution, *in situ* detection of hydrazine hydrate has been carried out using Au^{3+} ions as a colorimetric sensor. It is to be noted that once the Au^{3+} ions are reduced to Au NPs, the color of solution changes from pale yellow to reddish or bluish color. This is due to reduction of Au^{3+} ion to Au NPs by any residual hydrazine hydrate left in the reaction solution after complete reduction of GO to G. It has been reported that the interaction of Au^{3+} ions with hydrazine hydrate leads to the formation of inter-particle cross-linking between the freshly formed Au NPs, resulting in the formation of agglomerates of Au NPs [5]. In the present investigation, the dried graphene sheets have been obtained after heating the graphene solution at 120°C for 5h and thus hydrazine hydrate is expected to be completely removed. To confirm the absence of any hydrazine hydrate, the above mentioned methodology has been utilized. The dried graphene sheet has been dispersed in water and the supernatant obtained after filtration was treated with aqueous solution of HAuCl_4 (0.001M). No color change in the solution has been observed (figure S3). Hence, this experimental evidence clearly suggests that after heating the graphene stock solution at 120°C for 5h, freely available hydrazine hydrate has been completely removed.

On the other hand, in case of the supernatant obtained subsequent to the reduction reaction of GO to G, the addition of aqueous solution of HAuCl_4 (0.001M) at room temperature leads to change in the color of the solution to deep blue. Thus, it is possible to detect and confirm the residual hydrazine hydrate. The detailed experimental strategy is shown in figure S3.

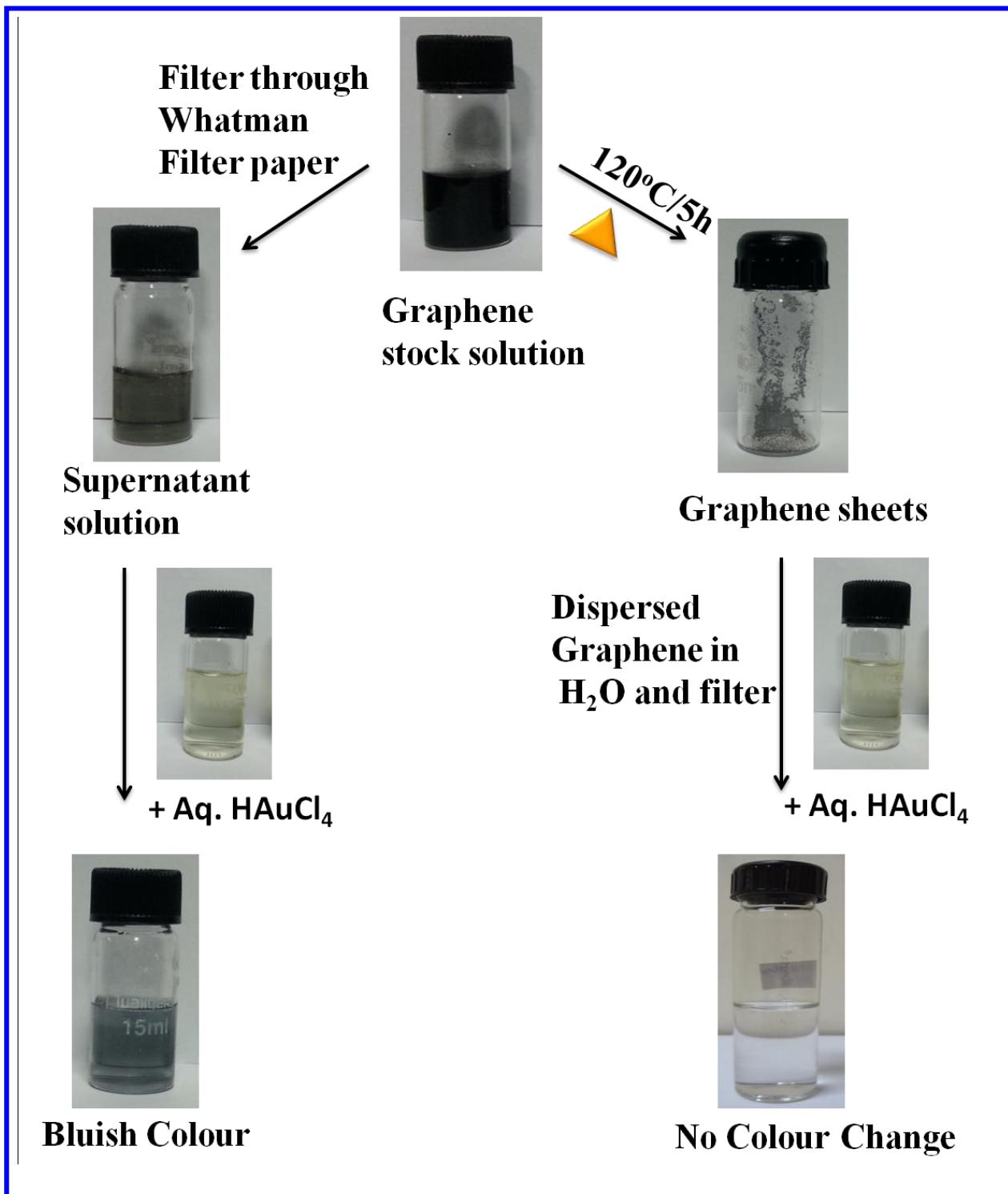


Figure S3: Complete experimental strategy for the detection of hydrazine hydrate in the reaction solution.

References

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