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Comment on " Porous Graphene for Ultrahigh Hydrogen Storage and CO Oxidation Multi-Functionalities".

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In a recent paper R.Kumar *et al* reported five-fold increase of hydrogen sorption by reduced graphene oxide (r-GO) after decoration with Pd nanoparticles.[1] This enhancement of hydrogen sorption was attributed to spillover effect and additional porosity created as a result of on- air microwave treatment. If true, this result would be a significant achievement as the value of 5.4 wt% at 77K for sample with specific surface area (SSA) of 586 m2/g is usually found only for carbon materials with SSA over 2500 m^2/g. Leaving aside controversy in observations of spillover effects for hydrogen sorption in carbon materials at near ambient temperature,[2] the hydrogen dissociation required for spillover mechanism is not expected at 77K. Moreover, the isotherms presented by R.Kumar et al for Pd/r-GO samples exhibit anomalous shape with almost linear increase of wt% up to ~70 bar H_2 pressure. Even more abnormal isotherm shapes are reported for precursor r-GO samples with almost zero uptakes up to 20 bar while for any other carbon materials this pressure is usually sufficient to achieve 80-100% of saturation value.[3-4] The shape of isotherms shown by R.Kumar *et al* has no analogues in literature on hydrogen sorption by carbon materials. Note also that modelling presented in the study by R.Kumar *et al* is performed for sub-nanometer size nanoparticles and holes while the actual SEM images show Pd particles in the 50-200 nm range (Figure 1 d,e in the paper by R.Kumar *et al*)[1] and with even larger holes produced after carbon support etching.

Our recent studies demonstrated that r-GO prepared using thermal exfoliation and activated r-GO samples follow rather precisely the standard for any carbon material SSA vs Wt% trends, exhibit standard Langmuir-type shapes of isotherms at 77K and almost linear isotherm shape at near-ambient temperatures.[5-6] To make sure that microwave treatment do not provide exceptions, we synthesized several samples of r-GO decorated with Pd nanoparticles using procedure reported by Kumar *et al*.[1] Our results confirm formation of holes in r-GO sheets around Pd particles after on-air microwave or simple heat treatment. Formation of holes indeed provides some increase of SSA (20-25% in our experiments) in agreement with results of theoretical modelling.[7] Overall characterization of our samples demonstrates that we produced material very similar to the one studied by R.Kumar *et al*. with SSA value of 319 m^2/g for precursor GO and up to 430 m^2/g for perforated samples. However, no enhancement of hydrogen uptake was observed due to addition of Pd nanoparticles. The Langmuir-type shapes of H_2 isotherms were observed for all samples, including both precursor r-GO and Pd decorated samples. The same type of isotherms was reported previously for Pd-free r-GO[5, 8] or other carbon materials.[4, 9] The values of H_2 uptake measured in our experiments precisely follow correlation with SSA reported in earlier studies.[5-6] Activation of Pd nanoparticles using hydrogen annealing (350^{0}C) also have not resulted in increase of hydrogen sorption. Considering abnormal shapes of reported isotherms and absence of reproducibility, we attribute hydrogen storage results reported by R.Kumar *et al* to artifacts of hydrogen uptake measurements.

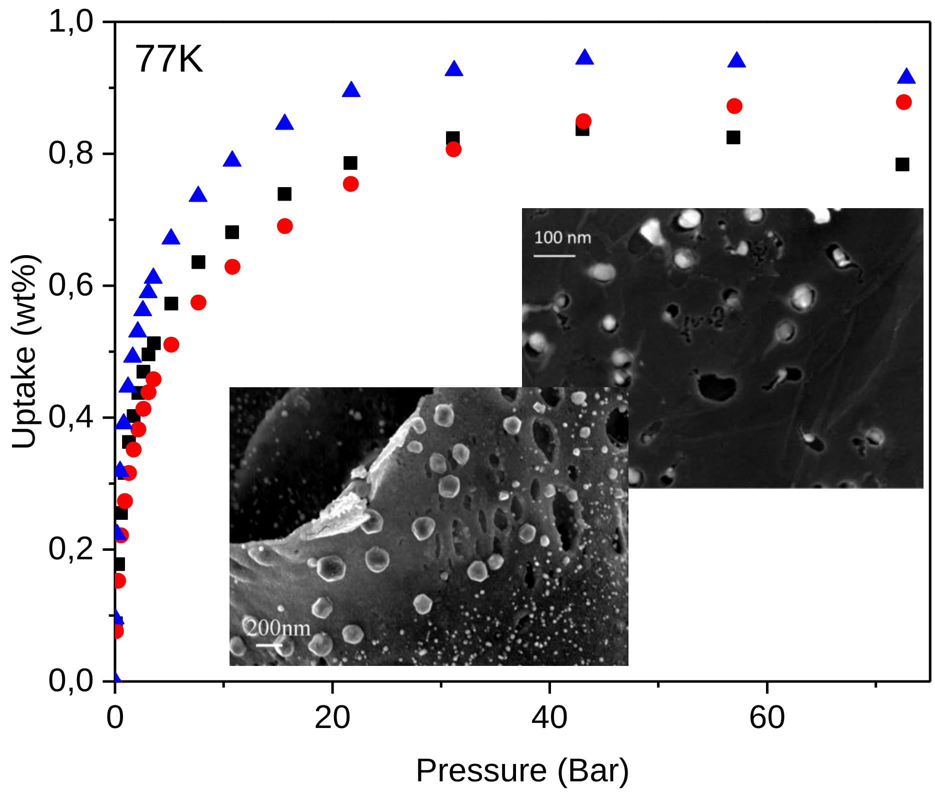

Figure 1. H_2 uptake isotherms recorded at 77K for Pd decorated samples prepared according to procedure described by H.Kumar *et al*. using microwave exfoliation and air etching: precursor r-GO prepared using microwave exfoliation (▲), Pd decorated and microwave treated r-GO (●), Pd decorated air annealed r-GO (■). Inset shows SEM images of r-GO decorated with Pd nanoparticles. Air-annealed samples show holes etched around Pd nanoparticles similarly to ref 1.

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