Support information

Synthesis of Graphene oxide:

Natural graphite powder, potassium permanganate were received from Alfa Aesar chemicals, Republic of Korea, palladium chloride, methanol, ethylene glycol were obtained Sigma-Aldich, Republic of Korea). Ascorbic acid was obtained from Daejung chemicals, Republic of Korea, sulfuric nitric, and nitric acid were received from Samchun pure chemicals, Republic of Korea. Analytical grade chemicals were purchased and used as received without further purification.

The graphene oxide was prepared by the modified the Hummer's process [J. W. S. Hummer, and R. E. Offeman, *J. Am. Chem.. Soc.* 1958, **80**, 1339]. In brief, natural graphite powder (4.0 g) was added to concentrated H_2SO_4 (70 mL) under stirring in an ice bath (0-2°C). Then, under vigorous stirring, potassium permanent (12.0 g) was added slowly to keep the temperature of the suspension lower than 20°C. After 15 min the reaction system was transferred to a 40°C oil bath and stirred for about 1 h. Then, 150 mL water was added, and the solution was stirred for 30 min at 100°C. Additional 500 mL water was added and followed by a slow addition of 30 mL H_2O_2 (30%). The mixture was filtered and washed with 1:10 HCl aqueous solution (500 mL) to remove manganese ions. The resulting solid (GO,GS1) was dried in air and diluted to 1000 mL, making a graphite oxide aqueous dispersion using ultrasonic irradiation.

Synthesis of the catalyst

The Pd@C over the reduced GO was obtained by employing the one pot solid sate reduction process. In brief, 16 mg of palladium chloride and 64 mg of GO (GS1) were mixed well using a mortar, after which about 20 mg of solid ascorbic acid was added to the mixture and ground well. After one minute the solid mixture was observed to slowly change in color from gray to black and take on a jelly-like consistency within one minute. The grinding process was continued for another 2 minutes and then the final mixture was dried in a hot air oven for about 2h at 90°C. The color change indicates the formation of the Pd nanoparticles over the GO. To ensure the effectiveness of the AA on the GO, about 40 mg of GO and 10 mg of AA were ground well using a mortar for about 5 min. (GS2). The same reaction was performed in an aqueous medium, in which 16 mg of palladium chloride and 64 mg of GO were dispersed in hot DI water (80°C) for 30 minutes. Then the resultant product was separated, washed with DI water and dried in a hot air oven for 2 hrs (GS3). Next, 25 mg of GO was dispersed in DI water and sonicated for about 30 min. About 50 mg of AA was added to the GO dispersion described above and kept aside (GS4). For carbon formation over the catalyst, i.e., Pd@C, a small part of the sample GS1 was subjected to microwave irradiation for about 5 minutes, at regular 30-second intervals. Similarly, Pd@C supported MWCNT and Vulcan XC were prepared by the above mentioned method.

Preparation of the catalytic electrode

First, 10 mg of the prepared catalyst was dispersed in 0.1 mL Nafion (0.05% ethanol)/0.9 mL water solution and 20 μL of the catalytic ink was dropped onto the GC electrode surface and vacuum dried at room temperature.

Characterization of the catalytic materials prepared

The catalysts prepared were initially characterized using powder X-ray Diffraction (XRD), using the Rigaku Instrument diffractrometer with Cu K_α radiation. The Fourier Transform Infrared (FTIR) spectra were recorded on a Perfkin Elmer (Spectra GX) spectrometer in the range of 400-4000 cm^{-1} and the Fourier Raman spectra were recorded using a Nanofinder

30 confocal Raman microscope (Tokyo Instrument Co., Japan) in the range of 500-3200 cm^{-1} with a He-Ne laser beam of 633 nm wavelength. The X-ray Photoelectron Spectra (XPS) were recorded on an Axis-Nova (Kratos Inc.) with an Al $K_{\alpha} = 1486.6$ eV excitation source. The surface Plasmon and the catalytic activity were monitored using the double beam UV-Vis spectrophotometer (Schimadzu UV-2550). Further characterization was performed employing Scanning Electron Microscopy (SEM) equipped with the Energy Dispersive X-ray Spectrometer (EDS) for the quantitative determination of the elements present in the catalyst on a JEOL, JSM-6200 equipped with an Ametek EDAX, at an accelerating voltage of 20 kV. The images from High Resolution Electron Microscopy (HRTEM) were recorded with JEOL, JEOL 2100 electron microscope operated at 200 kV. The thermal characteristics were tested utilizing a thermogravimetric analyzer (Thermo Plus EV 02, Rigaku Instruments) in a nitrogen atmosphere.

Electrochemical characterization of the catalytic materials

The electrocatalytic activity of the catalysts prepared was analyzed by the Cyclic Voltammetry (CV) technique using the electrochemical workstation (Biologics 320V) equipped with the standard three-electrode system and computer controlled software. The three-electrode system includes a saturated calomel (Hg/Hg_2Cl_2 in KCl) electrode serving as the reference electrode, a platinum wire serving as the counter electrode, and a catalyst coated glassy carbon electrode serving as the working electrode. The electrocatalytic activity of the catalysts prepared (Pd@C/RGO, Pd@C/CNT, Pd/GO and Pd/C) for alcohol oxidation was studied by performing CV in a 1.0 M KOH solution containing 0.5 M Ethylene Glycol (EG). To avoid oxygen interference, the nitrogen gas was purged before every experiment.

Catalytic reduction reaction

Typically, aqueous 4-nitrophenol (50 mL, 1x10^{-4}M) and aqueous sodium borohydride (50 mL 0.5x10^{-4} M) were transferred into a 30 neck round bottom flask. After 10 min, the carobocatalysts (50 mg Pd@C-RGO/Pd@C-MWCNT, Pd@C-VXC) was added into the mixture. The mixture was continuously stirred. Solution (1.0 mL) was sampled at certain intervals, diluted with cold deionized water (9.0 mL, ~3-5°C) and measured immediately by a double bean ultraviolet spectrophotometer in the range of 200-800 nm. (Shimadzu, UV-2550). After the experiment the catalyst was removed centrifugation, washed several times with DI water and dried in hot air oven at 90°C and reused the catalyst.

Experimental Results:

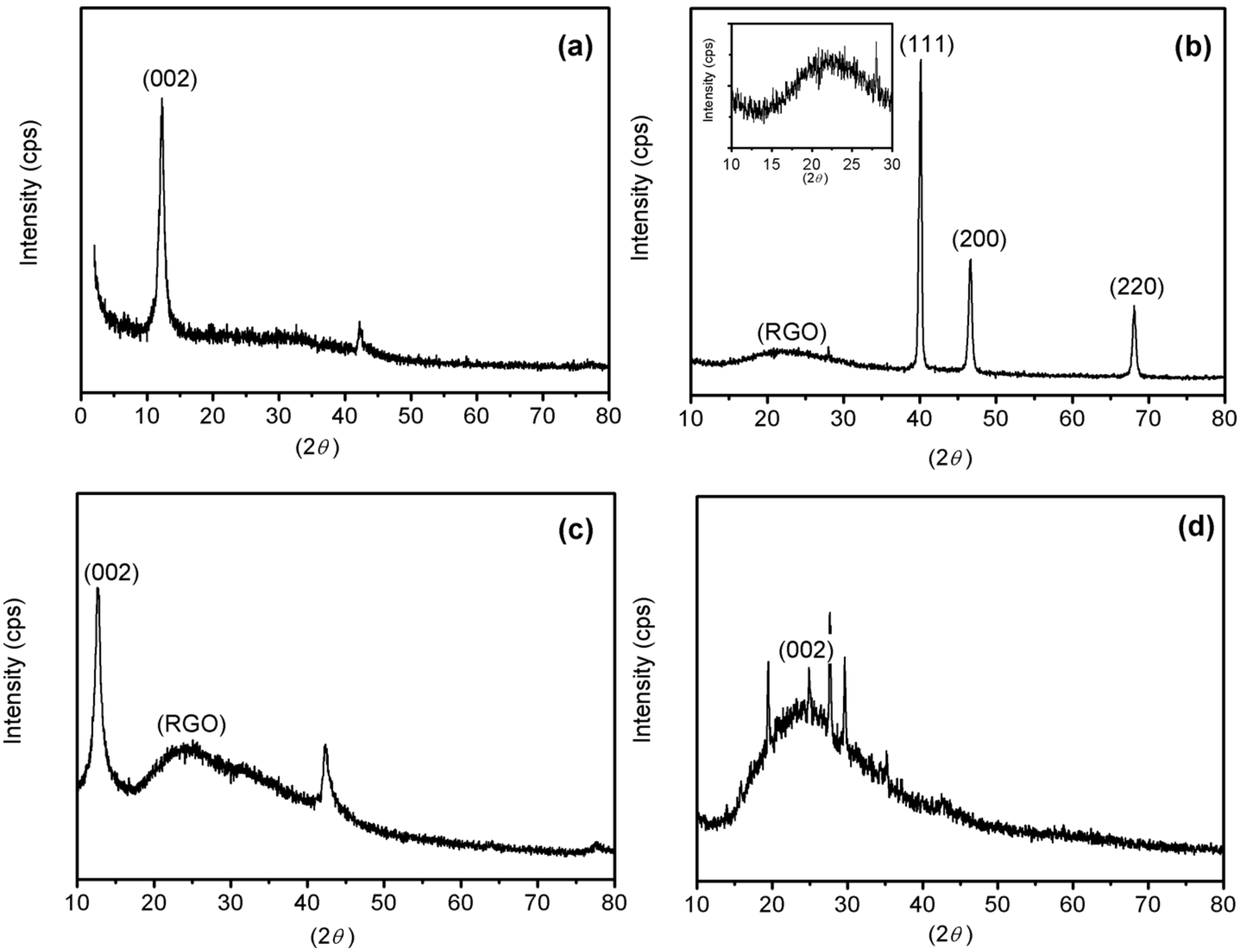


Fig. S1 XRD patterns of (a, GS1) GO, (b, GS2) Pd@C-RGO (Inset: formation of RGO), (c, GS3) Pd-PRGO and (d, GS4) RGO.

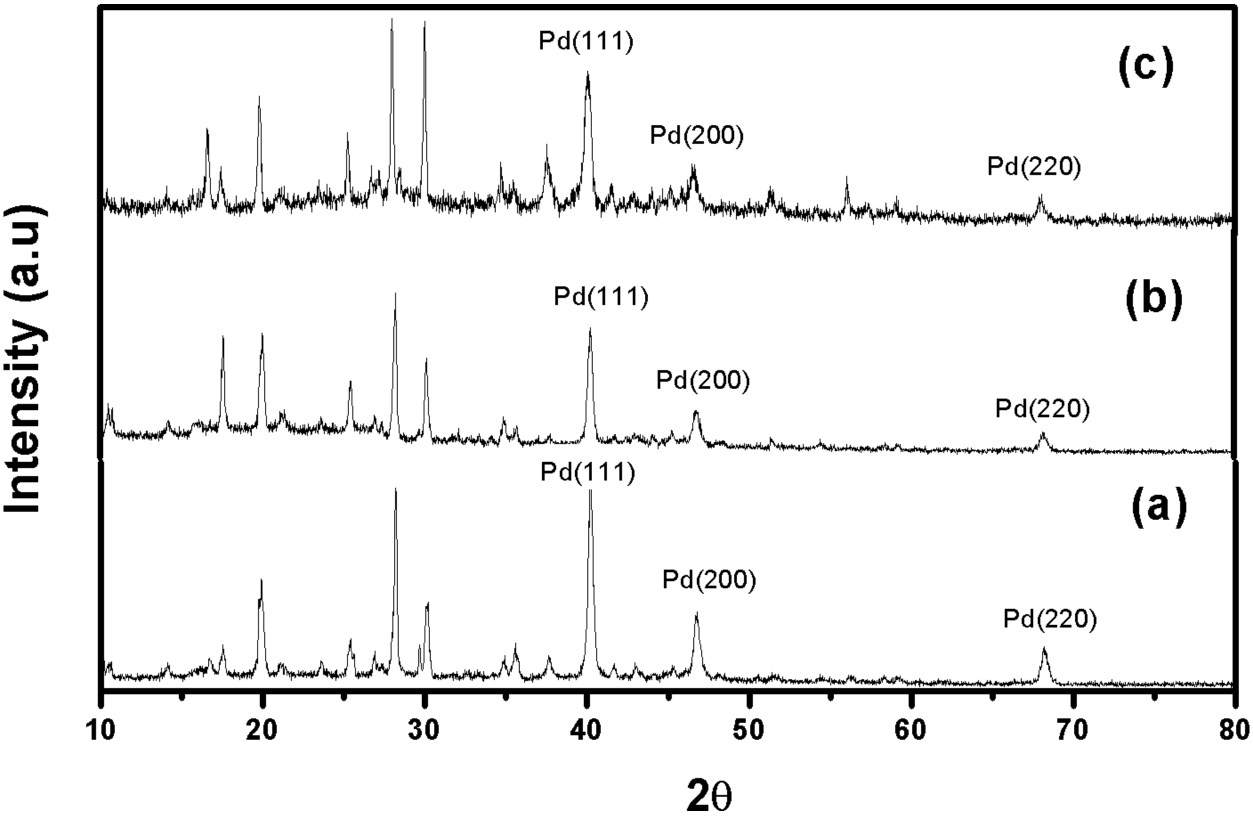


Fig. S2 XRD patterns of (a) Pd@C-VXC, (b) Pd@C-MWCNT and (c) Pd@C-RGO carbocatalysts prepared by microwave irradiation.

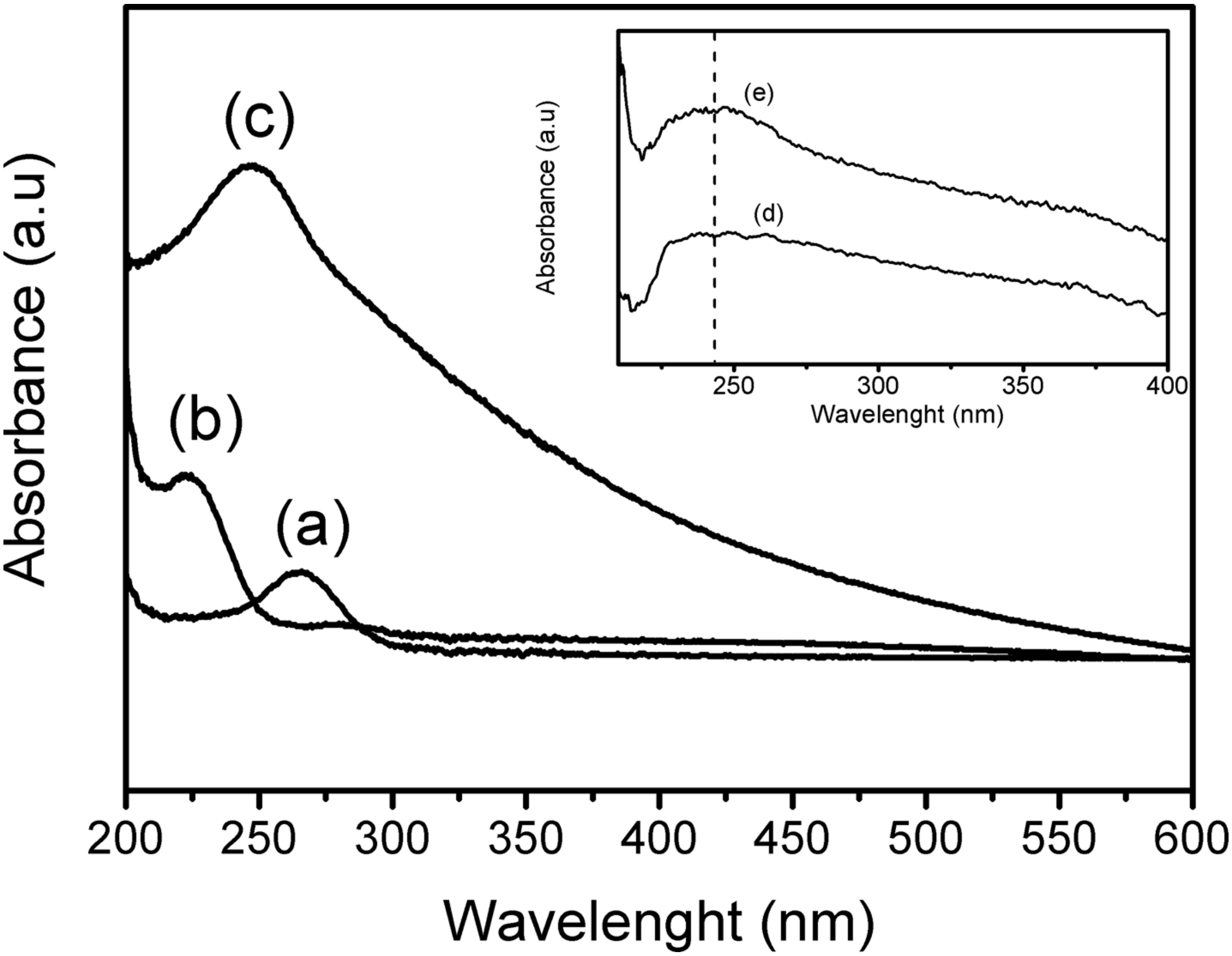


Fig. S3 UV-Vis spectrum of (a) GO, (b) colloidal Pd nanoparticles, (c) Pd@C-RGO carbocatalyst, (d) Pd@C-Vulcan XC and (e) Pd@C-MWCNT carbocatalyst

The surface plasmon of the carbocatalysts prepared was analyzed by the UV-Vis spectrophotometer (Fig. S3). The formation of the stable GO suspensions, colloidal Pd nanoparticles and Pd@C-RGO nanocomposite was monitored using UV-Vis spectroscopy. As shown in Fig. S3, the characteristic absorptions of the GO and palladium were observed at 265 nm and 231 nm, respectively. In general, the absorption peak of the GO dispersion was observed between 231 nm and 270 nm [D. Li, M. B. Muller, S. Gilje, R.B. Kaner, and G. G. Wallace, *Nature Nanotech.* 2008, **3** 101]. After the formation of Pd@C-RGO, the peak was observed at

247 nm and this shift in the absorption of GO suggested that the electronic conjugation within the graphene sheets had been restored after the reduction process. Besides, upon reduction using AA in the solid state reaction, the C=C plasmon peak at red shifted to 247 nm and this red shift was associated with the increase in the $\pi-$ electron density of the Pd@C-RGO and RGO samples. [Sun, Z. Yan, J. Yao, E..Beitler, Y. Zhu, and J. M. Tour, *Nature*, 2012, **468**, 54928, 29, A. O. Biying, V. R. Vangala, C. S. Chen, L. P. Stubs, N.S. Hosmane, and Z. Yinghuai, *Dalton. Trans.,* 2014, **43**, 5014]. Similarly, the Pd@C over the MWCNT and Vulcan XC showed the absorption maxima around 243 nm (Fig. S3 d & e).

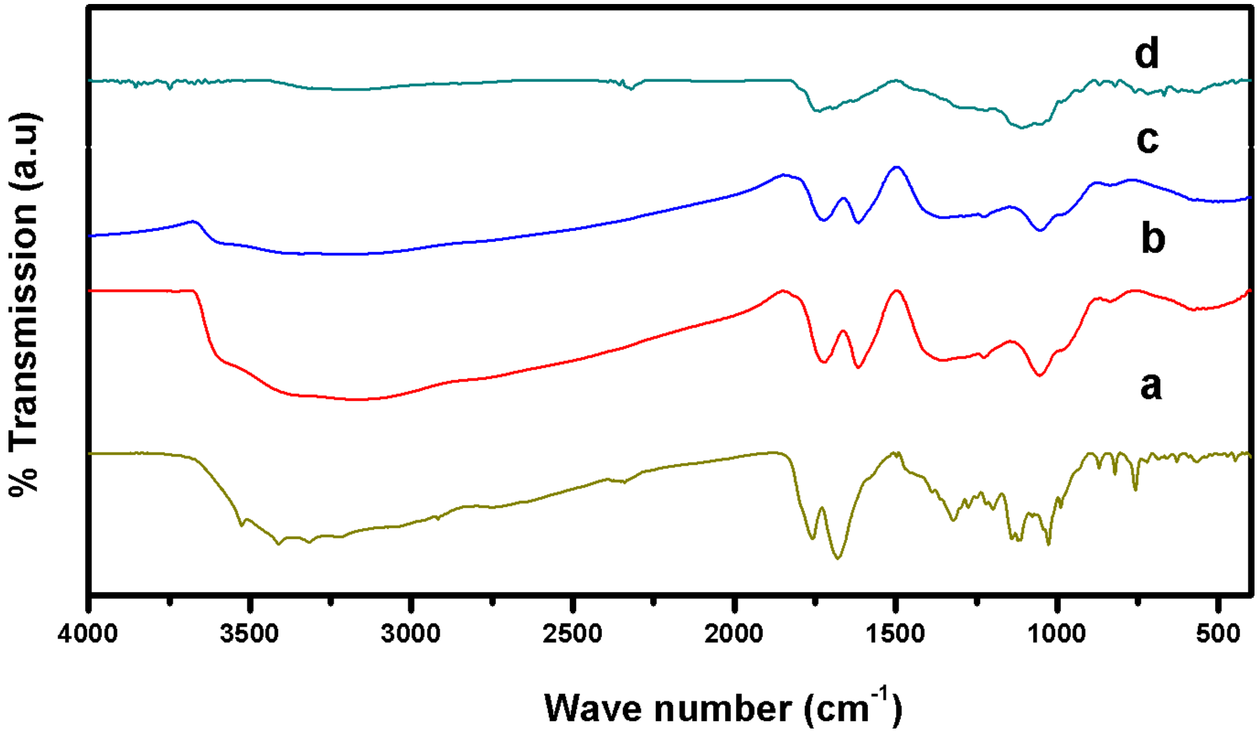
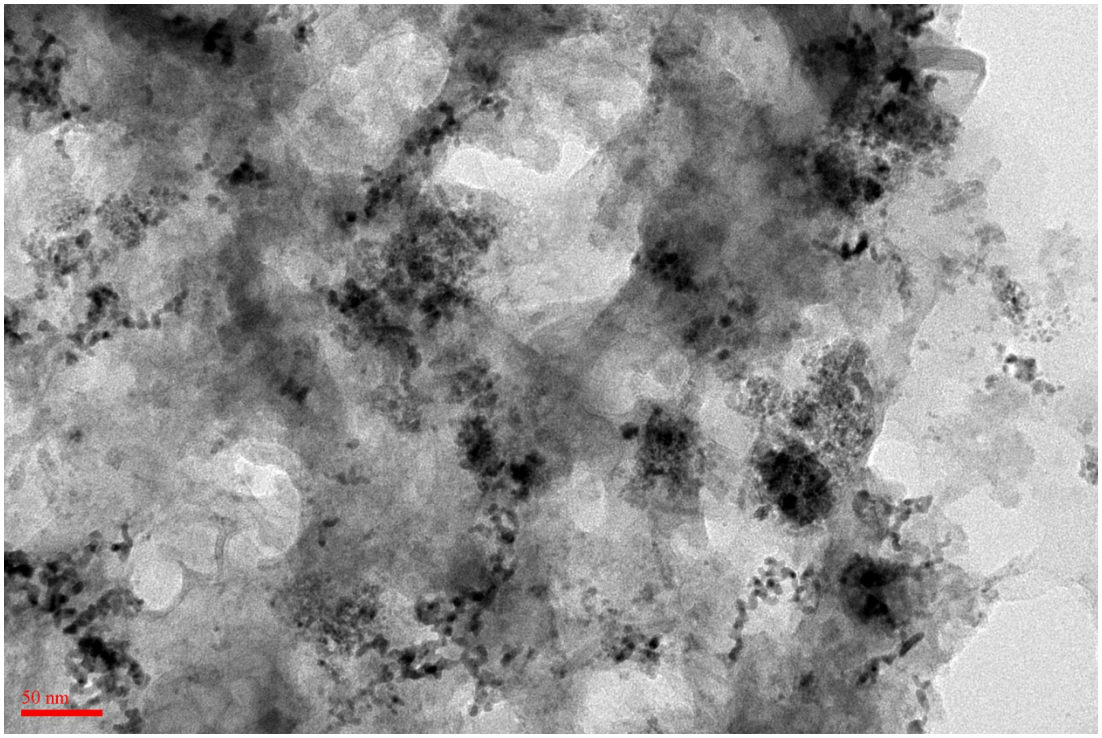


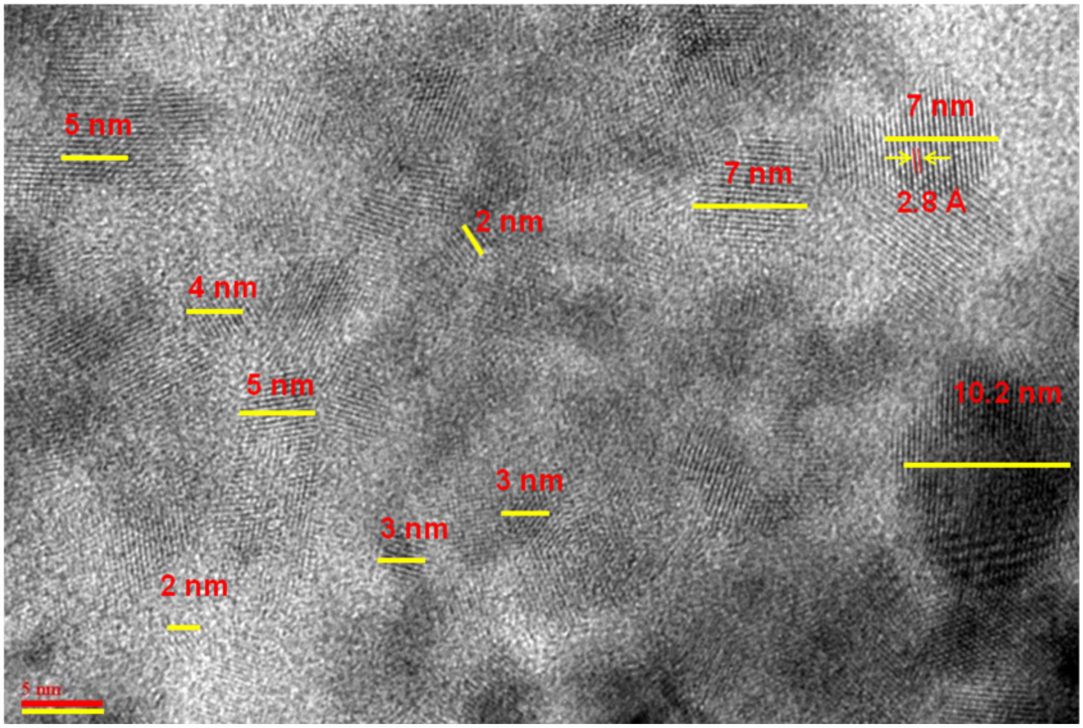
Fig. S4 FT-IR spectrum for (a) GO, Pd-RGO prepared by using (b) aqueous medium (Pd-PRGO) and (c) solid state process, (d) Pd@C-RGO carbocatalyst prepared by microwave irradiation.

Fig. S4 a-c shows the FTIR spectra of the GO, Pd@C-RGO and Pd-PRGO samples. The vibrational bands for the GO observed at 3250, 1734, 1623, 1374, 1227, and 1060 cm^{-1}

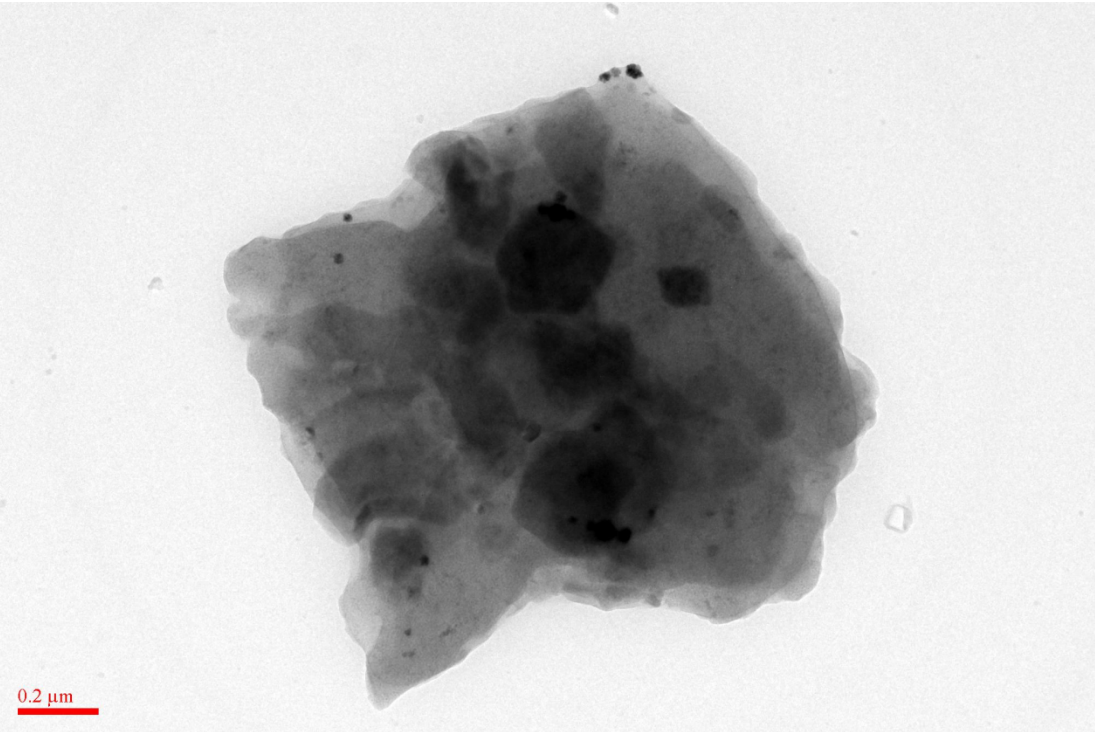
correspond to the stretching vibrations of the O-H (carboxyl or intercalated water molecules), C=O (carbonyl or carboxyl), C=C unoxidized, O-H (carboxyl or intercalated water molecules), C-OH (hydroxyl) and C-O (epoxy/alkoxy) [S. H. Kim, G. H. Jeong, D. Choi, S. Yoon, H. B. Jeon, S. M. Lee, and S. W. Kim, *J. Colloid. Inter. Sci.*, 2013, **89**, 85, S. Bose. T. Kuila, A. K. Mishra, N. H. Kim, and J. H. Lee, *J. Mater. Chem.*, 2012, **22**, 9696., S. Yang, J. dong, Z. Yoo, C. Shen, X. Shi, Y. Tian, S. Lin, X. Zhang, Scientific reports, 4, 2014: doi: 10.1038/srep04501]. On the other hand, the intensity of all the peaks diminishes markedly on the Pd-RGO and Pd@C-RGO samples, which indicates that the oxygen-containing functional groups on the surface had been removed in various degrees. The sample prepared in the aqueous medium exhibits a much higher degree of the stretching vibration of the –OH (3250 and 1650 cm^{-1}), whereas the sample prepared in the solid state process exhibits a much lower degree of $–OH_{str}$ vibrations and after the microwave irradiation an almost complete removal of the oxygen-containing functional groups from the catalyst is noted. This clearly indicates that the AA reduced the GO.

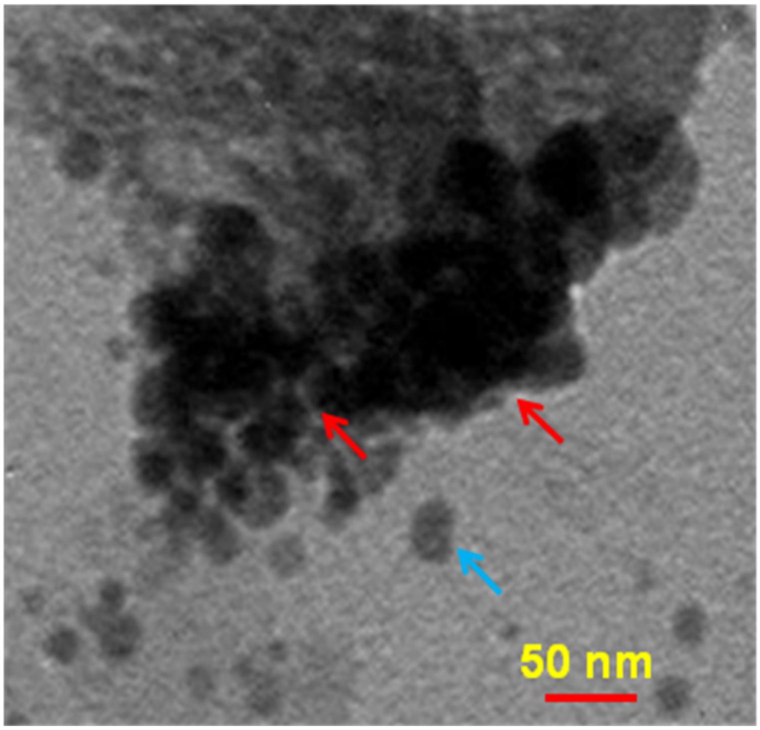
Pd-@C-RGO





Pd@C-VXC





The above TEM image of size controlled Pd@C- VXC carbocatalyst. The carbon coated over the Pd NPs (Pd@C, Red colored arrow) and uncoated Pd NPs (Blue colored arrow) were shown above the TEM image.

Pd@C-MWCNT

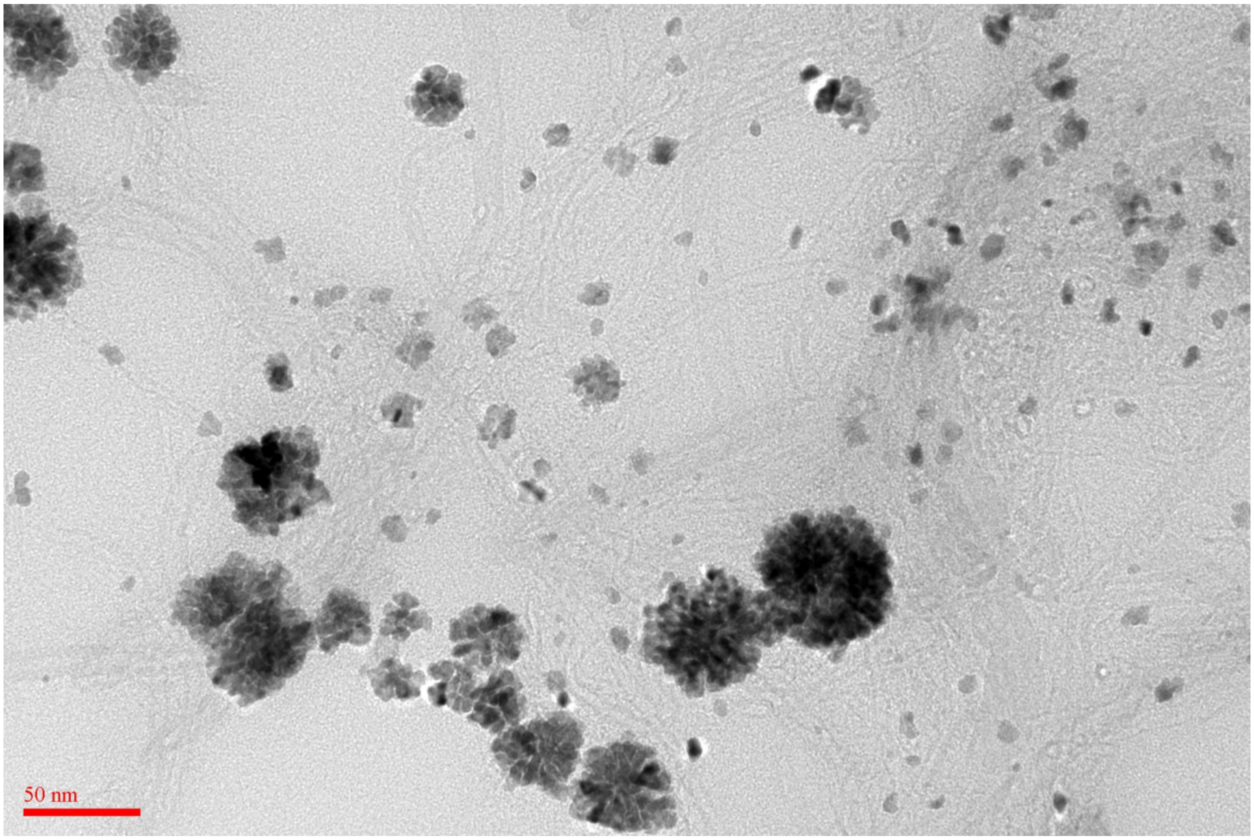
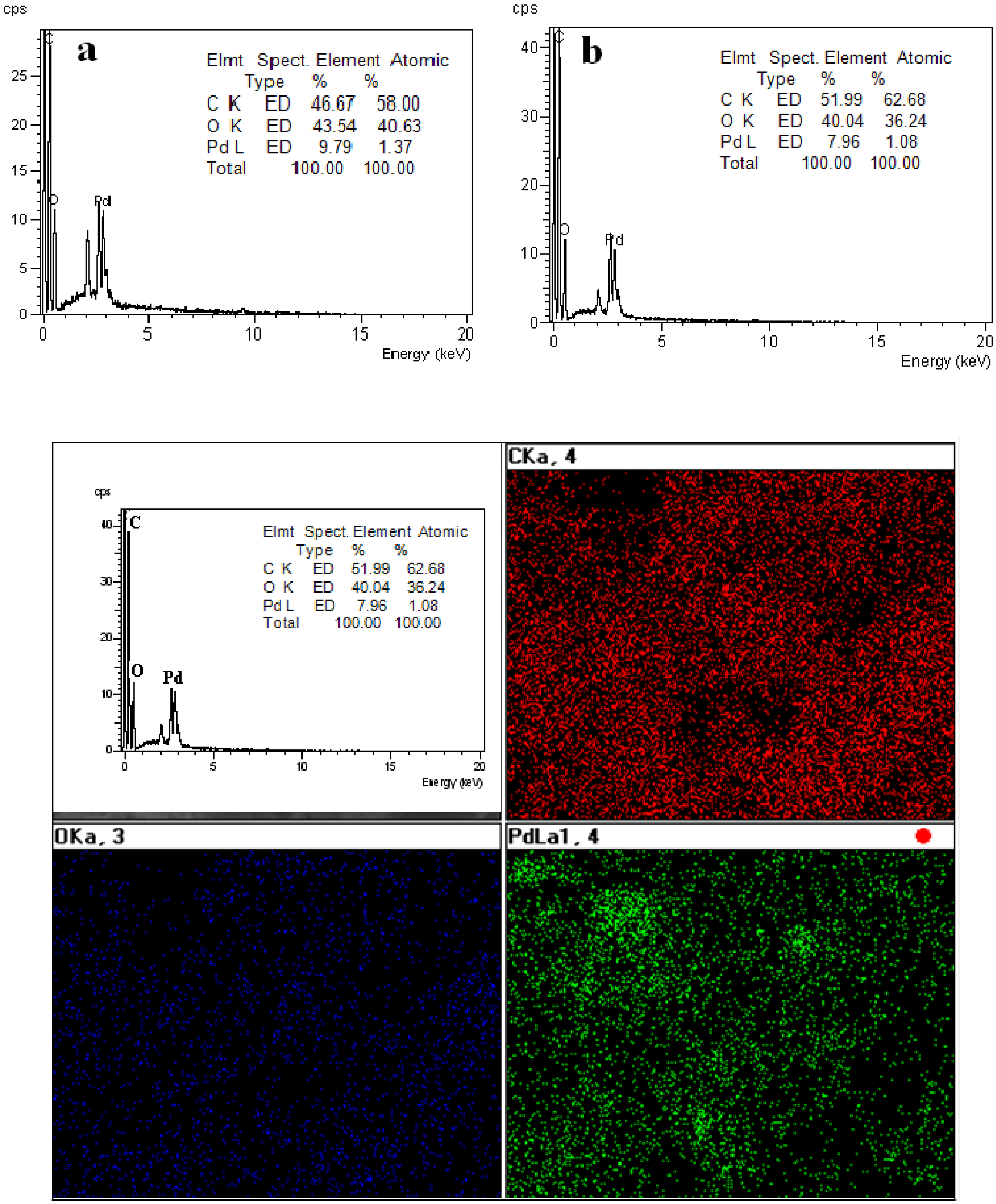


Fig. S5 The TEM micrographs of Pd@C at RGO, VXC, and MWCNT



a

Elmt	Spect. Type	Element %	Atomic %
C K	ED	46.67	58.00
O K	ED	43.54	40.63
Pd L	ED	9.79	1.37
Total		100.00	100.00

b

Elmt	Spect. Type	Element %	Atomic %
C K	ED	51.99	62.68
O K	ED	40.04	36.24
Pd L	ED	7.96	1.08
Total		100.00	100.00

Elmt	Spect. Type	Element %	Atomic %
C K	ED	51.99	62.68
O K	ED	40.04	36.24
Pd L	ED	7.96	1.08
Total		100.00	100.00

Fig. S6 The EDS analysis (a) Pd-RGO and (b) Pd@C-RGO and elemental mapping images for Pd@C-RGO.

The surface morphology of the carbocatalysts prepared was analyzed using the TEM and EDS analyses. The Pd nanoparticles (2-8 nm) over the GO prepared by solid state process was analyzed using TEM, revealing the formation of spherical-shaped Pd nanoparticles uniformly distributed over the RGO. The same sample when subjected to microwave irradiation, showed flower-like morphology and the carbon covered the Pd NPs are shown clearly (Pd@C-VXC). This was attributed to the dehydroascobate present along with the Pd nanoparticles, which gets carbonized to form Pd@C and it is these Pd@C particles that assemble to form the flower-like morphology over the support (Fig. S5). Also, on the MWCNT and VXC the Pd nanoparticles were formed as uniform flower-like structures with particle size ranging from 3-8 nm. Elemental analysis was performed to analyze the percentage of Pd, C and O present in the prepared carbocatalyst. Fig. S6 shows that the elemental analysis (EDS) spectra indicate the lower weight percentage of the Pd nanoparticles in the carbocatalyst. The elemental mapping of C, O and Pd is shown in Figs. S6, which indicate the uniform distribution of the elements in the material prepared. The EDS spectra for Pd/RGO and Pd@C-RGO is 46.67% and 51.99%, respectively. This indicates that the carbon materials are obtained after using microwave irradiation (support S6 a and S6 b).

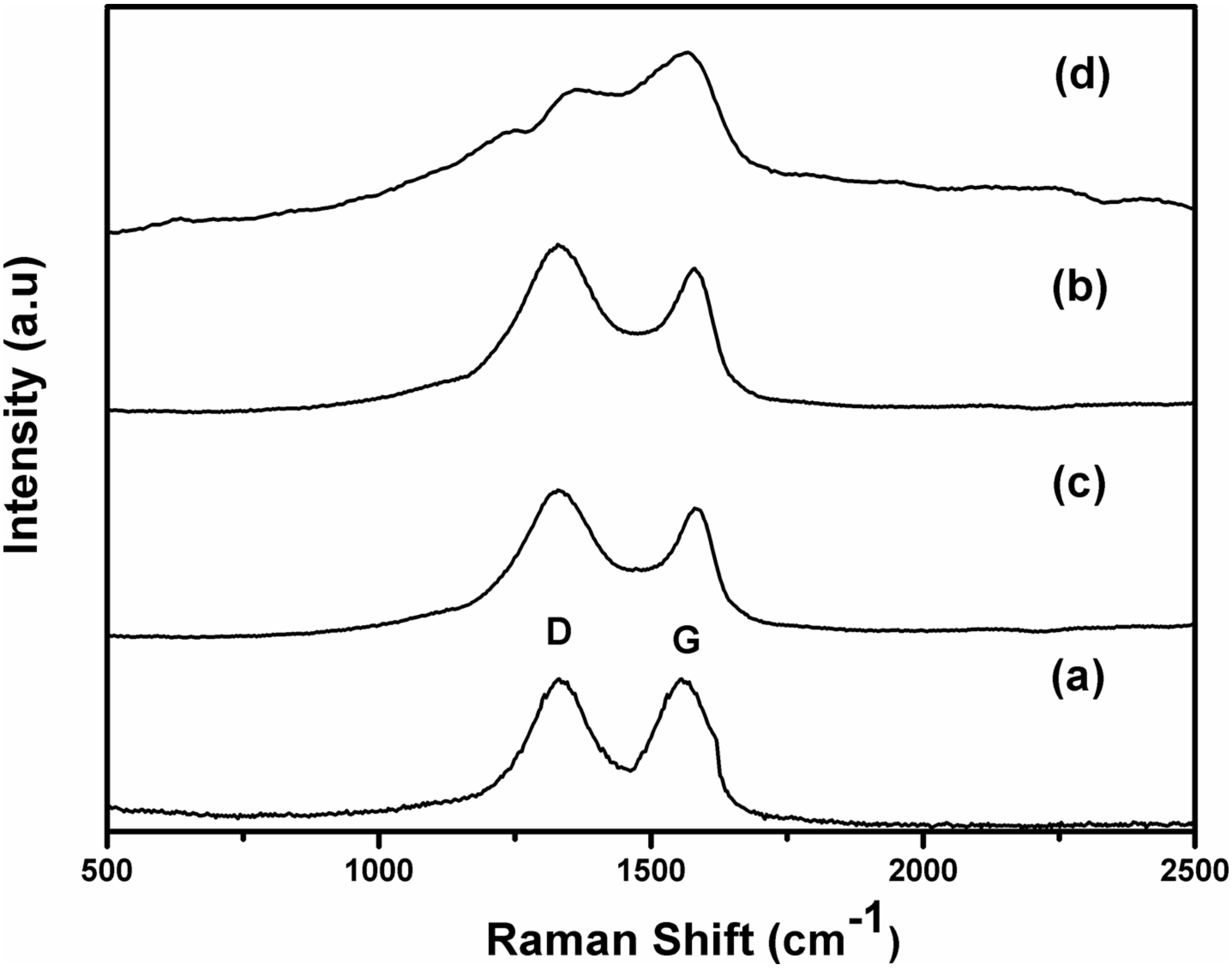


Fig. S7 Raman spectrums of (a) GO, (b) RGO, (c) Pd-RGO, and (d) Pd@C-RGO carbocatalysts.

Raman spectroscopic analysis is one of the most useful methods for the analysis of carbon-based materials, especially the graphene oxides. The Raman spectra of the GO, RGO, Pd-RGO and Pd@C-RGO materials, respectively. The GO exhibits two characteristic Raman peaks of the D (1359 cm^{-1}) and G (1593 cm^{-1}) bands. The D band corresponds to the breathing mode of the C-sp^2 atoms in the rings and also indicates the disorderness within the structure. The G band signifies the in-plane bond stretching motion in the C-C sp^2 atoms [12]. The I_D/I_G ratio for GO, RGO, Pd-RGO and Pd@C-RGO are 0.9901, 1.0784, 1.0780 and 0.9159, respectively. An increase in the I_D/I_G ratio indicates the formation of structural defects in the GO during the reduction process. As seen from Fig.S5. the I_D/I_G ratio of Pd-RGO is almost similar to that of the RGO. Whereas the I_D/I_G ratio of the Pd@C-RGO is very minimum at 0.9159 compared with that of the GO, RGO and Pd@C-RGO, a fact attributed to the carbon formed during the microwave irradiation. These results clearly indicate that the formation of the carbon product over the GO support occurs during the microwave irradiation process (Fig. S7).

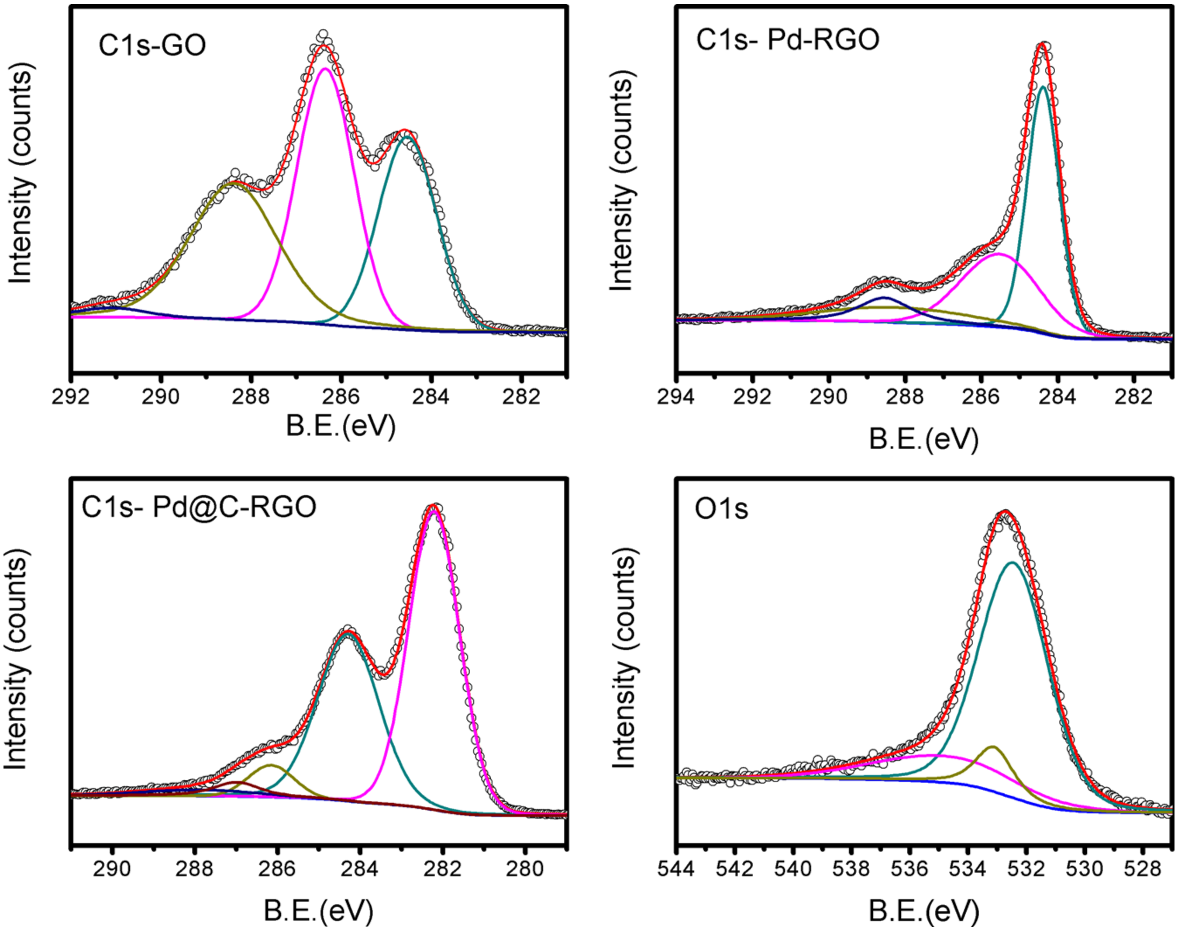
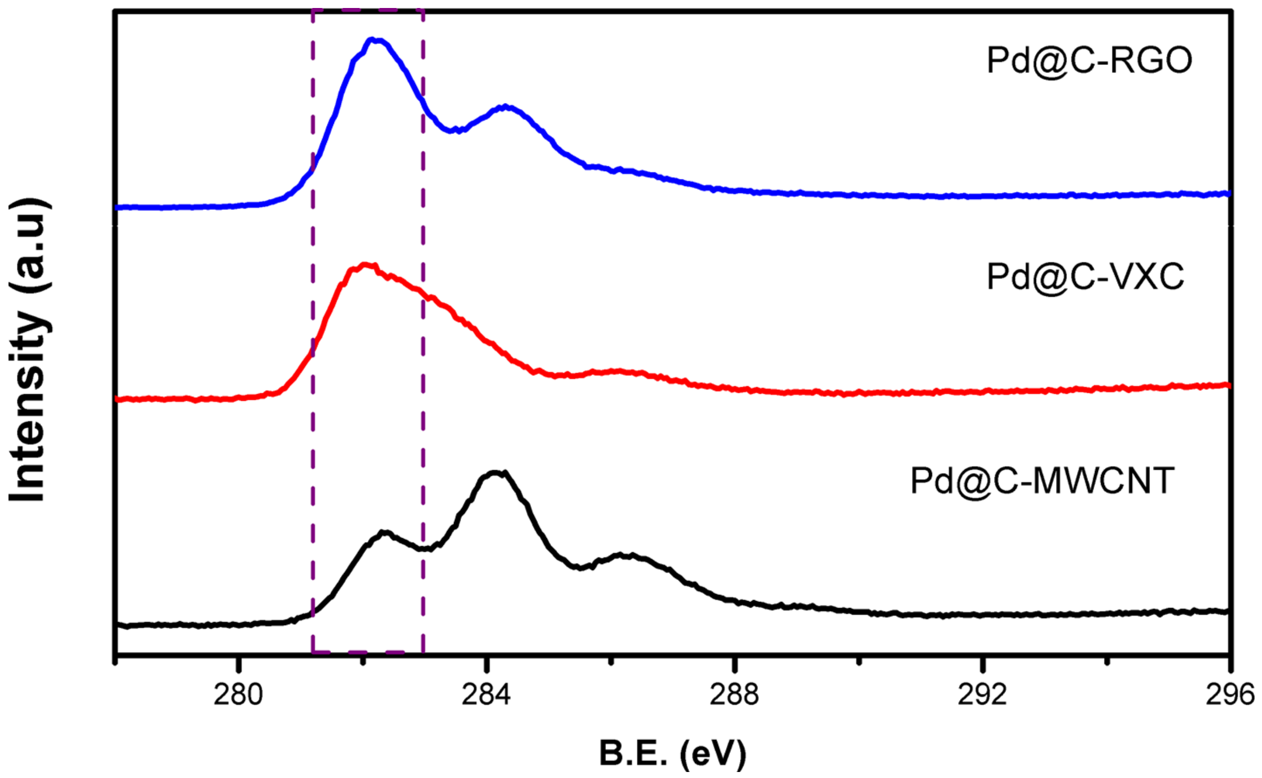


Fig. S8. XPS of C1s and O1s deconvoluated spectra of Pd@C at various carbon supports


Pd@C-RGO
Pd@C-VXC
Pd@C-MWCNT
Intensity (a.u)
280
284
288
292
296
B.E. (eV)

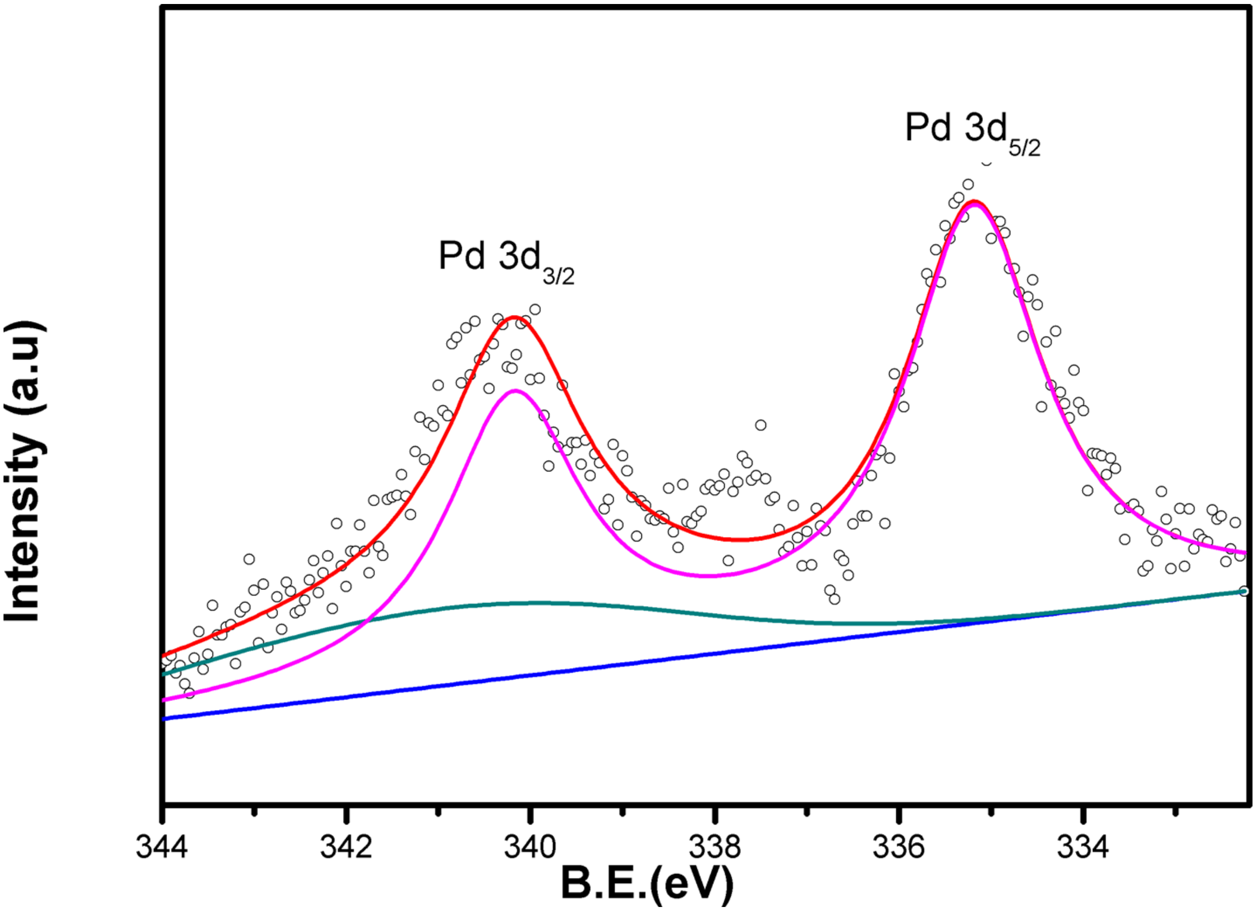


Fig. S9 XPS of C1s spectra of Pd@C at various carbon supports and Pd$_{3d}$ spectra of Pd@C-RGO.

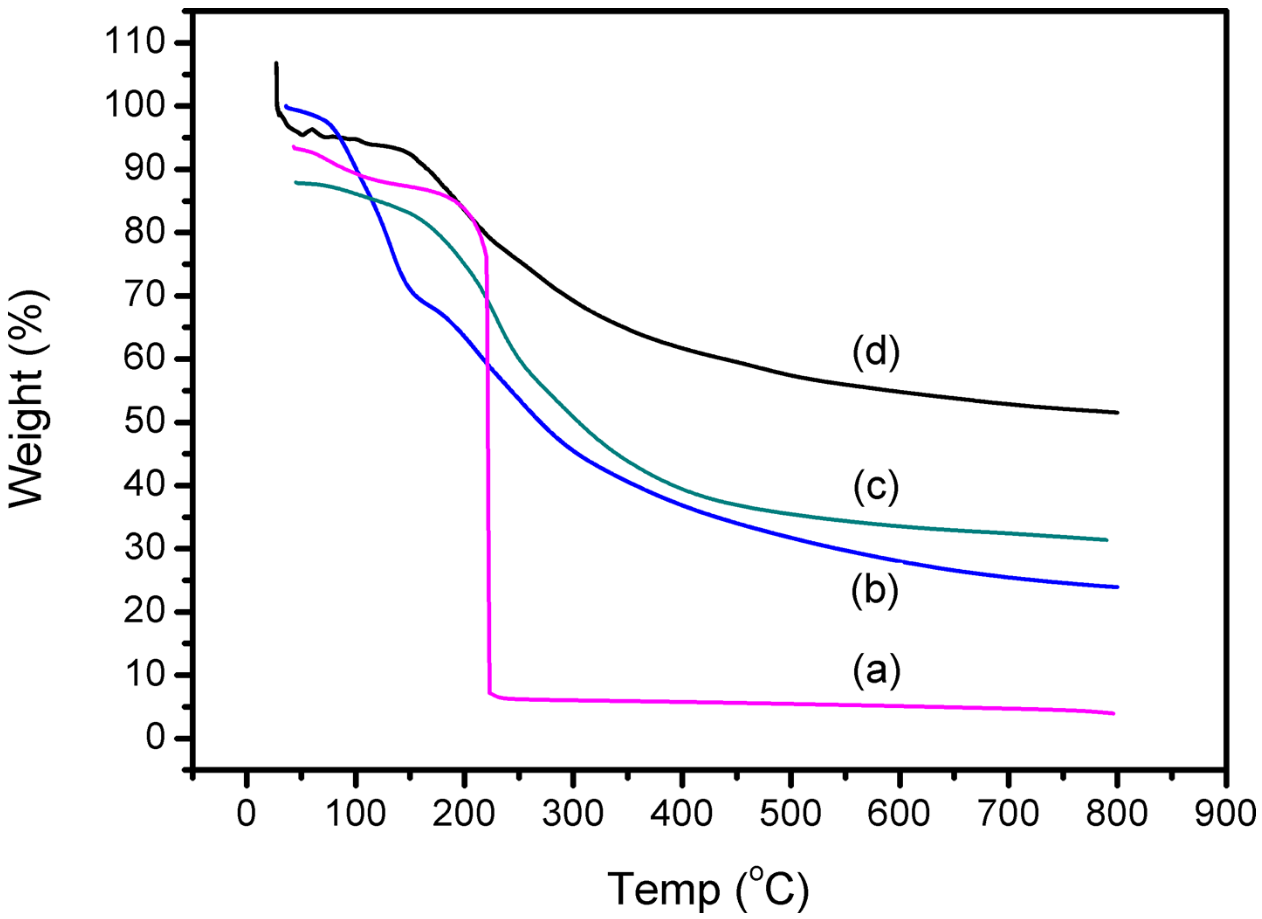


Fig. S10 Thermogravimetric analysis of (a) GO and (b) RGO, (c) Pd@C**C**-RGO and (d) Pd-RGO carbocatalyst.

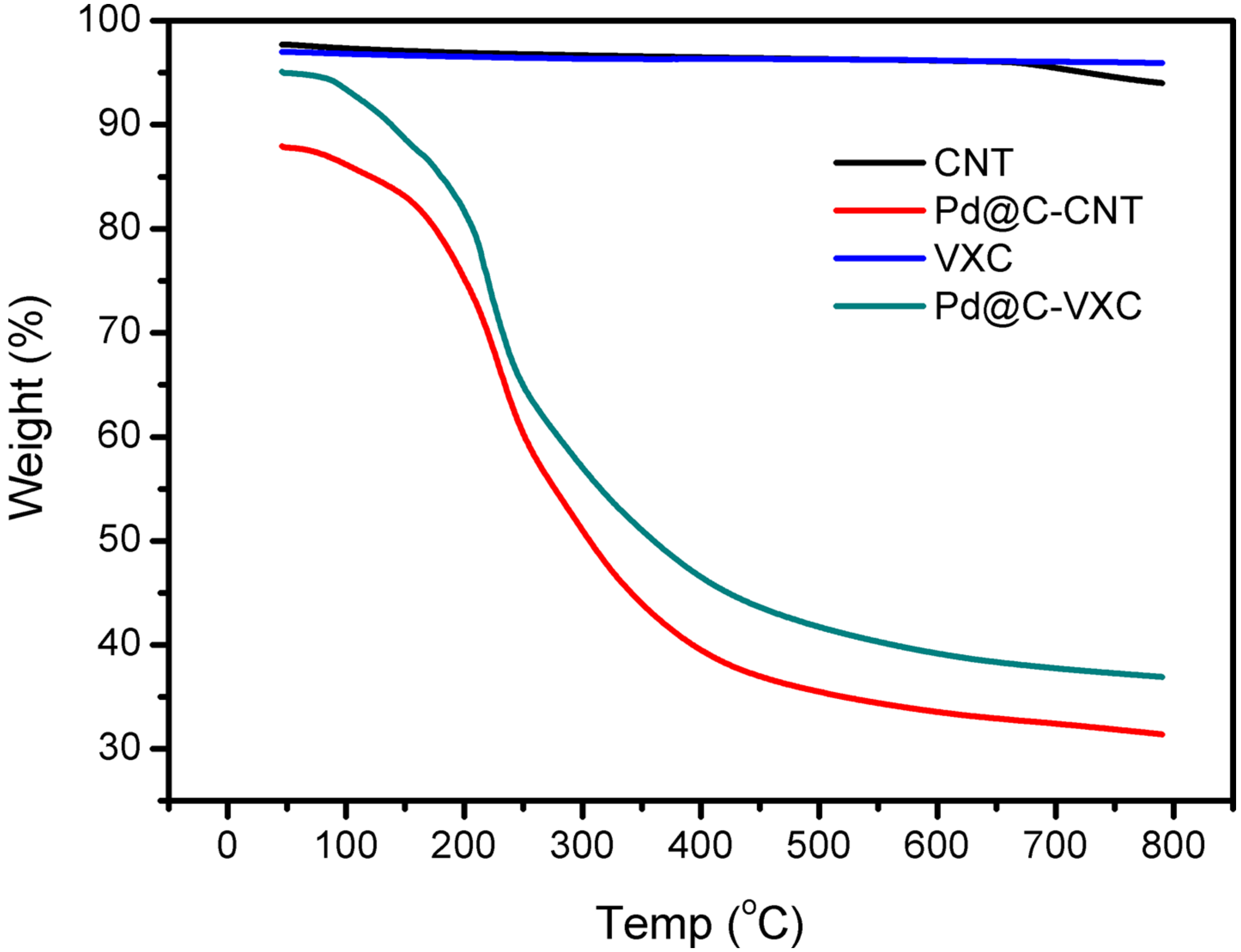


Fig. S11 Thermogravimetric analysis of MWCNT, VXC, Pd@C-MWCNT and Pd@C-VXC carbocatalyst.

The thermal stability of the Pd@C-RGO carbocatalyst thus prepared was analyzed by thermogravimetric analysis (TGA), from room temperature to 600°C in nitrogen atmosphere (Fig. S7). In the GO materials, the major weight loss occurred between 100-200°C, indicating the removal of the oxygen-containing functional groups present in the graphene [S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R. S. Ruoff, Carbon, 46, 1558 (2007)]. The TGA curve for Pd@C-RGO shows a major weight loss of about 90% at 220°C, indicating more oxygen containing functional groups were removed. On the other hand, the RGO, Pd-RGO and Pd@C-RGO showed higher thermal stability than the GO, the labile oxygen functionalities were removed upon reduction process. The RGO materials exhibit a two-step degradation in which the adsorbed water molecules are removed around 150°C, and a gradual weight loss of 65% observed at 600°C. However, in the presence of Pd, the thermal stability of improved markedly, although the Pd-RGO shows greater stability than the Pd@C-RGO. The improved thermal stability is due to the presence of the Pd nanoparticles and the Pd-RGO and Pd@C-RGO exhibit weight loss of 35% and 55% respectively. The higher weight loss of Pd@C-RGO is presumed to be due to the presence of carbon materials formed over the catalyst getting degraded around 200°C and the contents of the carbon material is higher in the Pd@C-RGO than the Pd-RGO. A similar trend was observed for Pd@C-MWCNT and Pd@C-VXC (Fig.S9).

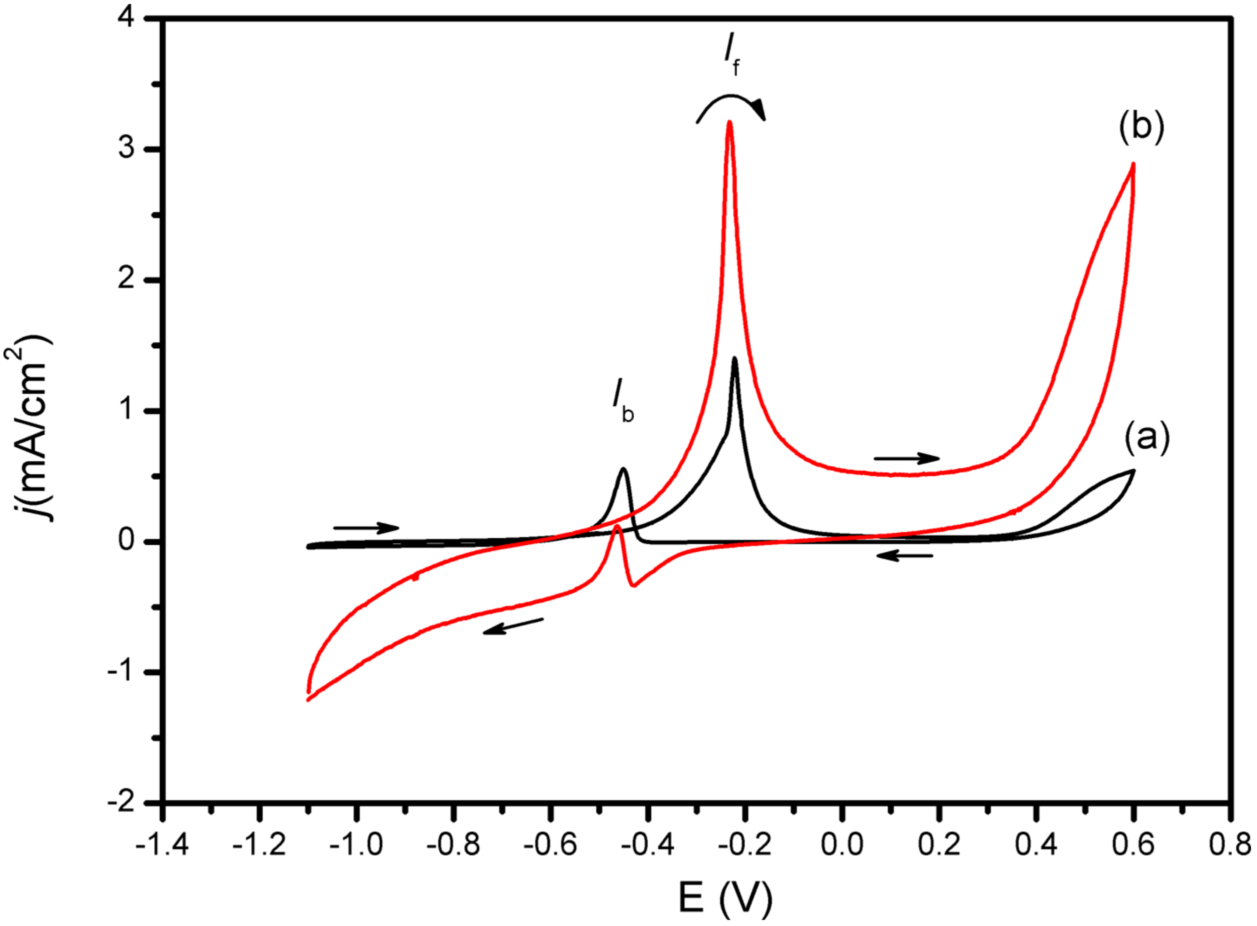


Fig. S12 CVs for the electrooxidation of Ethylene glycol over (a) Pd-RGO and (b) Pd@C-RGO carbocatalyst in nitrogen saturated 0.5 M EG + 1 M KOH solution.

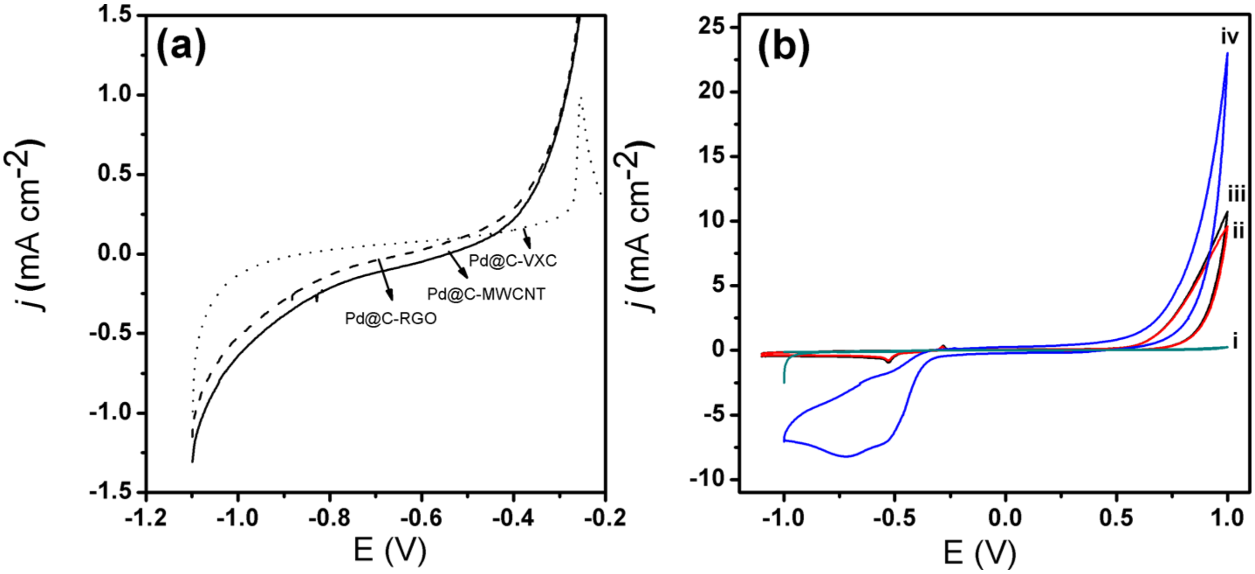


Fig. S13 (a) CV onset potentials for the electrooxidation of EG at various carbocatalyst, (b) Electrocatalytic activity of carbocatalyst towards oxygen evolution and oxygen reduction reactions. CV curves of OER and ORR at (i) bare GC electrode, (ii) Pd@C-VXC (iii) Pd@C-MWCNT and (iv) Pd@C-RGO cabocatalysts in nitrogen saturated 1 M KOH with a scanning rate of 25 mV/s.

We extended the CV potential range, the large anodic current appeared when the electrode potential was scanned between -1.1 V and +1.0 V, indicating the occurrence of the OER on the electrode surface. The bare glassy carbon electrode with the OER current was very minimal, although at the Pd@C-VXC and Pd@C-MWCNT electrodes, an almost equal peak current response is observed. The Pd@C-RGO exhibited the highest OER peak current response of 20 mA/cm^2.

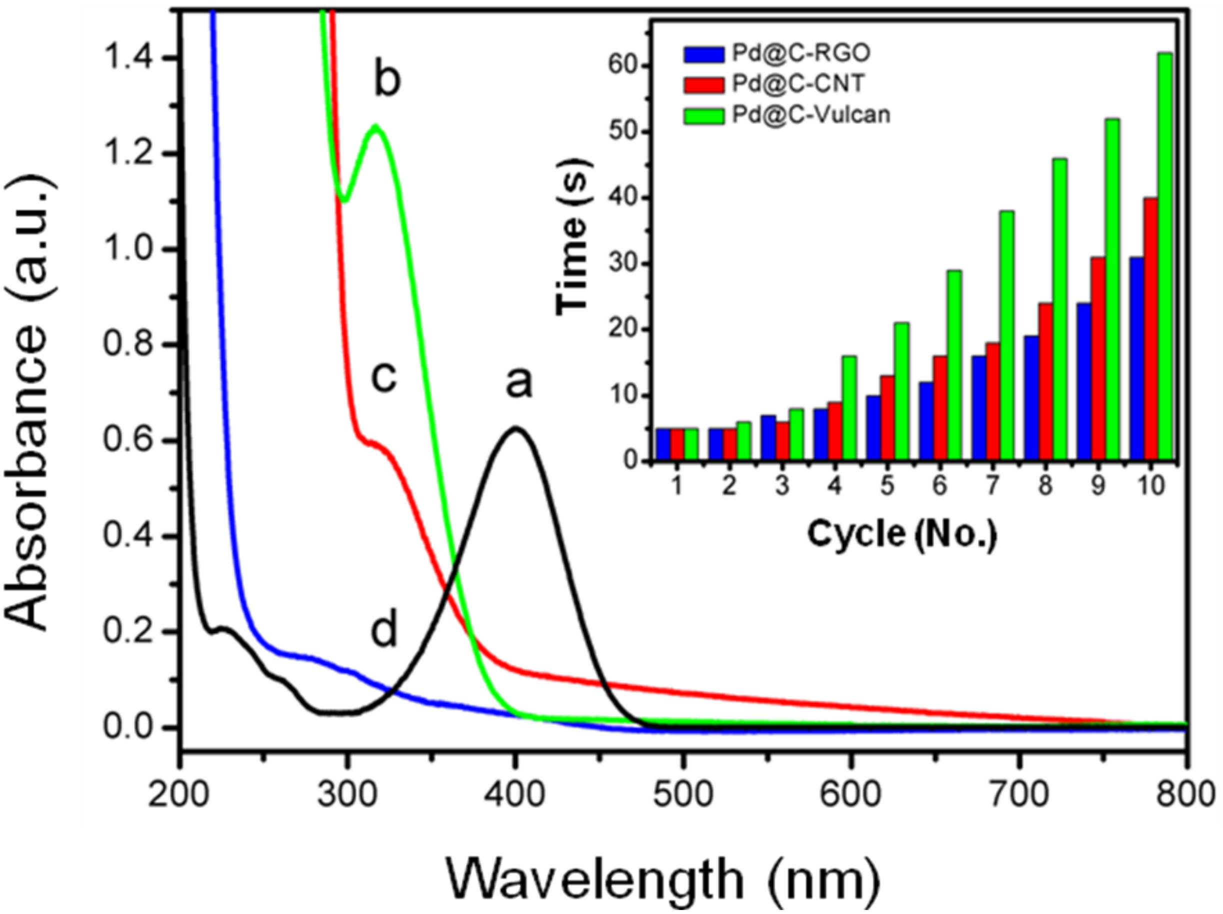


Fig. S14 UV-Vis spectra of 4-NP reduction (a) before and after 5 sec. with the addition of (b) Pd@C-VXC, (c) Pd@C-MWCNT and (d) Pd@C-RGO with $NaBH_4$ (Inset: The stability of the catalyst during 10 cycles of the same reduction reaction).

The catalytic activity of the Pd@C at the various supports was tested for the catalytic reduction of 4-nitropheneol (4-NP, $1x10^{-4}$M) to 4-amino phenol (4-AP) in the presence of sodium borohydride ($NaBH_4$, $0.5x10^{-4}$ M). The carbocatalysts exhibited excellent catalytic activity for the reduction of 4-NP in 5 s. The 4-AP formation was observed very clearly in the Pd@C-RGO carbocatalyst mediated reaction and the absorption peak for 4-AP was observed around 298 nm (Fig. S14)