Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Copper and Cobalt nanoparticles embedded in naturally derived graphite electrode for sensing of neurotransmitter Epinephrine

1. Materials and Methods:

1.1 Chemicals:

Epinephrine (>99%) was purchased from Sigma–Aldrich and used as received. Sodium tetrahydrido borate ($NaBH_4$), copper chloride dihydrate ($CuCl_2.2H_2O$), cobalt chloride ($CoCl_2$) and isopropyl alcohol were purchased form Merck and used as such. All other reagents and solvents such as hydrochloride, sulphuric acid and sodium hydroxide used were of analytical grade. Stock solutions of EP (1.0 mM) were prepared by dissolving the required amount of the compounds in double distilled water. The PBS solution with pH 7.2 was used as supporting electrolyte. All other reagents and solvents used were of analytical grade.

1.2 Preparation of carbon material:

The carbon catalyst was prepared from the cone of *pinus roxburghii* present in the Himalayan region (Solan, Himachal Pradesh, India). The cone was collected, cut it into pieces, washed with distilled water and dried in sun for 4-5 days and dried in a hot oven at 60ºC for 24 hours. The pine cone was treated with N/10 NaOH followed by washing with dilute HCl. The material was filtered under vacuum and washed with distilled water till all the washings are neutral. The material was dried at 45ºC and then heated in a tube furnace under nitrogen at 700ºC for 4 h. The furnace was cooled slowly to room temperature and the material was grounded to the fine powder with pestle and mortar to get the carbon material. The material was further stirred with sulphuric acid (conc.) at 30-35ºC for 5 h and filtered on a sintered glass funnel. The residue was washed with distilled water till all the washings were neutral. The wet solid was dried in an oven at 40-45ºC to get a free flowing powder that was used as such for supporting the Cu and Co nanoparticles.

1.3 Copper nanoparticles supported on carbon (Cu/G):

$CuCl_2.2H_2O$ (50 mg) was dissolved in isopropyl alcohol (30 mL) and carbon material (0.5 g) prepared in 2.2 was added to it. The Cu nanoparticles were deposited on the support after the reduction of $CuCl_2$ by the addition of 0.012 moles of $NaBH_4$ with the continuous stirring for 2.0 h. The mixture was stirred at room temperature till the evolution of gas stops. The stirring was stopped and the contents were allowed to settle down. The residue was filtered, washed with distilled water (5 X 30 mL) and dried in an oven at 40-45°C.

1.4 Cobalt nanoparticles supported on carbon (Co/G):

$CoCl_2$ (50 mg) was dissolved in isopropyl alcohol (30 mL) and carbon material (0.5 g) prepared in 2.2 was added to it. To this solution, $NaBH_4$ (0.012 moles) was added with the continuous stirring for 2.0 h. The stirring was stopped and the residue was allowed to settle, filtered, washed with distilled water (5 X 30 mL) and dried in an oven at 40-45°C.

1.5 Copper and Cobalt nanoparticles supported on carbon (Cu+Co@G):

$CuCl_2.2H_2O$ (26.5 mg, 0.18 mMol) and $CoCl_2$ (23.5 mg, 0.18 mMol) were dissolved in isopropyl alcohol (30 mL) and carbon material (0.5 g) prepared in 1.2 was added to it. To this solution, $NaBH_4$ (0.012 moles) was added with the continuous stirring for 2.0 h. The stirring was stopped and the residue was allowed to settle, filtered, washed with distilled water (5 X 30 mL) and dried in an oven at 40-45°C.

1.6 Characterization techniques:

The High Resolution Transmission Electron Microscopy (HRTEM), X-ray Energy Dispersive Spectroscopy (EDS) analysis and electron irradiations were performed in FEI Tecnai G^2 F30 microscope in which an electron beam produced from the field emission gun, operated at 300 KeV. X-ray photoelectron spectroscopy (XPS) using a Thermo Electron Corporation ESCA Lab250 spectrometer at 15kV and 150 W was employed to study the surface characteristic of synthesized samples. The crystalline phases and structures of the materials were characterized with X-ray diffraction (XRD) using a Rigaku D/max 2200V/PC diffractometer with Cu Ka radiation ($\lambda = 1.54178$ Å).The voltammetric study was done with cyclic voltammetric system BioLogic SP-200 and analyzed using EC Lab 10.37 software. In voltammetric detection conventional three-electrode system consisting of a modified glassy carbon (GCE) as working electrode, platinum auxiliary electrode and silver chloride as a reference electrode was employed for detection. All electrochemical measurements were performed using 0.1M PBS (Phosphate buffered saline) (pH−7.2) as the supporting electrolyte. The cyclic voltammograms were obtained by scanning the potential from -1.0 V to +1.0V V vs. Ag/AgCl and at a scan rate of 100 mVs^{-1}.

1.7 Electrode Modification Procedure:

The surface of the working electrode (GCE) was prepared by polishing in an aqueous slurry of alumina nanopowder (LabChem) using a SiC-emery paper. The electrode was put through the ultrasonic vibration for 5 minutes in double distilled water and ethanol is used to remove the remaining alumina particles on the surface of the electrode. A suspension of Cu@G (sample 1), Co@G (sample 2)and Cu+Co@G (sample 3) in N, N-dimethyl formamide (DMF) was prepared by dissolving 5.0 mg of each in 1.0 mL DMF using ultra sonication. The modified electrodes of GCE-Cu@G (Glassy Carbon Electrode Cu@G), GCE-Co@G (Glassy Carbon Electrode Co@G) and GCE-Cu+Co@G were prepared by drop-dry method. 5.0 µL drops of all the sample suspensions were dropped on the bare GCE electrode and then the solvent allows to evaporating at room temperature.

Figures

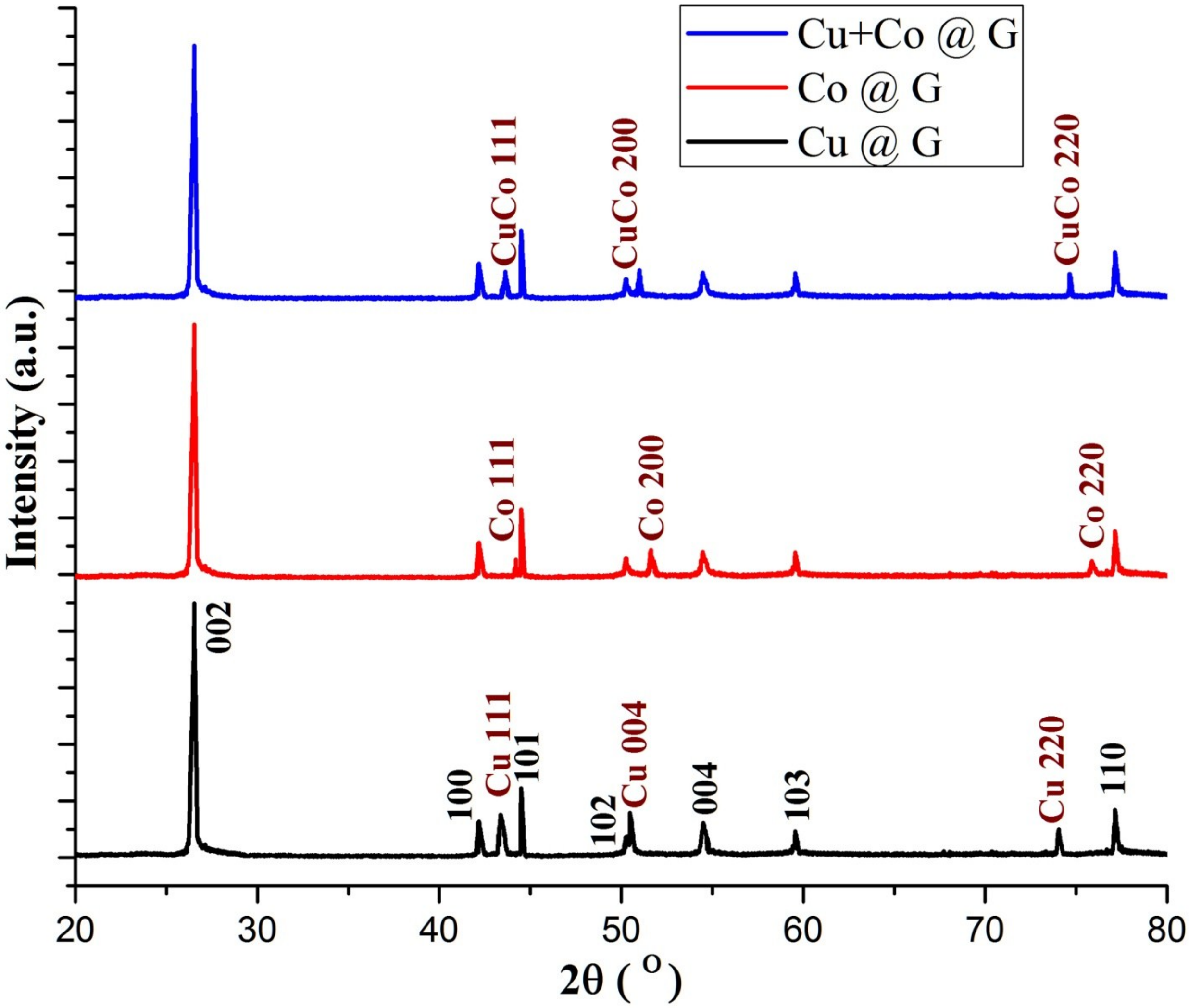

Fig.1S: XRD pattern of the metal embedded naturally derived graphite powder sample. The corresponding lattice planes are indicated near the peaks.

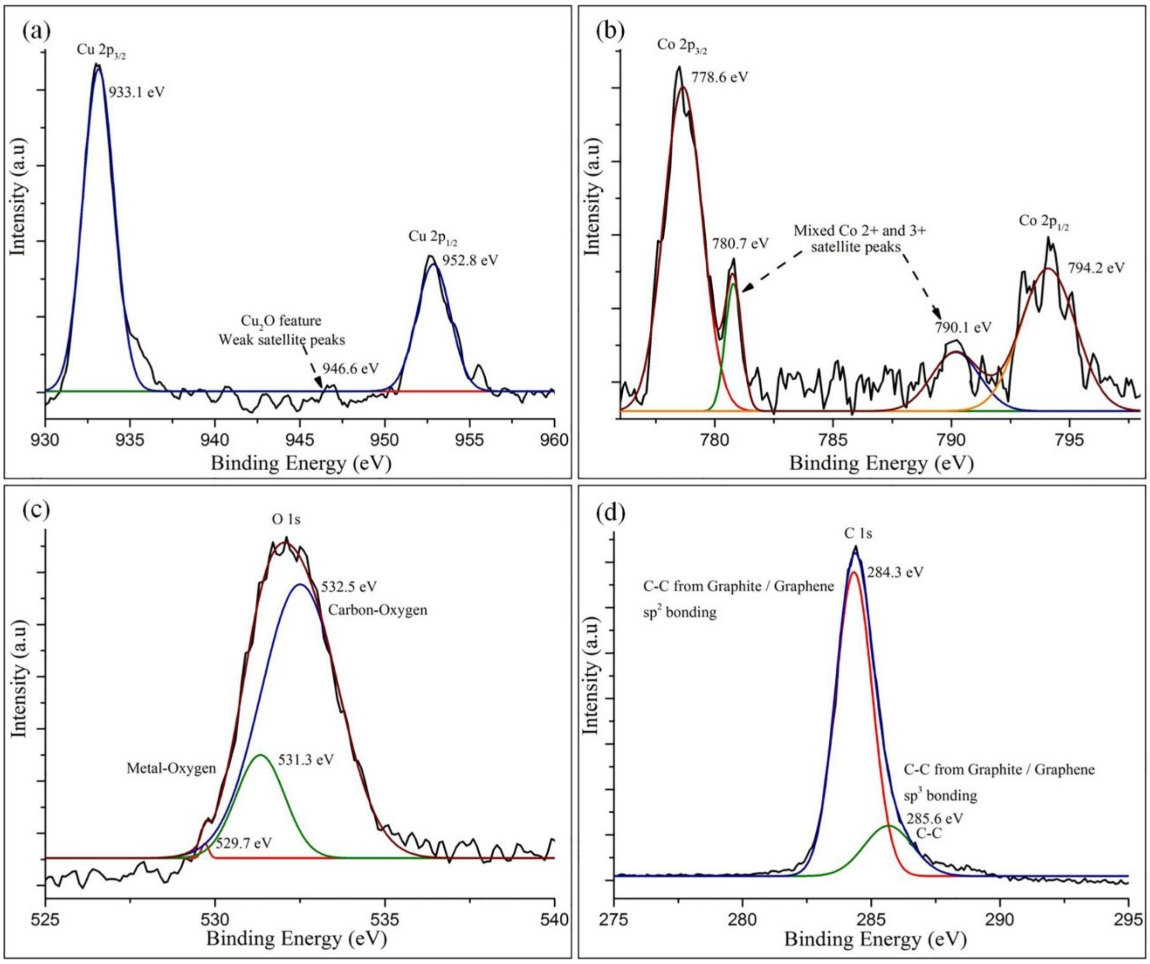

Fig.2S. (a), (b), (c) and (d) XPS narrow scan spectra of Cu (sample 1), Co (sample 2), O (sample 3) and C (sample 3), respectively. The deconvoluted spectra also plotted after baseline correction of obtained one.

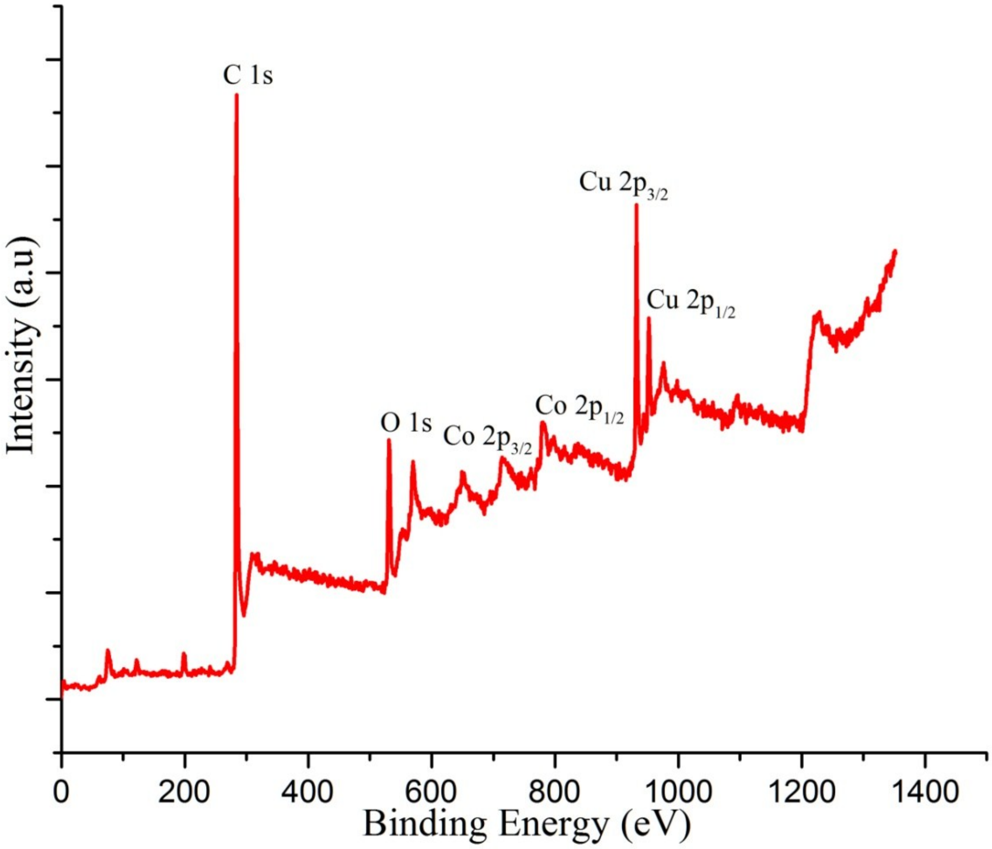

Fig. 3S. XPS Survey scan spectra of sample 3.

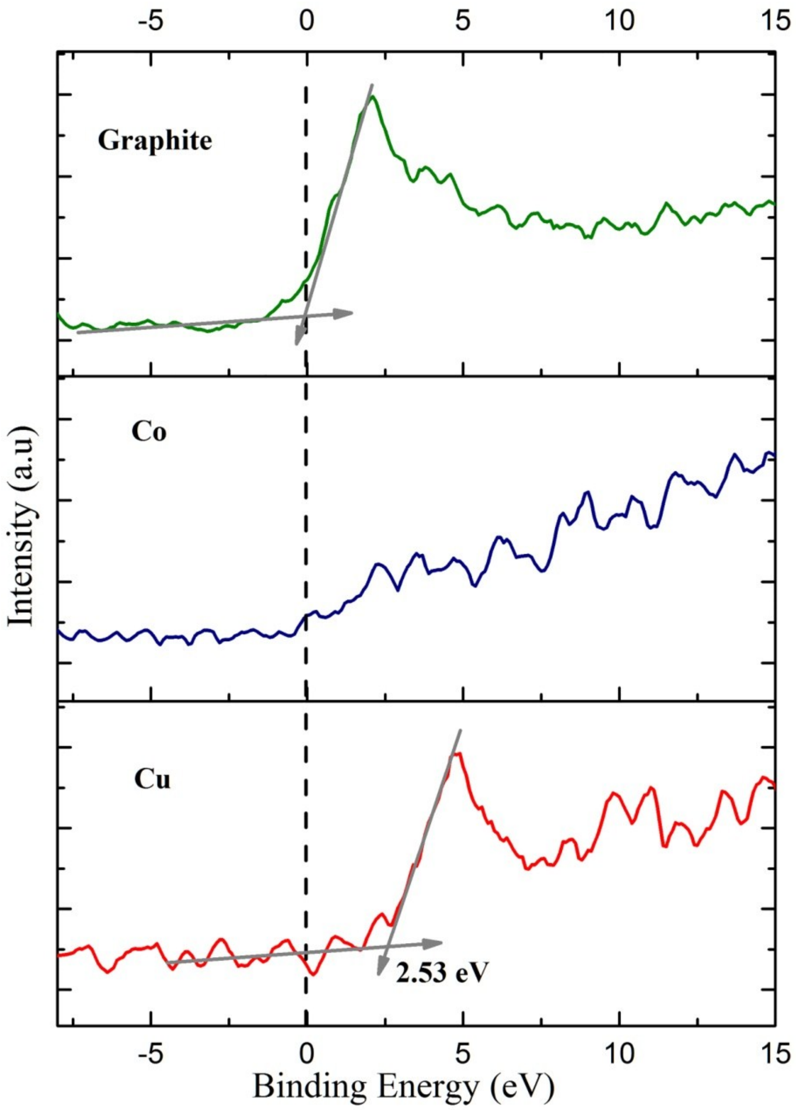

Fig.4S. The valence-band XPS spectrum of graphite (green), Co (blue) and Cu (red)

We scrutinize the valence band and the Fermi level of the samples to study the electronic band structure of metal embedded graphite. The valence-band (VB) XPS spectrum of graphite, Co and Cu is shown in Fig. 3S. The graphite structure has layers of fused hexagonal rings, with four atoms in the primitive cell. Its valence-band structure has eight filled bands instead of four. As expected, the result indicates a zero band gap for graphite. Graphite is the conductive material, whose Fermi level lies on the VBM (valence band maximum) and CBM (conduction band minimum). For the Co Cu, the spectra shown have been obtained from the experimental ones subtracting the graphite contribution, which does not show any structure around the Fermi edge. In the Cu VB spectrum, the 3d peak, which is located in bulk Cu at about 2.4 eV with respect to the Fermi level, moves towards higher binding energy 2.53 eV owing to the size and quantum confinement in the nanoscale system. There is no significance observation is recorded in the Co spectrum (which may caused by the presence of least amount).

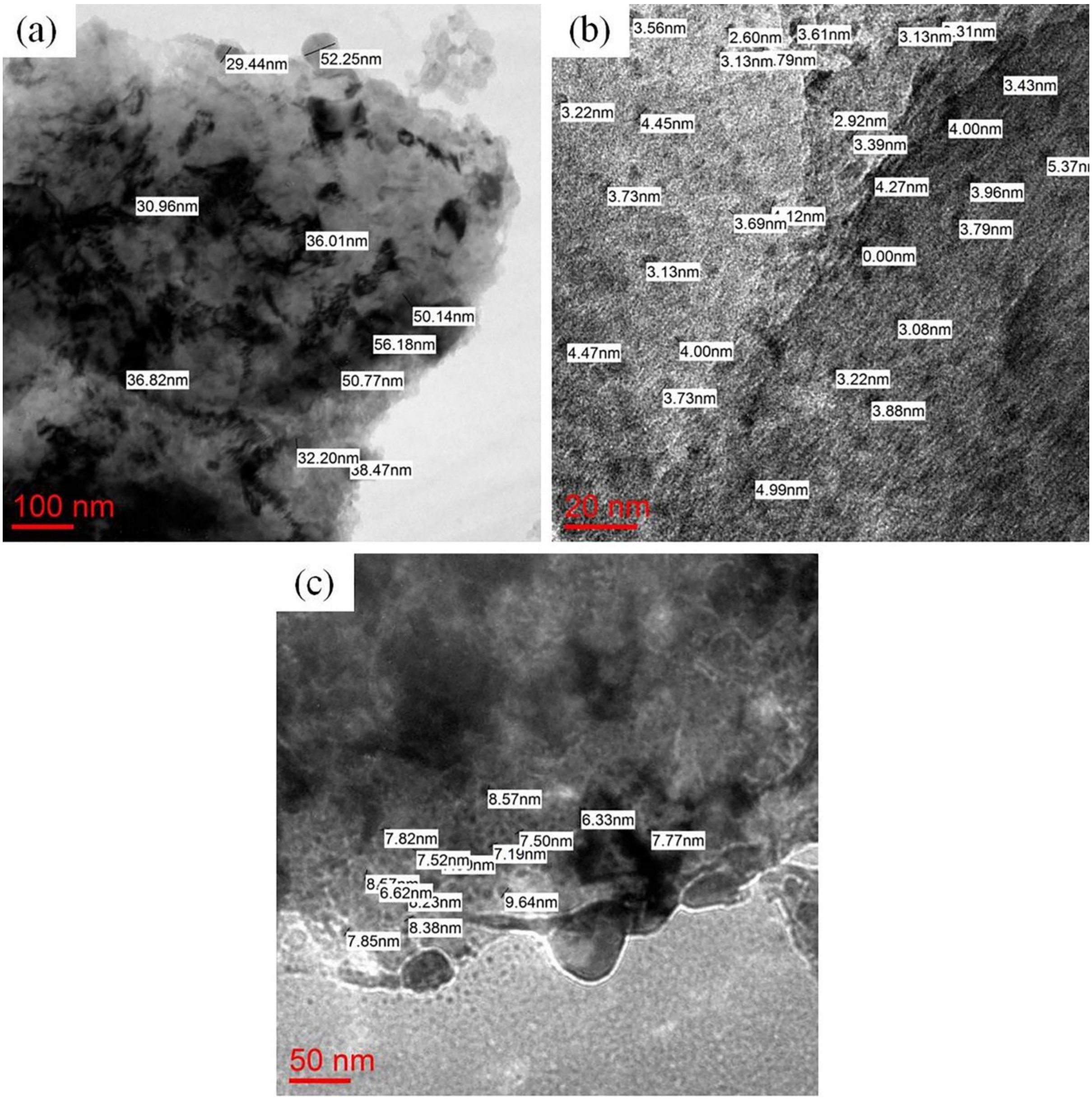

Fig.5S. (a-c) particle size analysis of sample 1,2 and 3, respectively from Raw TEM images.