

Supplementary information

## **Fabrication of branched nanostructures for CNT@Ag nano-hybrids: Application in CO<sub>2</sub> detection**

*Beant KaurBilling<sup>a</sup>, Prabhat K. Agnihotri<sup>a\*</sup> and NarinderSingh<sup>b\*</sup>*

Figure S1: SEM analysis of unpurified CNTs.

Figure S2: EDX spectrum of unpurified CNTs and CNT@Ag nano-hybrid.

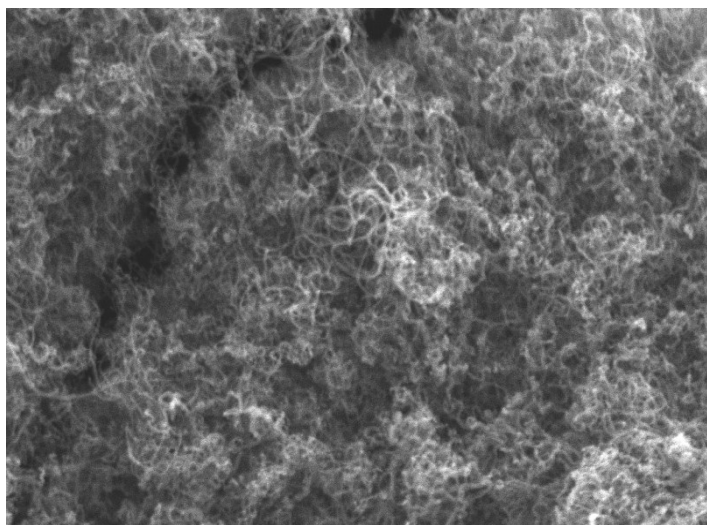
Figure S3: FTIR spectrum of unpurified and acid treated purified CNTs

Figure S4: SEM and EDX micrographs showing tree like structure with increased amount of reducing agent.

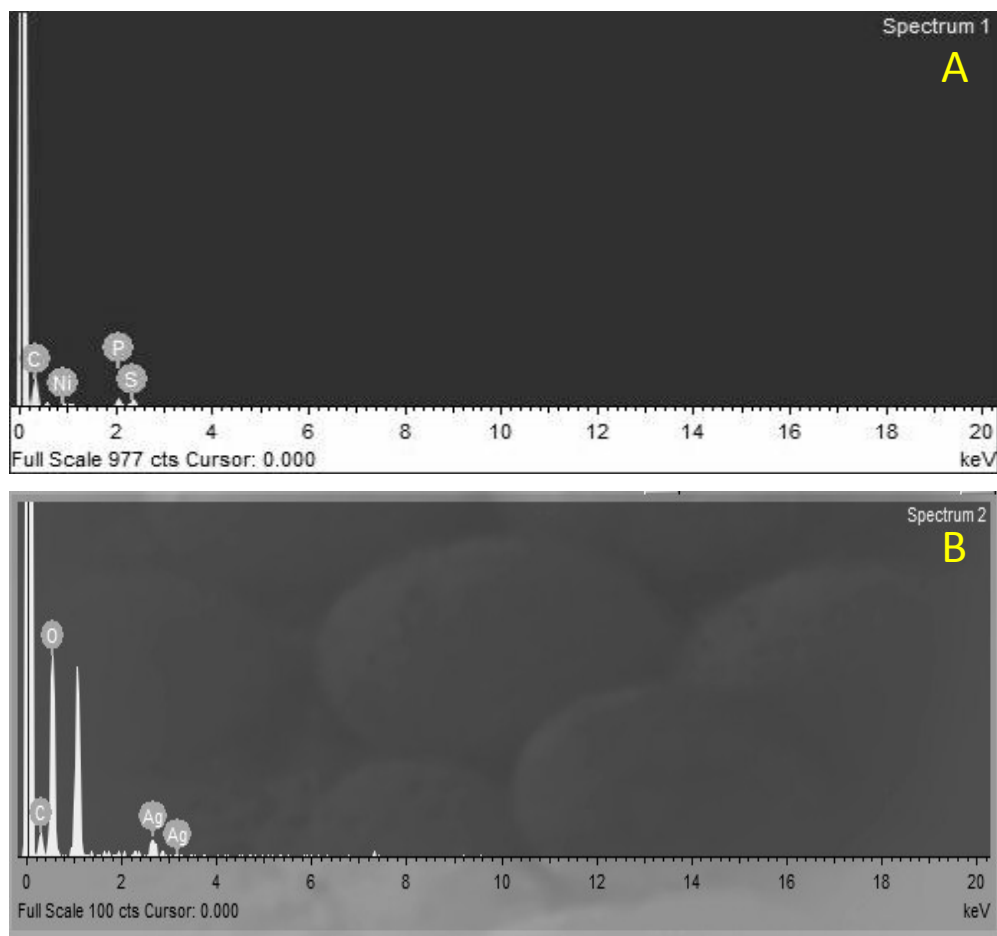
Figure S5: <sup>13</sup>C NMR spectra of CO<sub>2</sub> flushed CNT@Ag showing oxalate ion peak at 175 ppm.

Figure S6: Plot of response time of Host.CO<sub>2</sub> complex upon addition of different concentrations of CO<sub>2</sub> to Host solution in time interval of 1-150 minutes.

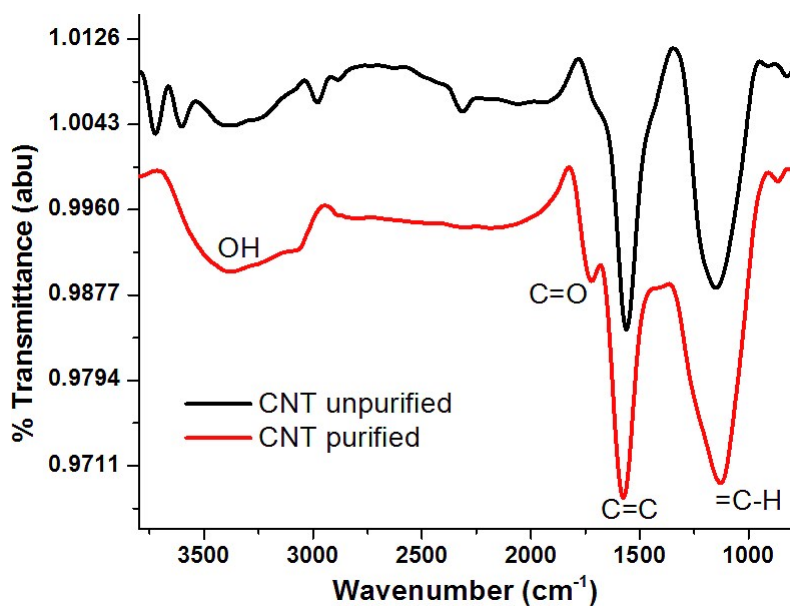
Table S1: Comparison data of published manuscripts vs proposed manuscript on detection of CO<sub>2</sub>.



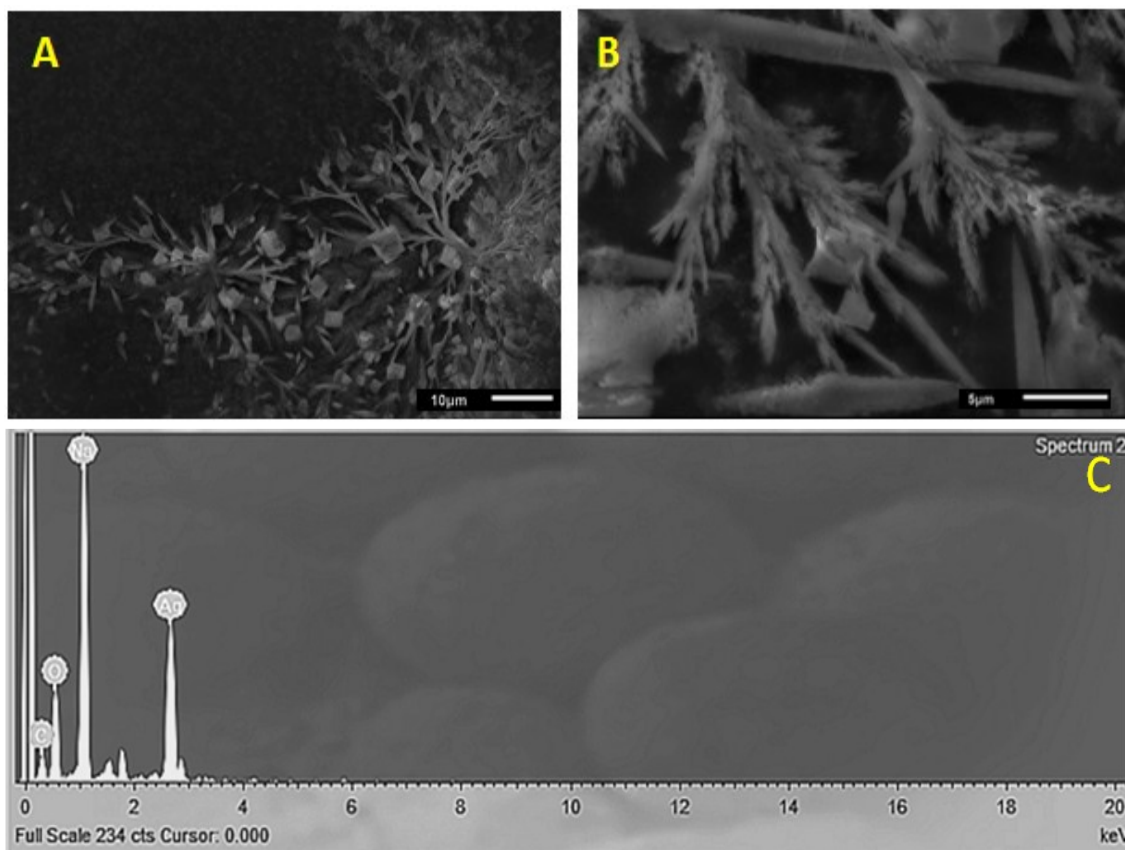
**Figure S1:** SEM analysis of unpurified CNTs.



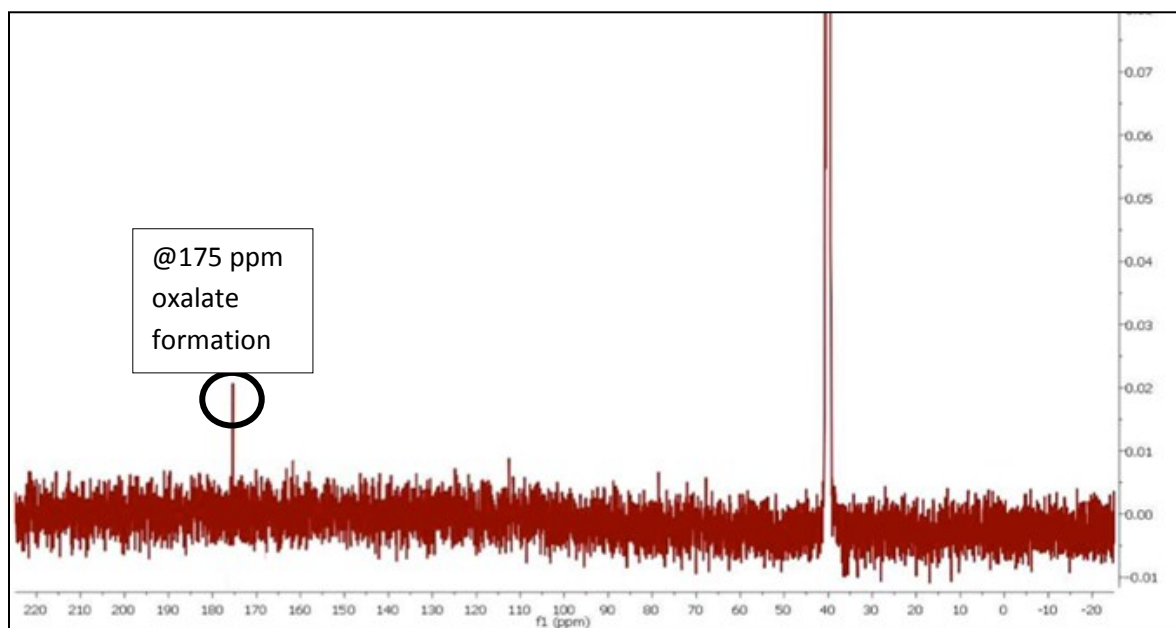
**Figure S2:** EDX spectrum of A) unpurified CNTs and B) CNT@Ag nano-hybrid.



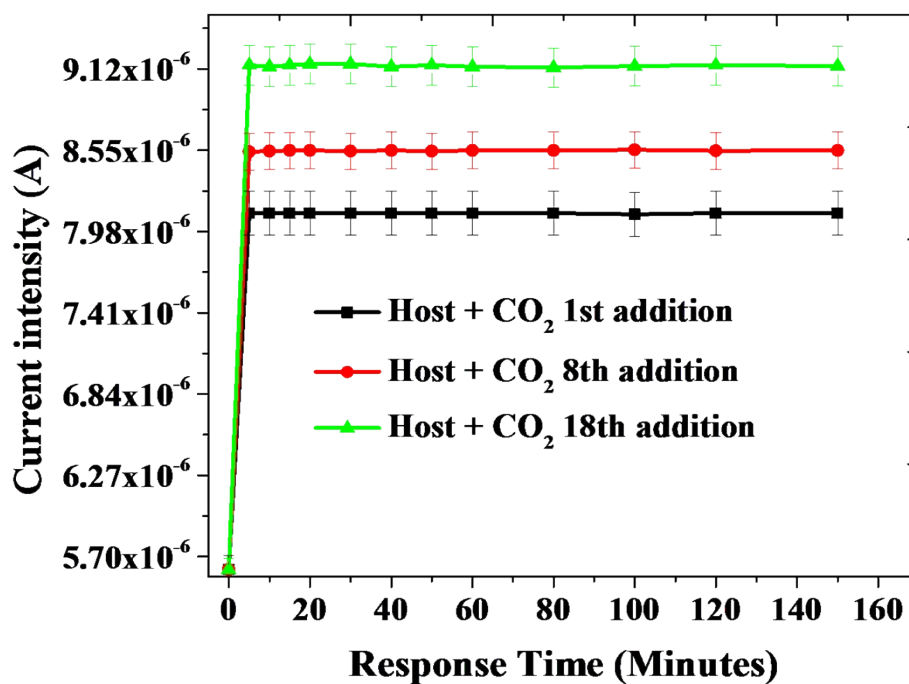
**Figure S3:** FTIR spectrum of unpurified CNTs vs acid treated purified CNTs



**Figure S4:** A) and B) SEM image showing tree like structure with the increased amount of reducing agent at different scales and C) EDX spectrum showing high concentration of Na as compared to other elements.



**Figure S5:**  $^{13}\text{C}$  NMR spectra of  $\text{CO}_2$  flushed  $\text{CNT@Ag}$  showing oxalate ion peak at 175ppm.



**Figure S6:** Plot of response time of  $\text{Host}.\text{CO}_2$  complex upon addition of different concentrations of  $\text{CO}_2$  to Host solution in time interval of 1-150 minutes.

**Table S1:** Comparison data of published manuscripts vs proposed manuscript on detection of  $\text{CO}_2$ .

Method followed for detection/adsorption	Material Used	Medium	Surface Area	Detection Limit	Reference
NMR Spectroscopy	Polyurethranes	Solid state	300ms/g	-	34
Fluorescent spectroscopy	Hexaphenylsilole	Aqueous	-	-	35
Fluorescent spectroscopy	Tetrapropyl benzobisimidazolium salts (TBBI)	$\text{CH}_3\text{CN}$	-	$1.2 \times 10^{-6} \text{M}$	36
Fluorescent	Tetraphenylethyle	Aqueous	-	$5 \times 10^{-6} \text{M}$	37

spectroscopy	ne derivative				
Colorimetric and Fluorescent spectroscopy	Polydiacetylene	Aqueous	-	-	38
Fluorescent spectroscopy	Imine and $\beta$ -ketoenamine based COFs	Aqueous	-	-	39
UV Absorption spectroscopy	Au nanoparticles	Aqueous	-	0.0024 hPa	40
Visible light plasmonic	Au-ZnO	Aqueous	12ms/g	-	41
Luminescence spectroscopy	ZnO MOF	Aqueous	-	-	42
Photoelectrocatalytic reduction	Semiconducting powder	-	-	-	43
Electrochemical	CNT@Ag nano-hybrid	Aqueous	525.07ms/g	52 X 10 <sup>-9</sup> M	Present Manuscript

Water resources such as oceans, rivers and lakes are major CO<sub>2</sub> sink. The oceans absorb 22 million tons of carbon dioxide every day.<sup>44</sup> Although this absorption is said to significantly reduce atmospheric greenhouse-gas levels, it has also been observed that such an excess of CO<sub>2</sub> may be altering the chemistry and biology of the oceans.<sup>45</sup> Higher uptake of CO<sub>2</sub> results in increase in acidity and decrease in pH of seawater. Mollusks, corals and a class of fish and sea urchins are the worst affected by the uptake of CO<sub>2</sub> by the seas. The current rate of change in ocean conditions is simply too high for many marine animals to adapt,<sup>46</sup> therefore to avoid further harm, authors chose to put an effort on the development of CNT@Ag hybrid sensor. It recognizes CO<sub>2</sub> in aqueous medium with a detection limit of 52nM. The novelty of sensor lies in the recognition of CO<sub>2</sub> in aqueous medium using electrochemical method. Detection limit is the major factor to distinguish present work from the literature reports. Present sensor can detect a minimum amount of 52nM of CO<sub>2</sub>, which shows a clear progress in detection of CO<sub>2</sub> among all literature reports. The novelty of sensor lies in the recognition of CO<sub>2</sub> in aqueous medium using electrochemical method. Also, we can see that tedious carbon chains were first synthesized and then employed for sensing applications. In present method, no such tedious organic compounds were synthesized but nano-hybrids were fabricated from CNTs and Ag nanoparticles. Also electrochemical studies

compared of CV, DPV and LSV are easy to understand. Moreover, CO<sub>2</sub> conversion to useful material has also been done in present manuscript, which has made this work superior. In addition to all above factors, CNT@Ag nano-hybrid offers more surface area, that is why it exhibits more sensitivity towards CO<sub>2</sub> detection.