Unraveling Hydrogen Adsorption Kinetics of Bimetallic Au-Pt Nanoisland-Functionalized Carbon Nanofibers for Room-Temperature Gas Sensor Applications

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SUPPORTING INFORMATION

SEM elemental analysis:

Surface morphology and elemental mapping of Au-Pt nanoislands on the surface of carbon nanofibers are evaluated using scanning electron microscopy shown in figure S1. Surface of the carbon nanofibers are anchored by bimetallic Au-Pt nanoparticles throughout. It was observed that the nanoparticles are uniformly surface anchored above the carbon nanofibers. Elemental mapping of bimetallic CNFs@Au-Pt NIs reveals the uniform distribution of Au-Pt nanoparticles.
Figure S1 a) SEM image, b) Live map image and elemental mapping of c) combined d) Carbon e) Pt and f) Au of CNFs@Au-Pt NIs.

XPS Analysis:
The XPS full survey spectra (figure S2a) of CNFs@Pt NIs hybrids display four predominant peaks at 532, 400, 284 and 71-75eV corresponding to O1s, N1s, C1s and Pt4f substantiates the presence of elements, such as oxygen, nitrogen, carbon and platinum. High resolution XPS spectra for the C1s region around 285 eV are shown in figure S2a. The C1s signal was deconvoluted into four components. The first peak at 284.7 eV was attributed to C=C bonds and is believed to have originated from an amorphous carbon phase or from adventitious carbon. The second peak at 285.9 eV is characteristic of C–OH groups. Third peak at 288.94 eV corresponds to C=O bonds. The last small broad band at 290.6 eV was assigned to the shakeup π–π* satellite, which is a common feature of graphitic carbon in XPS. The deconvoluted high-resolution O1s spectra of CNFs@Pt NIs indicate the presence of C=O (531.08 eV), C-OH (532.46 eV) and COOH (533.52 eV), which are well agreement with the identifications from O1s spectra. As
illustrated in Figure S2b the deconvoluted N1s spectra of carbon nanofibers indicate the presence of four types of nitrogen bonding states in the support material, such as pyridinic nitrogen (398.48 eV), pyrrolic nitrogen (400.07 eV), graphitic N (401.95 eV) and pyridinic-N-oxide (404.5 eV). A high-resolution spectrum of Pt 4f was found to be emerged as a doublet peak with a 4f 7/2:4f 5/2 with intensity ratio of 4:3, which is originated from the spin orbital coupling of 4f photoelectron transitions. In addition to this, the non-symmetrical peaks of Pt 4f orbital suggest the presence of more than one oxidation state. Hence, these peaks were further deconvoluted and fitted into four peak signals. According to literature, the lowest binding energy components associated with the most intense peaks at 70.78 and 74.2 eV can be attributed to zero valent metallic state platinum nanoparticles. The second pair of higher binding energy peaks appearing at 71.88, 75.26 eV and 76.1 eV are assigned to platinum oxide and hydroxides namely, PtO and Pt (OH)₂. Moreover, there are no other peaks substantiate the purity of the sample, and the predominant Pt 4f peaks confirmed the successful synthesis of the Pt monometallic nano islands over the surface of carbon nanofibers. Therefore, it can be concluded that Pt existed in metallic state in the CNFs@Pt nanohybrids.
Figure S2: The high resolution XPS spectrum of a) C1s b) N1s c) O1s and d) Pt4f of CNFs@PtNIs.

The XPS full survey spectra (figure S3a) of CNFs@Au NIs hybrids display four predominant peaks at 532, 400, 284 and 84 eV corresponding to O1s, N1s, C1s and Au4f substantiates the presence of elements, such as oxygen, nitrogen, carbon and gold. High resolution XPS spectra for the C1s region around 285 eV are shown in figure S3a. The C1s signal was de-convoluted into four components. The first peak at 284.7 eV was attributed to C=C bonds and is believed to have originated from an amorphous carbon phase or from adventitious carbon. The second peak at 286.24 eV is characteristic of C–OH groups. Third peak at 288.4 eV corresponds to C=O bonds. The last small broad band at 290 eV was assigned to the shakeup $\pi-\pi^*$ satellite, which is
a common feature of graphitic carbon in XPS. The deconvoluted high-resolution O1s spectra of CNFs@Au NIs indicate the presence of C=O (530.6 eV), C-OH (532.2 eV) and COOH (533.8 eV), which are well agreement with the identifications from N1s and O1s spectra. The Au 4f spin orbital splitting spectra exhibit two strong peaks emerging at 83.7 and 87.3 eV, corresponding to the BEs of Au 4f \(_{7/2}\) and Au4f \(_{5/2}\). Moreover, there are no other peaks substantiate the purity of the sample, and the predominant Au 4f peaks confirmed the successful synthesis of the Au monometallic nano islands over the surface of carbon nanofibers. It can be concluded that Au existed in metallic state in the CNFs@Au nanohybrids.

![Figure S3](image)

Figure S3 The high resolution XPS spectrum of a) C1s b) N1s c) O1s and d) Au4f of CNFs@Au NIs.
Figure S4  a) XPS spectra of CNFs@Pt, CNFs@Au, and CNFs@Au-Pt NIs and b &c) Comparison of high resolution XPS spectra of Au$4f$ and Pt$4f$ of CNFs@Pt, CNFs@Au and CNFs@Au-Pt NIs.

Current –Voltage characteristics of CNFs@Pt and CNFs@Au-Pt NIs:

Current voltage (I-V) measurements were performed using Keithley, 2420 source measurement unit enabling two-probe method, corresponding I-V characteristics between -5 to +5 V ranges is shown in Figure S5.
**Figure S5** I-V characteristics of CNFs@Pt and CNFs@Au-Pt NIs in different conditions.

I-V characteristics of CNFs@Pt and CNFs@Au-Pt NIs synthesized via chemical reduction performed in different conditions (N₂, H₂ and synthetic air) to study the influence of hydrogen gas versus conductivity of the sample. It was found that, upon exposure to H₂ gas the conductivity of the CNFs@Pt and CNFs@Au-Pt NIs was enhanced owing to the increase in charge carrier concentration with the introduction of reducing gas like hydrogen.

**Gas sensor characteristics:**

The selectivity of the sensor towards various gases was compared with response towards H₂ gas (Figure S6a). The analyte gases include hydrogen, ammonia, acetone, hydrogen sulphide (H₂S), ethanol and nitrogen dioxide (NO₂) to study the selectivity of CNFs@Pt NIs and CNFs@Au-Pt NIs materials. Response time and recovery time of CNFs@Au-Pt NIs towards various concentration of H₂ gas was depicted in figure S6b.
Figure S6. a) Selectivity of CNFs@Au-Pt NIs sensor towards other gases (ammonia, acetone, hydrogen disulphide, ethanol and NO₂) b) Response time and recovery time of CNFs@Au-Pt NIs

Figure S7. a) Dynamic gas sensor response and b) sensitivity plot of CNFs@Au-Pt NIs towards H₂ gas(5%-10%).

Influence of humidity over H₂ gas sensing of CNFs@Au-Pt NIs has been studied and found that there is a small interference of humidity with the sensor response. As the humidity increases the response towards H₂ was found to be decreased. This is due to the fact that at higher humidity ranges, the water molecules are likely to be adsorbed on the surface of the CNFs@Au-Pt NIs.
preventing the adsorption of hydrogen molecules. Therefore, number of sites for adsorption decreases which results in the decrease in H₂ sensor response. But after 90% RH sensor response increased, this may be due to the condensation of water vapour inside the chamber increased. Also, with humid air, one probable reaction is that the water vapour get dissociated on the bimetallic Au-Pt surface giving rise to more H⁺ and OH⁻ ions as shown in equation 1. Increase in adsorbed H⁺ further result in decrease in resistance.

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \ldots ..(1) \]

**Figure S8.** Effect of humidity on gas sensing properties of CNFs@Au-Pt NIs.

**Table no. S1** Comparison table of H₂ sensing performance with other previously reported H₂ sensors.

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<th>Sl no.</th>
<th>Material</th>
<th>Temp (°C)</th>
<th>Sensitivity</th>
<th>Conc.</th>
<th>Response time</th>
<th>Recovery time</th>
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References:


