Electronic Supplementary Material (ESI) for Chemical Science.


# An efficient on-board metal-free nanocatalyst for controlled room temperature hydrogen production

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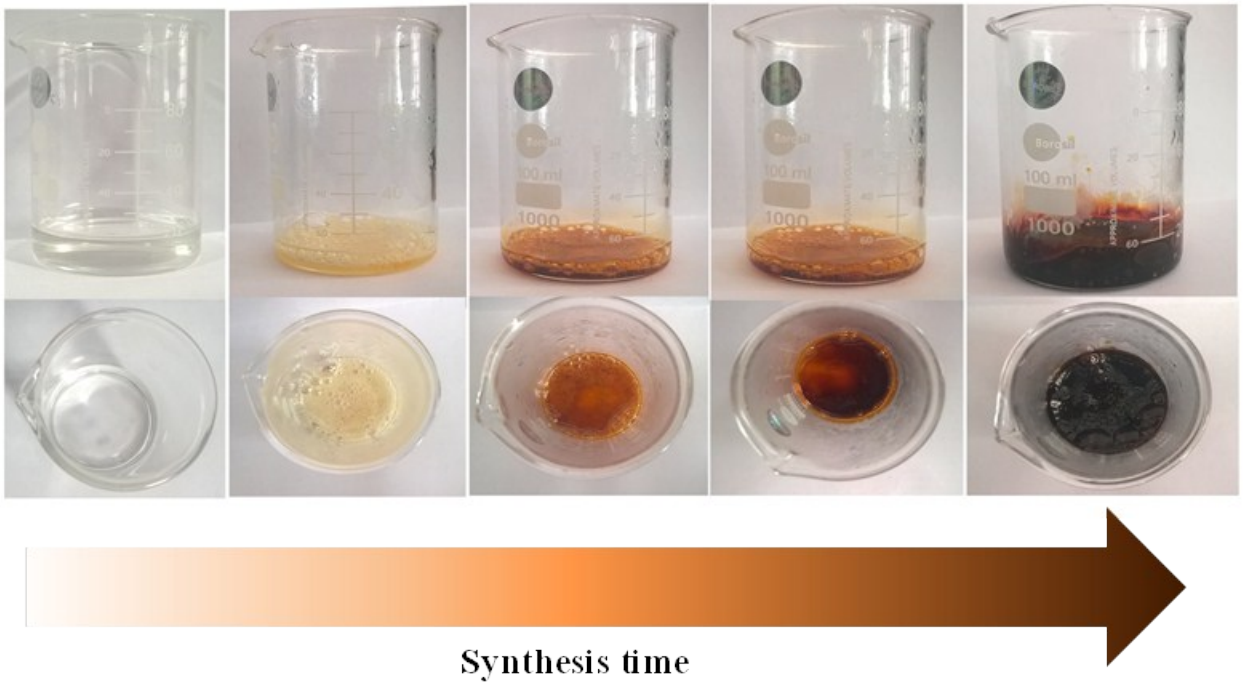


Figure S1. Colour change of the precursor solution during CND synthesis

To verify our assumption described in scheme 1 the same synthesis procedure was performed without the nitrogen source, urea. Here the synthesis time was fixed at 3.5 min (same as the best performed sample). A brown gel was formed and assigned as sample D. The HRTEM image of sample D is shown in figure S2. The average particle size of the CNDs was found to be ~4 nm.

The lattice spacings of 0.24 and 0.33 nm, corresponding to (1120) and (002) planes respectively are clearly visible which confirm the formation of CNDs. The SAED pattern (figure S2b) is indicative of amorphous nature that may be due to the nanocrystalline nature of the same.

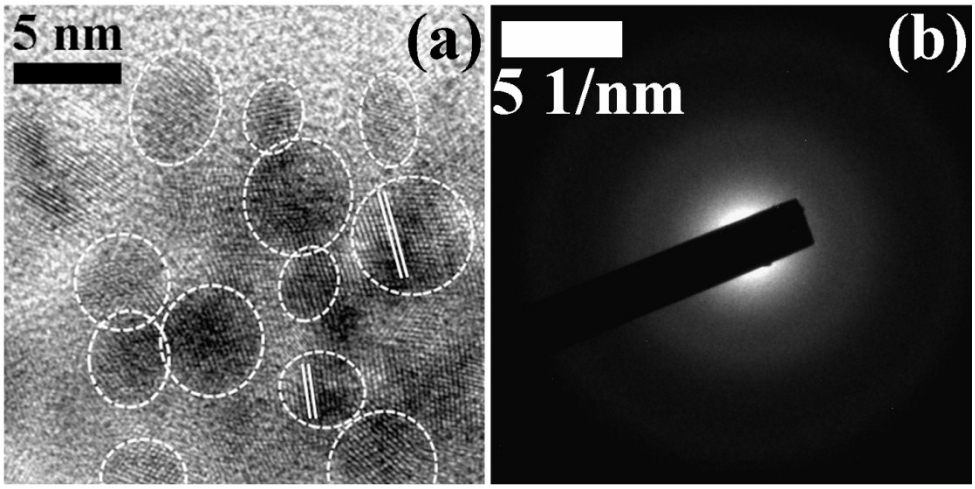


Figure S2 (a) HRTEM image; (b) SAED pattern of sample D.

Detail elemental analysis of sample D was performed by XPS (figure S3a-d). The survey scan confirms the presence of C and O in the sample. From the high resolution scan of C1s, peaks at 284.5, 287.2 and 288.6 eV associated with C-C/ C=C, C=O and O-C=O, respectively were found. Peaks at 531.8 and 533.2 eV related to C-OH/ O-C-O and C-O-C respectively are observed in O1s spectrum. In addition, a very low N1s intense peak near 400.2 eV was observed which is assigned to N-$O_x$. The presence of nitrogen for this sample is believed to be due to atmospheric nitrogen.[1,2] From the XPS data atomic percentage of carbon, oxygen and nitrogen were calculated for all the samples and compared in table S1. It may be noted that sample B contains the highest amount of nitrogen while sample D contains the least.

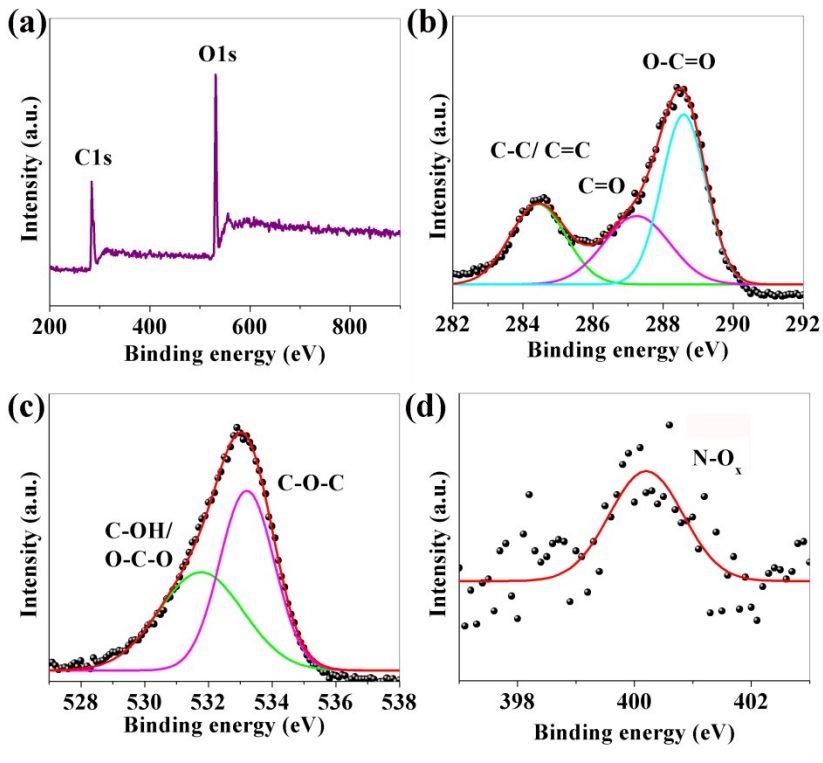


Figure S3. (a) XPS survey scan; (b-d) XPS high resolution survey scan of C1s, O1s and N1s region of sample D.

| Sample | Carbon (%) | Oxygen (%) | Nitrogen (%) |
|---|---|---|---|
| A | 70.06 | 20.05 | 9.89 |
| B | 58.18 | 26.63 | 15.19 |
| C | 66.20 | 21.19 | 12.61 |
| D | 59.37 | 39.60 | 1.07 |

Table S1. Comparison of atomic % of C, O and N for sample A, B, C and D.

$H_2$ production performance of sample D was also verified using $NaBH_4$ (0.05 M), catalyst (4 mM) and 50 ml of water at room temperature. The results are compared with that of without catalyst

and sample B (figure S4). It is observed that sample D lowers the hydrolysis activity of $NaBH_4$ (without catalyst) which supports our assumption towards the positive role of $NH_4^+$ ion in hydrolysis of $NaBH_4$.

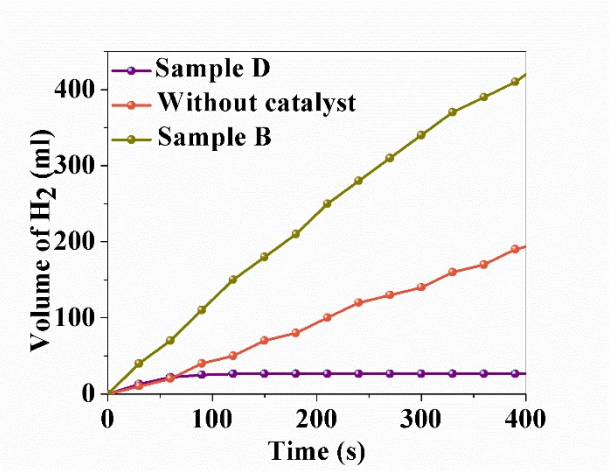


Figure S4. Comparison of kinetics for $H_2$ generation for Sample B, D and without catalyst

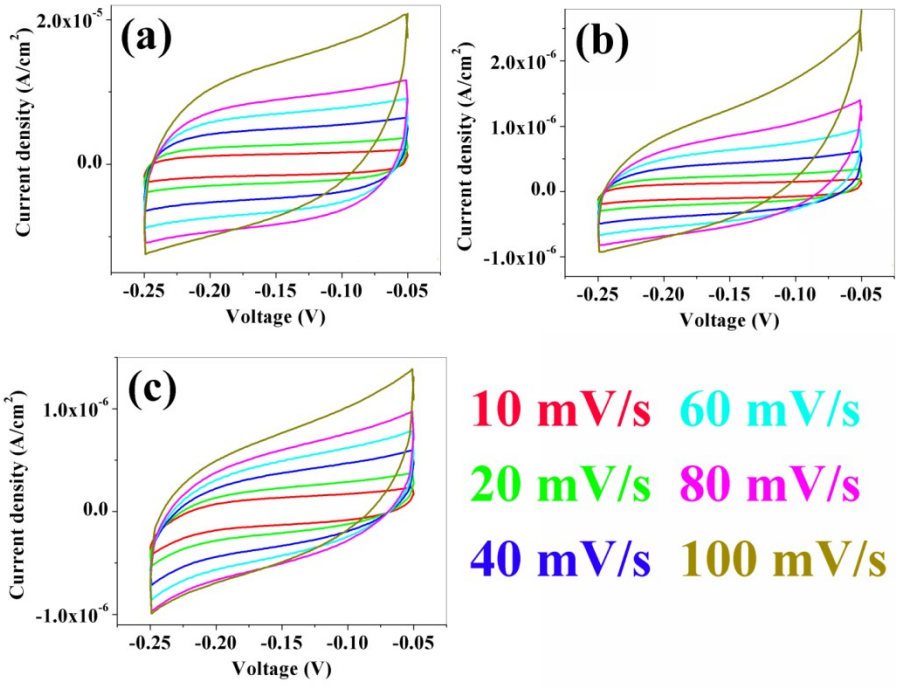


Figure S5. (a-c) CV measurements of sample A, B and C, respectively.

## References


1. G. R. Rao and C. N. R. Rao, *J. Phys. Chem.*, 1990, **94**, 7986.
2. Y. Y. Q. Zhonga, W. Caia, J. Dinga, J. Mol. Catal. A: Chem., 2015, **398**, 344.