Supporting Information

Neodymium Decorated Graphene as a Highly Proficient Electrocatalyst for Hydrogen Production

Lifang Chen, [§] *Rizwan Ur Rehman Sagar,* [§, *] *Sehrish Aslam,* [ð] *Yiqun Deng,* [§] *Shahid Hussain,* [¤] *Waris Ali,* [£] *Chao Liu,* [§] *Tongxiang Liang* [§, *] *and Xinmei Hou* [€, *]

[§]College of Rare Earths, Jiangxi University of Science and Technology, 86 Hong Qi Road, Ganzhou 341000, PR China
[ð]Shenzhen Engineering Lab of Flexible Transparent Conductive Films, School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen, 518055, China
[€]Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, P.R. China
[¤]School of Materials Science and Engineering, Jiangsu University, China
[£]Department of Physics, Govt Islamia College Civil Lines (GICCL), St. Nagar Road Lahore, 54000, Pakistan

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Schematic and parameters of Fabrication

A double zone CVD system is used for the fabrication of Nd-Gr-NF composite material. Nd-source was placed in Zone-I and heated at high temperature (1200-1400°C). while the nickel foam was placed in downstream in Zone – II (Fig. S1a). The heating time of Zone-I and Zone-II was synchronized and both zones reached at particular temperature at the same time (Fig. S1b). The hydrogen (25%) mixed argon gas was provided throughout of the experiment. When the temperature of Zone- II reaches as 1100°C, ethylene (C_2H_4) gas as carbon source was inserted.

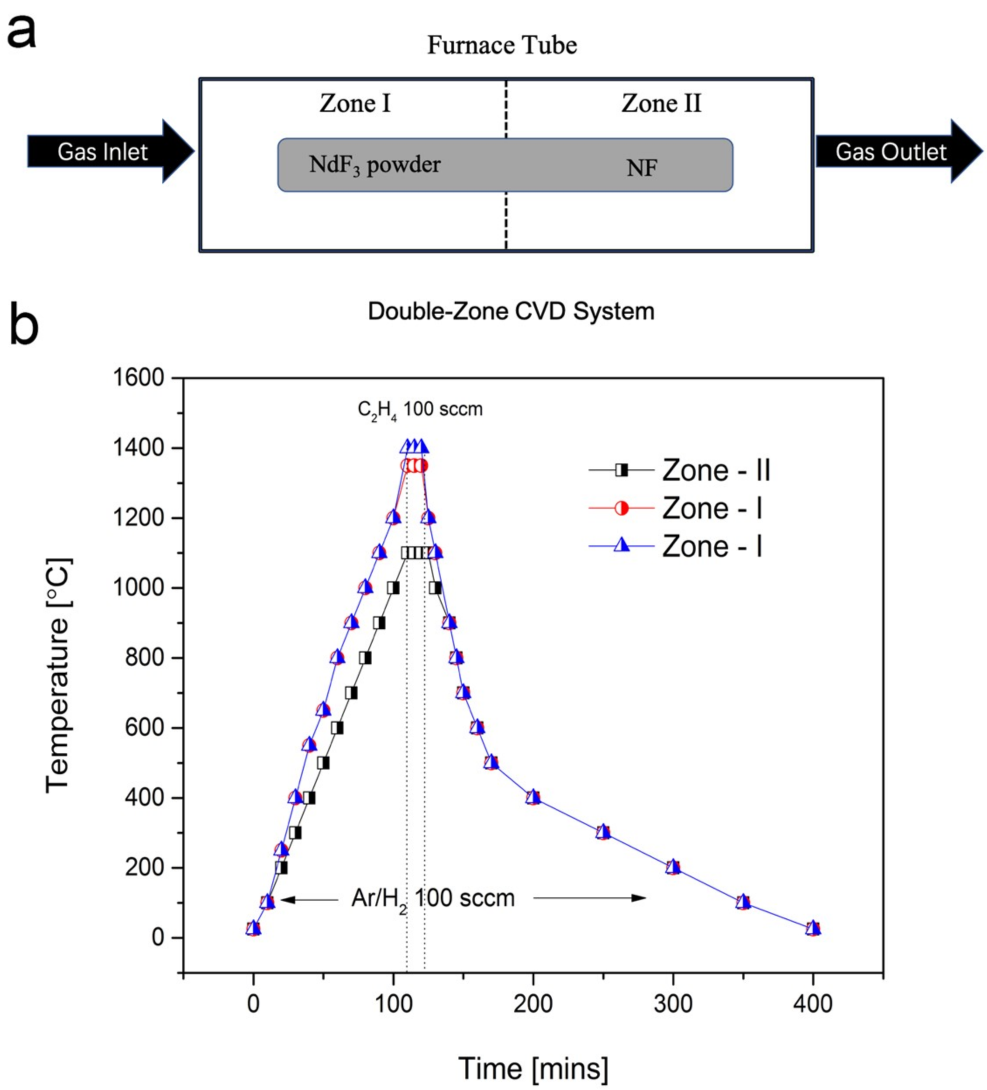

Fig. S1 (a) Schematic of double zone CVD system and (b) growth conditions (temperature *vs.* time (flow of gases))

Table. S1 Each experiment was repeated numerous times on identical conditions

Material/Temperature of Zone – I of CVD	Material/Temperature of Zone – I of CVD	Growth Time (mins)	Special Morphology
No Material	Nickel Foam/1100°C	5-10	Graphene on nickel foam (No special morphology)
NdF3/1100°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Graphene on nickel foam (No special morphology)
NdF3/1200°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Nd-Graphene on nickel foam (No special morphology)
NdF3/1250°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Nd-Graphene on nickel foam (No special morphology)
NdF3/1300°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Nd-Graphene on nickel foam (No special morphology)
NdF3/1350°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Nd-Graphene on nickel foam (ball-like morphology)
NdF3/1400°C	Nickel Foam/1100°C	20 for Zone-I 10 for Zone-II	Nd-Graphene on nickel foam (fiber-like morphology)

Growth Mechanism

Li et al.[1] already described the growth mechanism of graphene on copper and nickel substrates. The nickel has ability to absorb the carbon atoms. There are numerous steps to perform the experiment to get Nd-Gr-NF composites. The C-atoms will absorb in nickel and come again on the surface of nickel upon cooling to form the graphene, but nickel cannot absorb the Nd atoms. The C-atoms arrange to form graphene, but the Nd-atoms remain on the surface and upon cooling, start agglomerating to form different kind of morphologies on the surface of graphene. Fig. S2 indicates the formation of the composite.

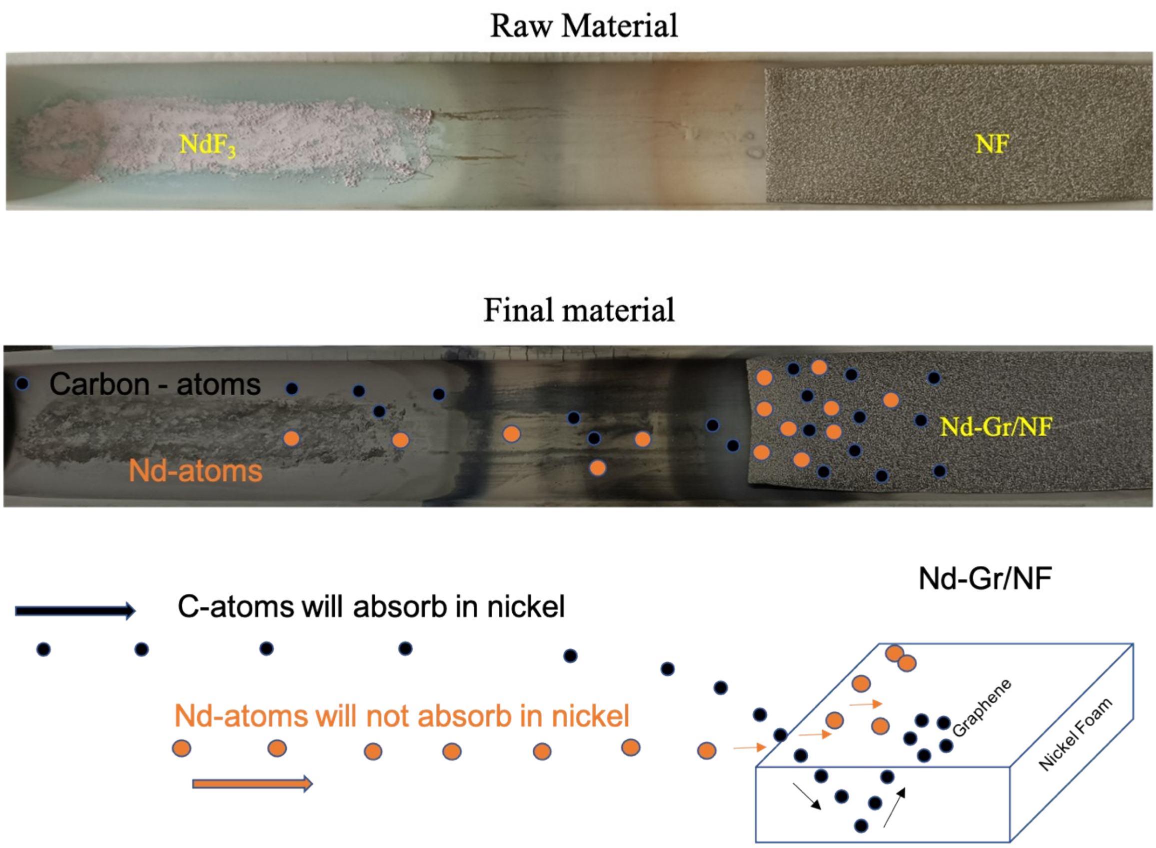

Fig. S2 A comparison of the situation when loading the prepared samples and after the experiment, and the schematic of growth mechanism.

Etching of nickel to get Gr-Nd samples

The transfer of the sample is possible after etching the nickel and pure graphene foam like material can be obtained as reported in the literature.[2-9] However, normally $FeCl_3$ and HCl are used for wet-etching process. These both can also etch Nd on the surface of nickel foam. That's why we have compared transfer free sample and transferred sample's XRD to find out the presence of Nd. In XRD, Nd peaks are missing.

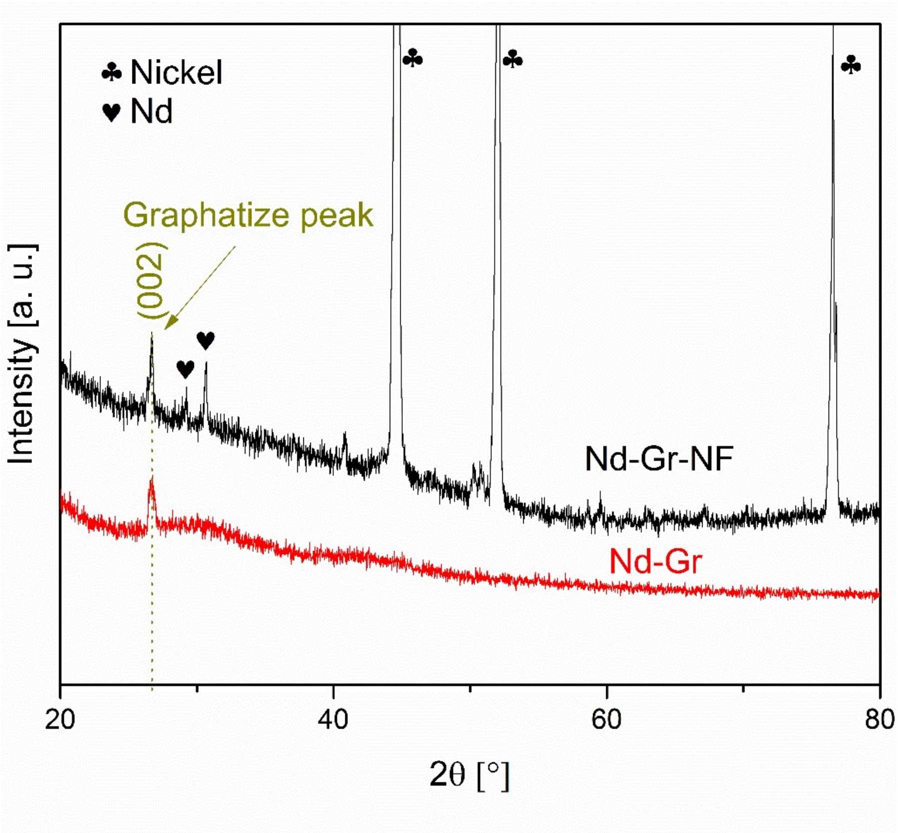

Fig. S3 The XRD of Nd-Gr-NF and nickel etched Nd-Gr samples [10]

SEM of controlled growth of Nd on Gr/NF

A smooth surface of the nickel foam was observed under the SEM (Fig. S4a) which converts into rough upon the fabrication of graphene (Fig. S4b). The surface of nickel foam becomes dirty upon the deposition of neodymium (Nd) (Fig. S4c and S4d). As the pyrolysis temperature increases, the neodymium material on the graphene foam nickel increases. It can be seen from the figure that the neodymium active materials of Nd-Gr/NF-1300°C and Nd-Gr/NF-1400°C are uniformly distributed on the graphene foam nickel (Fig. S4e and S4f).

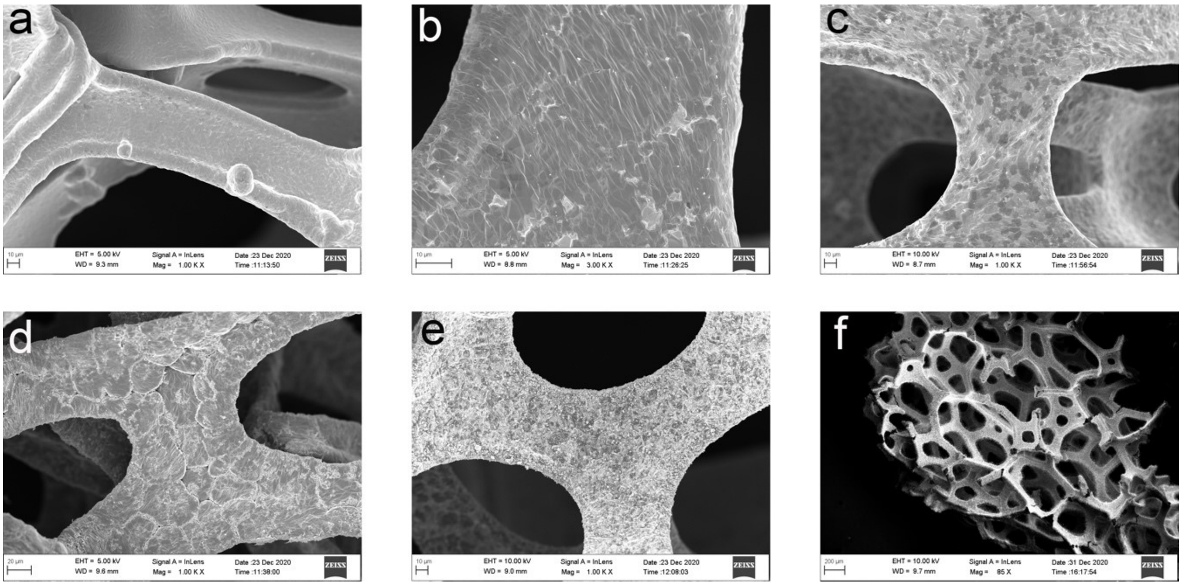

Fig. S4 Surface of nickel foam (a), graphene grown on nickel substrate (b), Nd-Gr/NF-1200°C, (c) Nd-Gr/NF-1250°C, (d) Nd-Gr/NF-1300°C (e) Nd-Gr/NF-1350°C (f) Nd-Gr/NF-1400°C

HRTEM of transferred graphene and Nd-graphene

Graphene with Nd and without Nd was transferred from nickel foam for the structural analysis. The high-resolution image of graphene without Nd shows a d-spacing of 0.33 nm and the distance between layers of graphene is about 0.33 nm (Fig. S5a). This indicates that graphene on nickel foam was multilayered. The SAED pattern of graphene shows random bright dots which indicates the layers of graphene were also randomly oriented. Though, XRD did not provide any peaks of Nd upon transferring of graphene from nickel but HRTEM shows that there are small Nd-particles inside the graphene sheets which results the SAED pattern into rings (Fig. S5c and S5d).

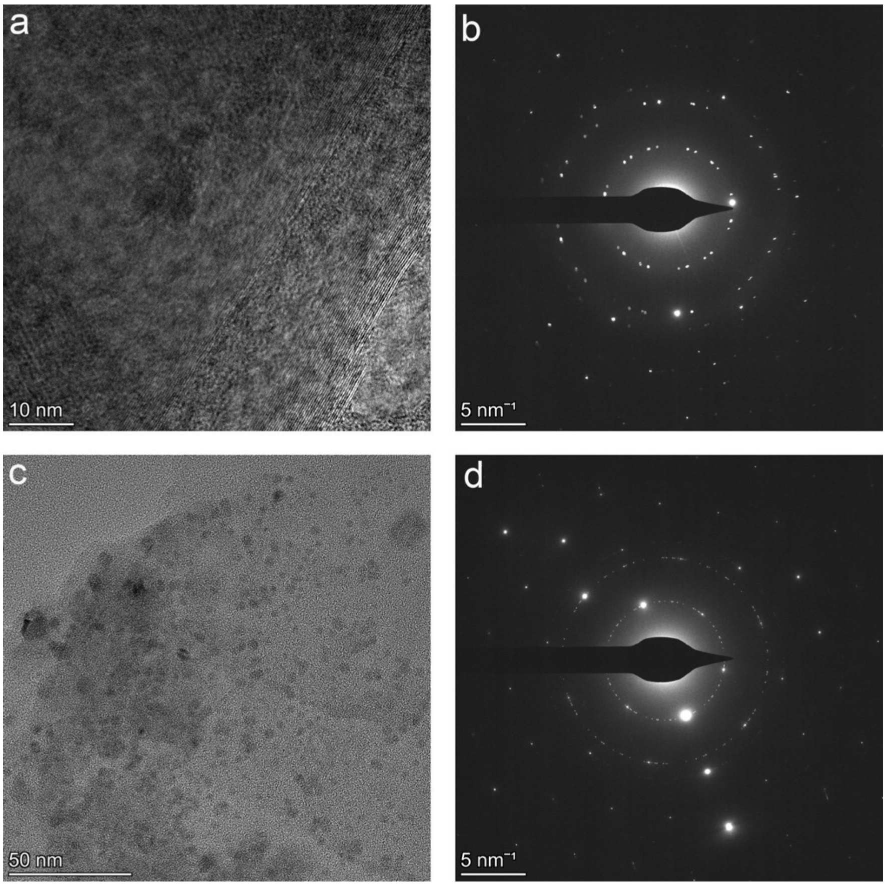

Fig. S5 HRTEM of transferred as-grown graphene on nickel foam (a) and its corresponding SAED pattern (b). The transferred Nd-graphene with small Nd-particles (c) and corresponding g SAED pattern (d).

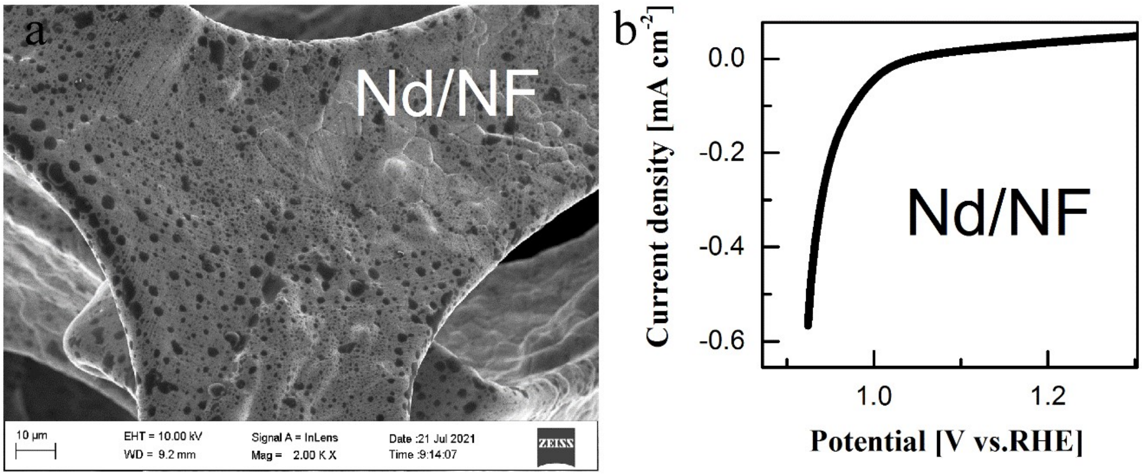

Fig. S6 Nd deposited on nickel foam (NF) (a) and corresponding LSV in. KOH medium (b)

Stability and ESCA normalized LSV

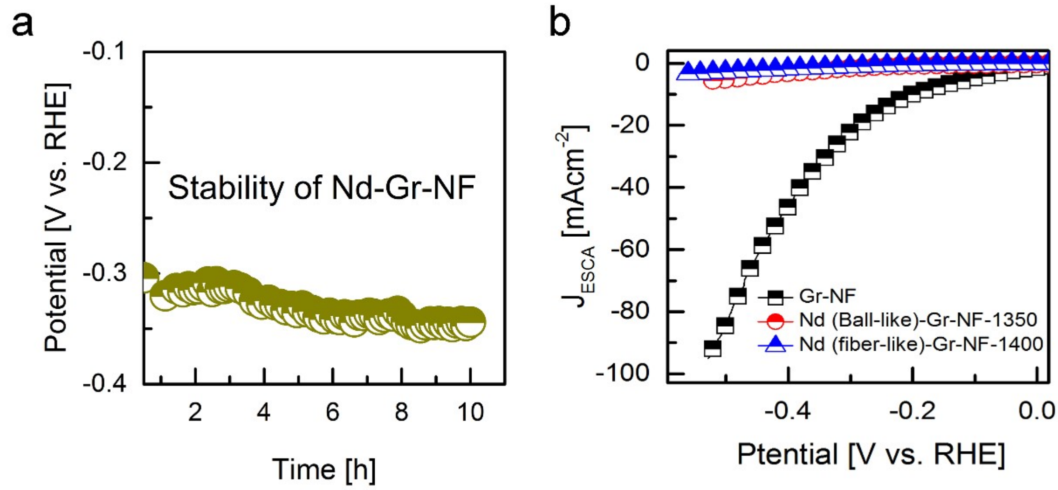

Fig. S7 Stability for 10 hours (a) and ECSA normalized LSV's of Gr-NF, Nd-Gr-NF-1350 and Nd-Gr-NF-1400

Characterizations after stability

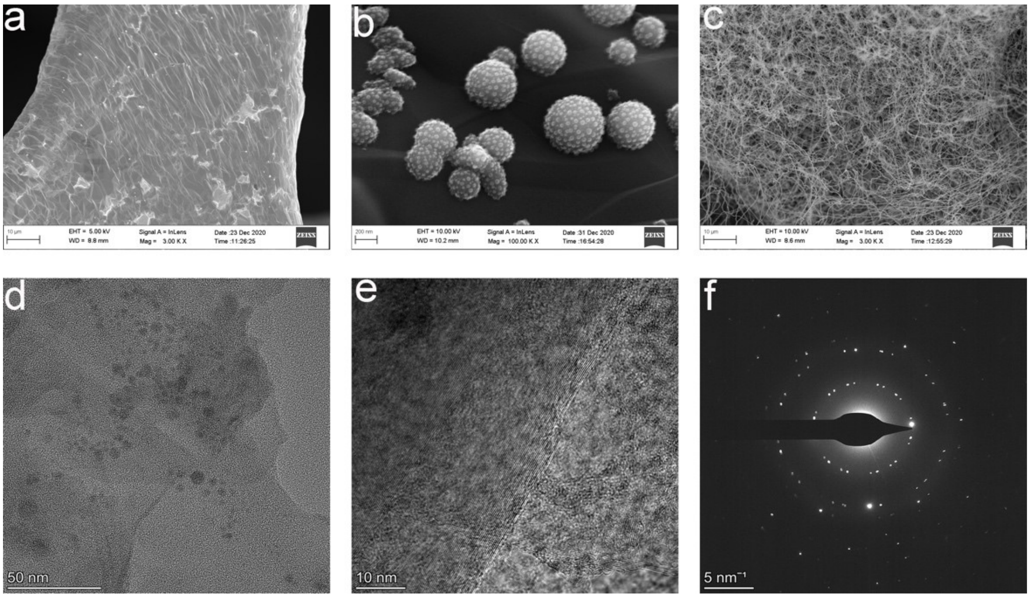

Fig. S8 SEM of graphene (a), Nd-balls on graphene (b), and Nd-fiber on graphene grown on nickel foam (c). HRTEM of ball-like Nd in graphene sheets (d), high-resolution HRTEM (e), and SAED pattern (f).

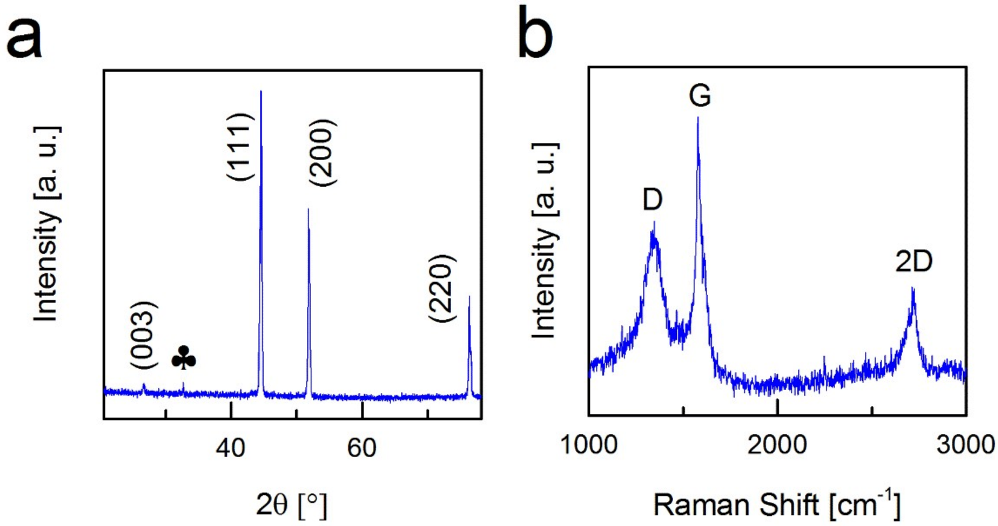

Fig. S9 XRD of Nd-Gr-NF (a) and Raman spectroscopy (b)

179-188.
3. R. U. Rehman Sagar, M. Zhang, X. Wang, B. Shabbir and F. J. Stadler, *Nano Materials Science*, 2020, **2**, 346-352.
4. R. U. R. Sagar, N. Mahmood, F. J. Stadler, T. Anwar, S. T. Navale, K. Shehzad and B. Du, *Electrochim Acta*, 2016, **211**, 156-163.
5. R. U. Rehman Sagar, B. Shabbir, S. M. Hasnain, N. Mahmood, M. H. Zeb, B. N. Shivananju, T. Ahmed, I. Qasim, M. I. Malik, Q. Khan, K. Shehzad, A. Younis, Q. Bao and M. Zhang, *Carbon*, 2020, **159**, 648-655.
6. R. U. R. Sagar, M. Galluzzi, A. García-Peñas, M. A. Bhat, M. Zhang and F. J. Stadler, *Nano Res*, 2019, **12**, 101-107.
7. R. U. R. Sagar, M. Galluzzi, C. Wan, K. Shehzad, S. T. Navale, T. Anwar, R. S. Mane, H. G. Piao, A. Ali and F. J. Stadler, *ACS Appl Mater Interfaces*, 2017, **9**, 1891-1898.
8. S. Aslam, R. U. R. Sagar, H. Kumar, G. Zhang, F. Nosheen, M. Namvari, N. Mahmood, M. Zhang and Y. Qiu, *Chemosphere*, 2020, **245**, 125607.
9. M. H. Zeb, B. Shabbir, R. U. R. Sagar, N. Mahmood, K. Chen, I. Qasim, M. I. Malik, W. Yu, M. M. Hossain, Z. Dai, Q. Ou, M. A. Bhat, B. N. Shivananju, Y. Li, X. Tang, K. Qi, A. Younis, Q. Khan, Y. Zhang and Q. Bao, *Acs Appl Mater Inter*, 2019, **11**, 19397-19403.
10. R. U. Rehman Sagar, X. Zaiping, J. Iqbal, S. U. Rehman, H. Ashraf, C. Liu, J. Zeng and T. Liang, *Materials Today Physics*, 2021, DOI: https://doi.org/10.1016/j.mtphys.2021.100460, 100460.

References