Support Information

Highly dispersed nanodiamonds supported on few-layer graphene as robust metal free catalysts for ethylbenzene dehydrogenation reaction

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Experimental information:

Synthesis of highly dispersed ND nanoaggregates

The highly dispersed ND nanoaggregates was synthesized by a milling process of commercial ND powders reported by Osawa et al.[1] 2 g commercial ND powder was added a small mill equipped with a 15 mL zirconia vessel and a single-bladed zirconia agitator were used for the stirred media-milling. Zirconia beads of 30 um in diameter were employed. The mill was tightly closed with cover, and the content agitated at a peripheral speed of 10 m s^{-1} for 3 h under cooling with running water. At the end of milling, beads were separated by filtration and/or centrifugation and the slurry diluted with water to 0.2% concentration and subjected to sonication to obtain a clear colloidal solution of highly dispersed ND nanoaggregates.

Synthesis of HD-ND/graphene catalysts:

The commercial few-layer graphene support bought from the Sixth Element Company (Changzhou, China) were dispersed into ethanol by sonication. Then the as-prepared HD-ND nanoaggregates colloidal solution was added into the graphene ethanol solution. After stirring for 10 h, the solvent was removed by vacuum rotary evaporation at 40 ^{o}C and the obtained precipitate was dried at 120 ^{o}C overnight. The HD-ND/graphene catalysts with different ND weight loadings can be synthesized by tuning the concentration of ND in the initial solution.

Characterization and Catalytic performance test:

The samples were characterized by SEM (Nova NanoSEM 450, FEI). The images of transmission electron microscopy (TEM) were observed on a Tecnai G2 F20 operated at 200 kV. X-ray diffraction (XRD) patterns of the samples were obtained using a D/MAX-2500 PC X-ray diffractometer with monochromatized Cu Ka radiation (λ=1.54 Å). Raman spectroscopy was tested by a LabRam HR 800 using a 632.8 nm laser. The catalytic tests were carried out for the commercial ND powder, HD-ND/graphene catalysts and the pure graphene with the DH of ethylbenzene to styrene. The experiments were tested using 50 mg catalysts at 550 ^{o}C in a fixed-bed quartz reactor. The mixture reactants were introduced to the reactor with a total flow rate of 10 mL min^{-1} (2.6 % ethylbenzene) at atmospheric pressure for 20 h. The

helium was used as a balance gas. The reaction product was analyzed by gas chromatography (Agilent 7890A) with FID and TCD detectors. EB conversion of the blank experiment was just 0.12%, which was ignored here.

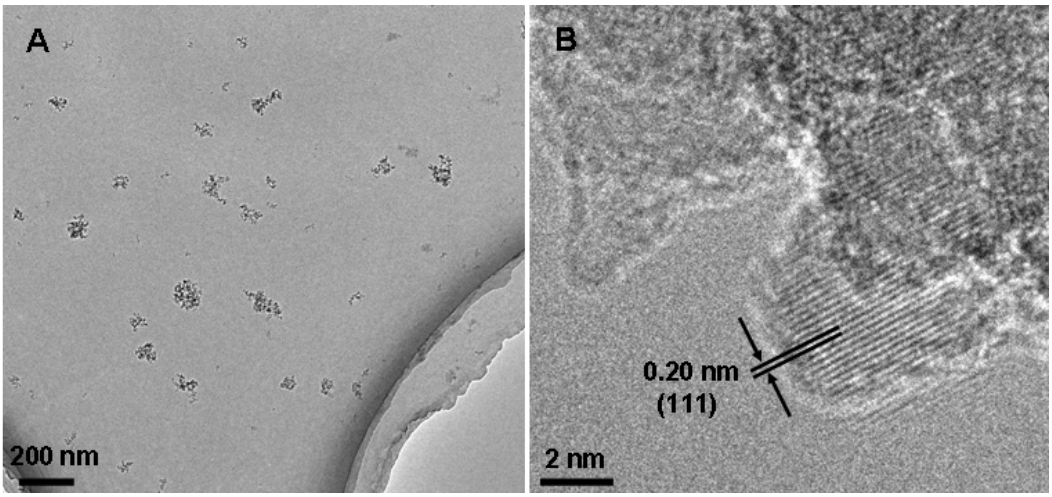

Fig. S1 TEM images of the (A) commercial ND aggregates collected after sonicating in water and the HRTEM image of (B) one single HD-ND nanoparticle.

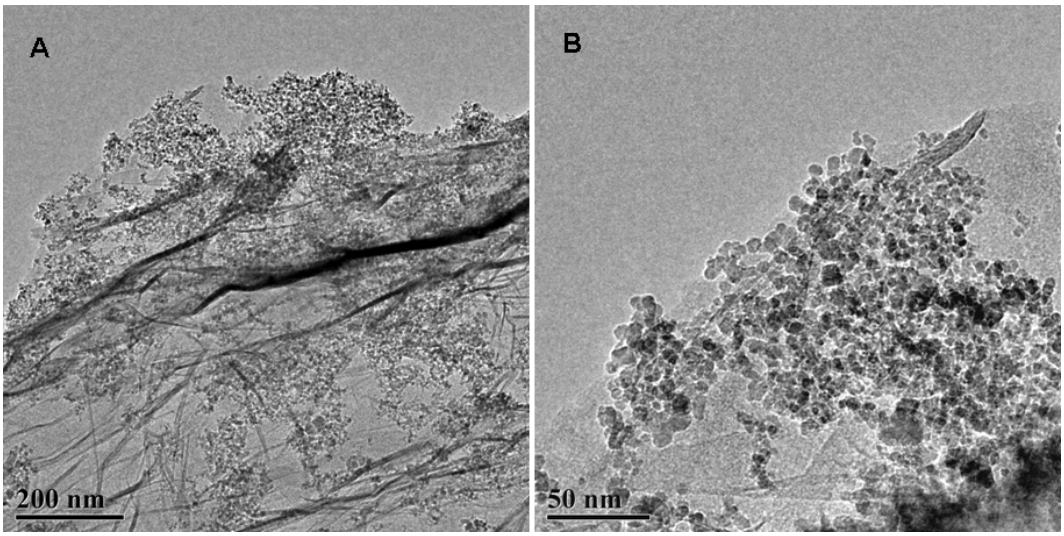

Fig. S2 TEM images of the HD-ND/graphene catalyst. The weight loading of ND is 12 wt%.

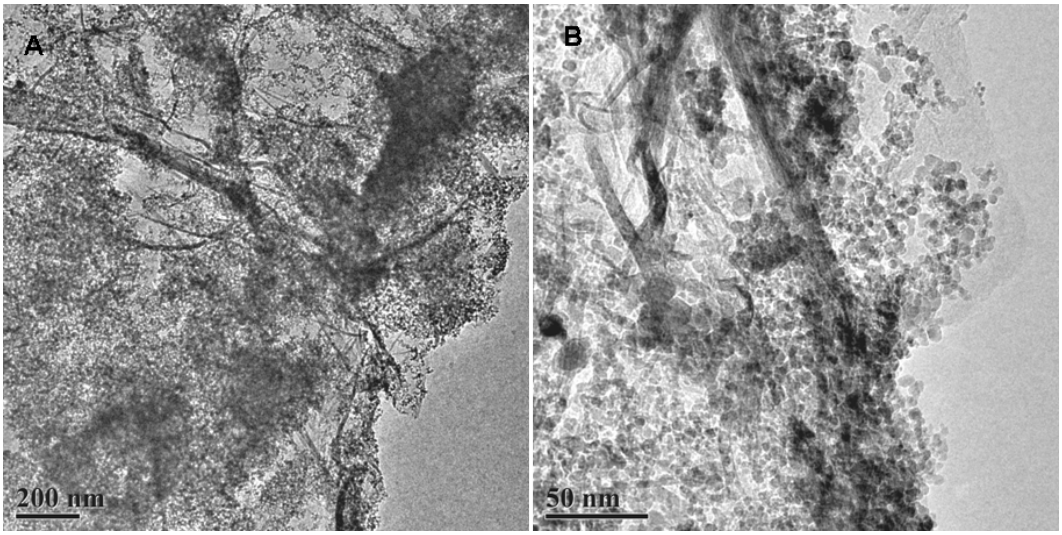

Fig. S3 TEM images of the HD-ND/graphene catalyst. The weight loading of ND is 30 wt%.

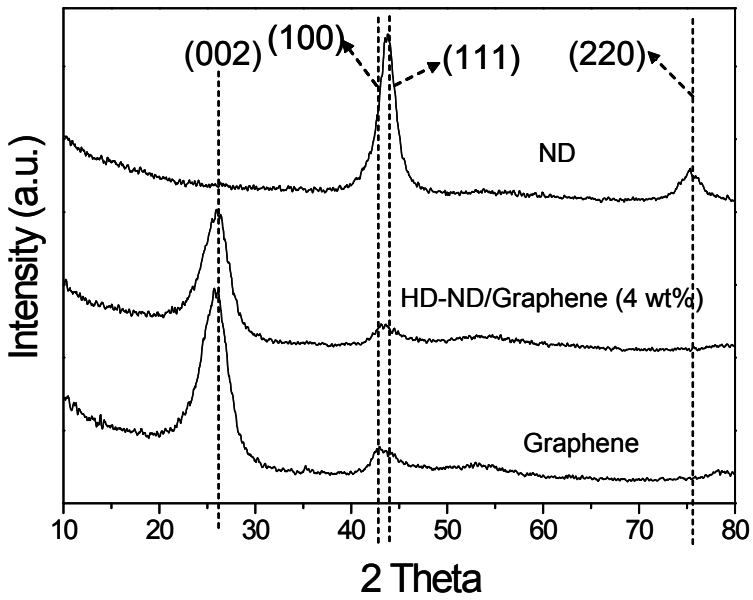

Fig. S4 XRD patterns of the commercial ND powders, HD-ND/graphene (4 wt%) and the pure graphene support.

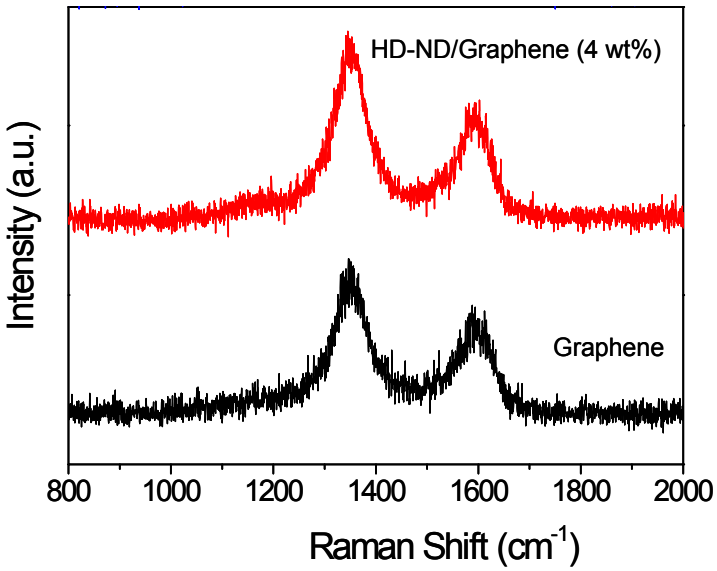

Fig. S5 Raman spectra of the graphene support and HD-ND/graphene (4 wt%) catalyst.

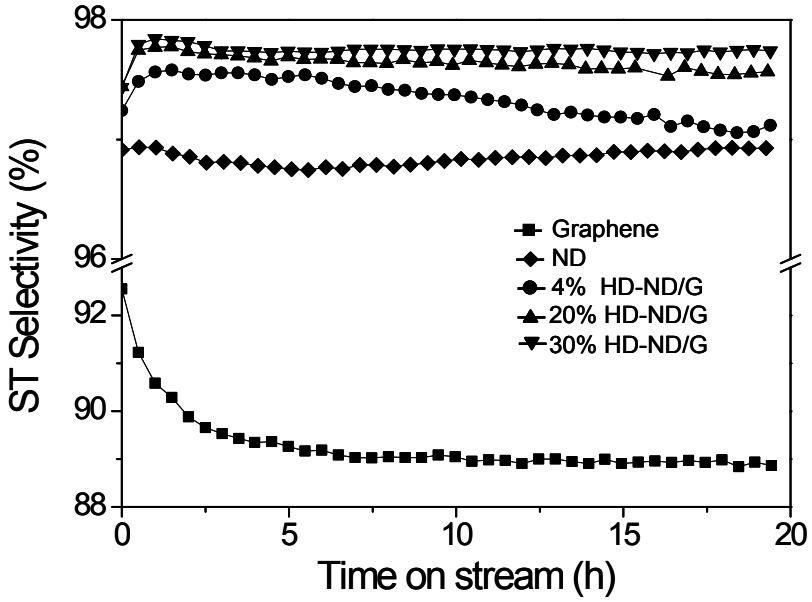

Fig. S6 Catalytic performance over few-layer graphene, HD-ND/graphene catalysts with different ND weight loading (4 wt%, 12 wt%, 30 wt%) and commercial ND powders. Reaction conditions: T = 550 ^{o}C, Flow rate = 10 ml min^{-1}, 2.6% ethylbenzene with He balance.

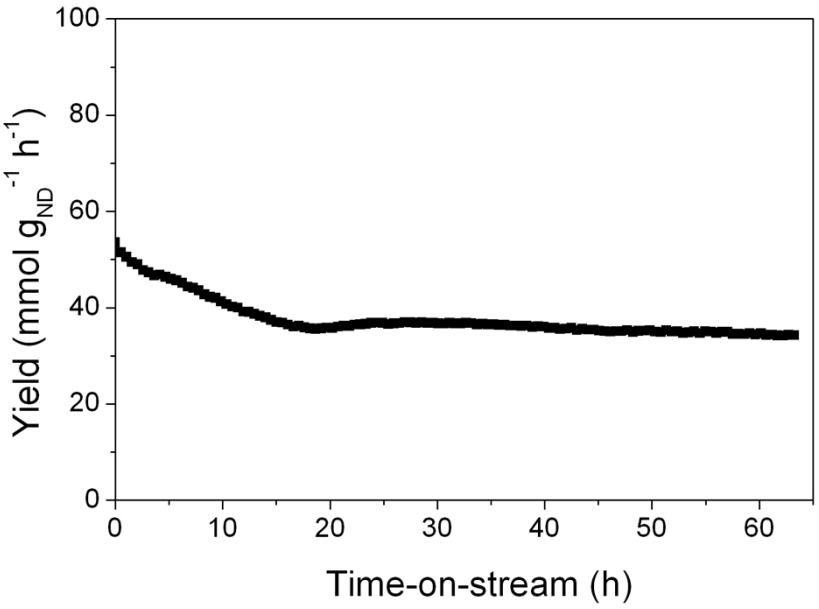

Fig. S7 The long term test over the HD-ND/graphene catalysts with 4% ND weight loading. Reaction conditions: T = 550 ^{o}C, Flow rate = 10 ml min^{-1}, 2.6% ethylbenzene with He balance.

References

1 A. Krüger, F. Kataoka, E.Osawa, Carbon, 2005, **43**, 1722.