

# Eco-Friendly and Solvent-Less Mechanochemical Synthesis of ZrO<sub>2</sub>–MnCO<sub>3</sub>/N-Doped Graphene Nanocomposites: A Highly Efficacious Catalyst for Base-Free Aerobic Oxidation of Various Types of Alcohols

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## 1. Preparation of GO and NDG

Graphite oxide (GO) was synthesized from graphite powder using a previously reported modified Hummers method [1,2]. Briefly, a mixture of 0.5 g of graphite powder and 0.5 g of NaNO<sub>3</sub> in 23 mL of H<sub>2</sub>SO<sub>4</sub> was stirred for 10 min in an ice bath in a 100-mL flask. Thereafter, 3 g of KMnO<sub>4</sub> was slowly added to this mixture until the color of the mixture was changed to dark green. The mixture was allowed to stir thoroughly for several minutes. After this, the ice bath was removed, and the mixture was placed in a water bath and slightly heated to 35 to 40 °C. Stirring continued for another 1 h, which resulted in the formation of thick paste. Subsequently, deionized water (DI) (40 mL) was added to the mixture, and stirring continued at ~90 °C for another half of an hour. After 30 min, at the same temperature, more DI water (100 mL) was added to the mixture, and subsequently 3 mL of H<sub>2</sub>O<sub>2</sub> was also added. This resulted in an immediate change in the color of the mixture from dark brown to light yellow. After cooling, the mixture was filtered and washed several times (3 times using 100 mL of water each time). After washing, a thick brown paste was obtained, which was dispersed in DI water (100 mL) and subjected to a centrifuge for a short time (~2–3 min) at a low speed of 1000 rpm. Similarly, this step was repeated around 4–5 times, using the same amount of water, until all of the floating particles were removed. Finally, the as-obtained mixture was dispersed again in 100 mL of DI water and was centrifuged at a high speed of 8000 rpm to remove any remaining small pieces of GO. After this, the resultant paste was re-dispersed in water via mild sonication to obtain a solution of GO.

The as-synthesized graphite oxide (200 mg) was dispersed in 40 mL distilled water and sonicated for 30 min to obtain graphene oxide (GRO) sheets. The resulting suspension was taken in a round bottom flask, to which 4 ml of NH<sub>4</sub>OH and 4 ml hydrazine hydrate was added simultaneously.

Afterwards, the reaction mixture was stirred for a few minutes, the dispersion of reaction mixture flask was put in a water bath controlled at 90 °C for 3 h the flask was equipped with cooling condenser. After the 3 h of reaction, the product was collected after been filtered through micropore filters, washed by deionized water and freeze-dried.

## 2. Ball Milling procedure

The graphite oxide powder was milled using Fritsch Pulverisette P7 planetary ball mill (FRITSCH Milling and Sizing, Industriestraße 8, 55743 Idar-Oberstein, Germany). The Graphite Oxide Powder and Stainless Steel balls (5mm Diameter) with ball to powder weight ratio of 11:1 were introduced into the Stainless Steel Container. The milling of the powder was performed for 16 hours. And in order to maintain the temperature inside the container, the milling process was paused at regular intervals.

## 3. Characterization

An FE-SEM (JSM 7600F JEOL, JEOL, Tokyo, Japan) and EDX (JEOL, Tokyo, Japan) attached to the SEM were employed to study the composition and morphology of the sample. For the SEM study, the samples were mounted onto a stub with carbon-based double-sided tape and then sputter coated with approximately 10 nm of platinum. For imaging, the samples were oriented perpendicular to the incoming electron beam. SEM images were taken using an operating voltage of 5 kV and a working distance of 4.5 mm over different magnifications. The XRD analysis of the as prepared nanocatalysts were carried out using a D2 Phaser X-ray diffractometer (Bruker, Karlsruhe, Germany), Cu K $\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ), the step size is 10 seconds and acquisition time is 2 hrs. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded as KBr pellets using a Perkin- Elmer 1000 FTIR spectrophotometer (Perkin Elmer, Waltham, MA, USA). BET surface area was measured on a NOVA 4200e surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL 33426, USA), the nanocomposites pre-treatment for N<sub>2</sub> adsorption analysis is carried out at degassing temperature 120 °C for 3 hrs. Thermogravimetric Analysis was carried out using TGA/DSC1 (Mettler Toledo AG, Analytical, Schwerzenbach, Switzerland). Benzyl alcohol conversion was analysed using a gas chromatography (GC) (GC 7890A, Agilent Technologies Inc., Santa Clara, CA, USA, equipped with a flame ionization detector (FID) and a 19019S-001 HPPONA column), equipped with a flame ionization detector (FID) and a 19019S-001 HPPONA column)

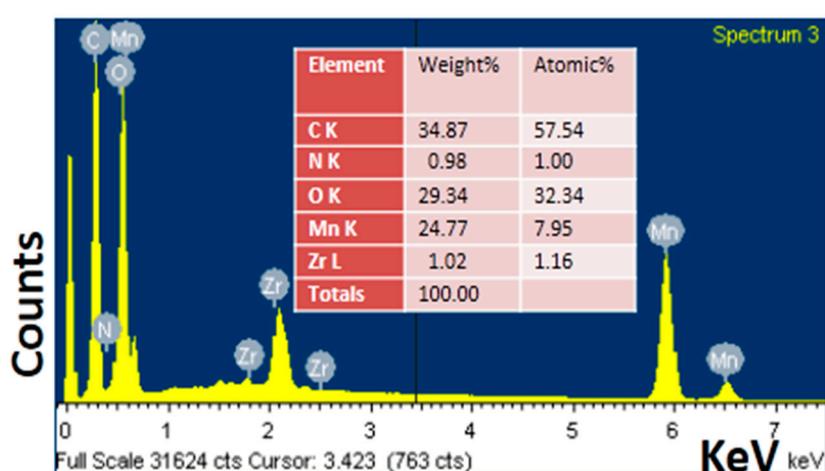


Figure S1. EDX spectrum of (1%)NDG/MnCO<sub>3</sub>-(1%)ZrO<sub>2</sub> nanocomposite.

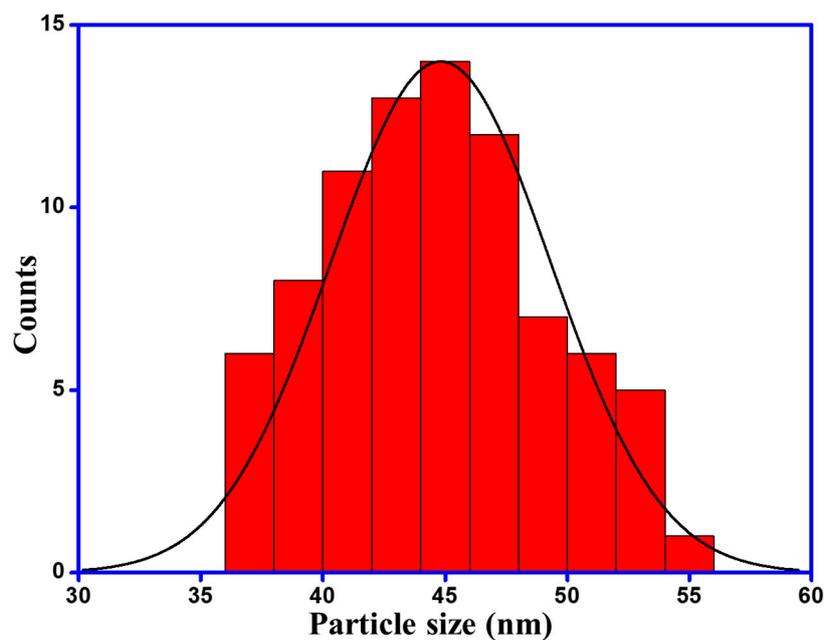


Figure S2. Particle size distribution of (1%)NDG/MnCO<sub>3</sub>-(1%)ZrO<sub>2</sub> nanocomposite.

## References

1. Hummers, W.S., Jr.; Offeman, R.E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339.
2. Cote, L.J.; Kim, F.; Huang, J. Langmuir–Blodgett assembly of graphite oxide single layers. *J. Am. Chem. Soc.* **2008**, *131*, 1043–1049.