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Supporting information

Shape and size controlled synthesis of Cu nanoparticles-wrapped on RGO nanosheet catalyst and their outstanding stability and catalytic performance in the hydrogenation reaction of dimethyl oxalate

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Synthesis of GO NSs using modified Hummer method

Modified Hummers method was utilized to synthesize graphene oxide from the oxidation of high purity graphite powder. 96.0 ml Conc H₂SO₄ was added gradually to a mixture of 2 gm purified graphite flakes and 1 gm of sodium nitrate with keeping in ice bath. After around 30 min of vigorous magnetic stirring, 6 gm of KMnO₄ was added gradually and very carefully and stirred for 2 h under 20 °C as maintained by using ice bath. The mixture was placed in an oil bath whose temperature was maintained around 35 °C by a hot plate and magnetically stirred for 20 h after which the mixture turned into heavy brownish pasty color. Then, 150 ml di- water was added gradually within vigorous stirring. When the temperature increased with huge toxic gas bubbling, the more di-water was added until the solution diluted with 240 ml. When the diluted suspension color changed into brilliant yellow, 5 ml of H_2O_2 as strong oxidizing agent was added to it. After 2 h of continuous stirring, the mixture was filtered and washed by rinsing and centrifugation with mixture of 10% HCl. Then ultra-pure ethanol and di-water was added for several times to increase the pH value towards neutral. The resulting filtered mixturewas dried in oven for 24 h approximately at temperature 70 °C, and finally, solid GO powder was obtained.

| Type of Catalyst | S _{BET} (m2/g) | Pore | Cu ⁺ /(Cu ⁺ +Cu ⁰) % | TOF value |
|--------------------------------|-------------------------|---------|--|----------------------------|
| | | diamete | | (h ⁻¹) |
| | | r (nm) | | |
| Cu/RGO (US) | 43.8 | 8.1 | 27 | 4.8 |
| Cu/RGO (NH ₄ OH) | 21.9 | 7.3 | 28.3 | 15.3 |
| Cu/RGO (US/NH ₄ OH) | 37.4 | 18.4 | 34 | 17.1 |
| Cu/RGO (10 wt%) | 49.6 | 8.2 | 26.3 | 12.6 |
| Cu/RGO (25 wt%) | 37.4 | 18.4 | 34 | 17.1 |
| Cu/RGO (45 wt%) | 37 | 19.1 | 26 | 14 |

Table S1 Physico-chemical properties of the prepared catalysts

| Ref | Reaction temperature (°C) | H2/DMO Ratio mol mol ⁻¹ | |
|-----------|----------------------------------|------------------------------------|--|
| 1 | 200 | 80 | |
| 4 | 210 | 300 | |
| 12 | 80 | 17.5 | |
| 13 | 220 | 110 | |
| 32 | 220 | 80 | |
| 38 | 180 | 150 | |
| 39 | 210 | 200 | |
| This work | 210 | 200 | |

Table S2 Reaction condition for the catalysts used in the comparison of the catalytic activity (Related to Table. 1)



Fig. S1 TEM images for the Cu/RGO catalyst (US)



Fig. S2 XPS survey and analogues high resolution images of Cu 2p for Cu/RGO catalysts (a,b) synthesized in different reaction condition and (b) synthesized in presence of ultrasound and ammonia within different Cu wt% loading.



Fig. S3 XPS and HR-XPS to as-prepared, reduced and spent Cu/RGO catalyst to show the shift in the bending Energy values after reducing and used catalyst.



Fig. S4 H2-TPR for Cu/RGO catalysts synthesized (a) in different reaction condition and (b) synthesized in presence of ultrasound and ammonia within different Cu wt% loading.



Fig. S5 MG and DMO conversion ratio for the spent Cu/RGO catalyst after 300 h of reaction time.



Fig. S6 TEM and HRTEM image for the spent Cu/RGO catalyst