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SUPPORTING INFORMATION

Highly Active g-C_3N_4 as a Solid Base Catalyst for Knoevenagel Condensation Reaction under Phase Transfer Conditions†

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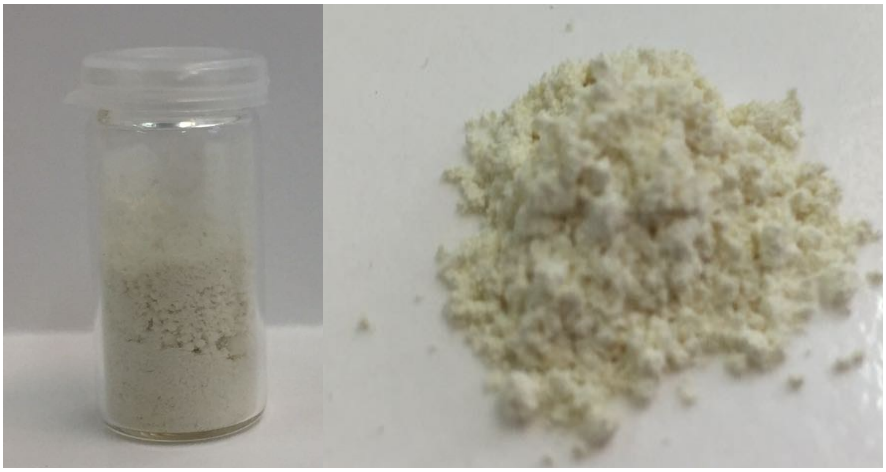

Figure S1: Physical appearance of g-C_3N_4 catalyst.

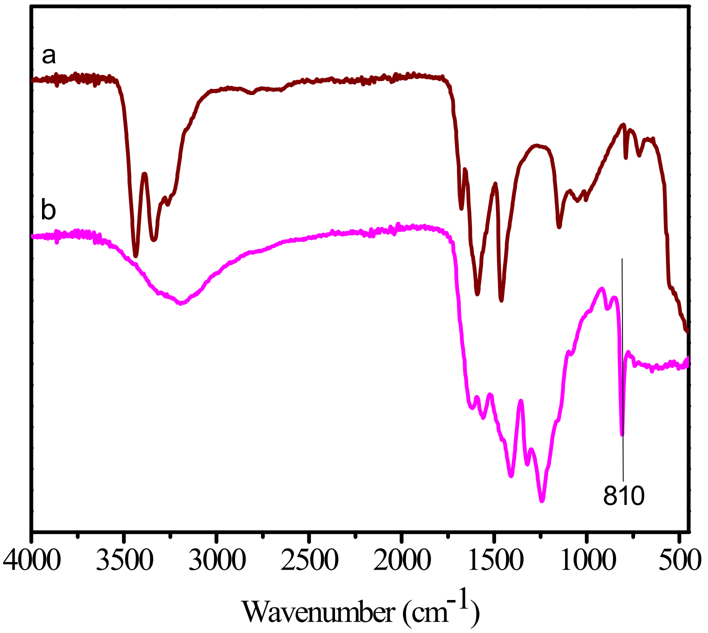

Figure S2: FT-IR spectra; a) Urea, b) g-C_3N_4.

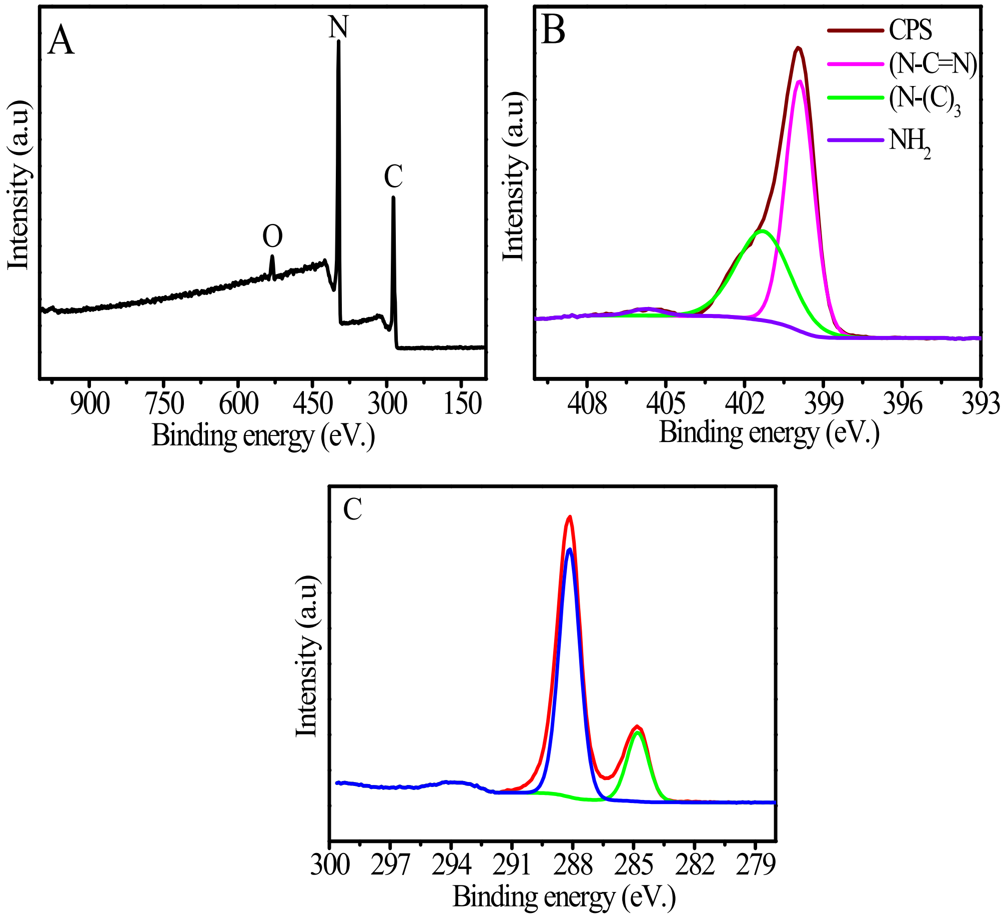

Figure S3: XPS spectra: (A) full scan g-C_3N_4, (B) high resolution XPS spectra in the N 1s region of g-C_3N_4, (C) in the C 1s region of g-C_3N_4.

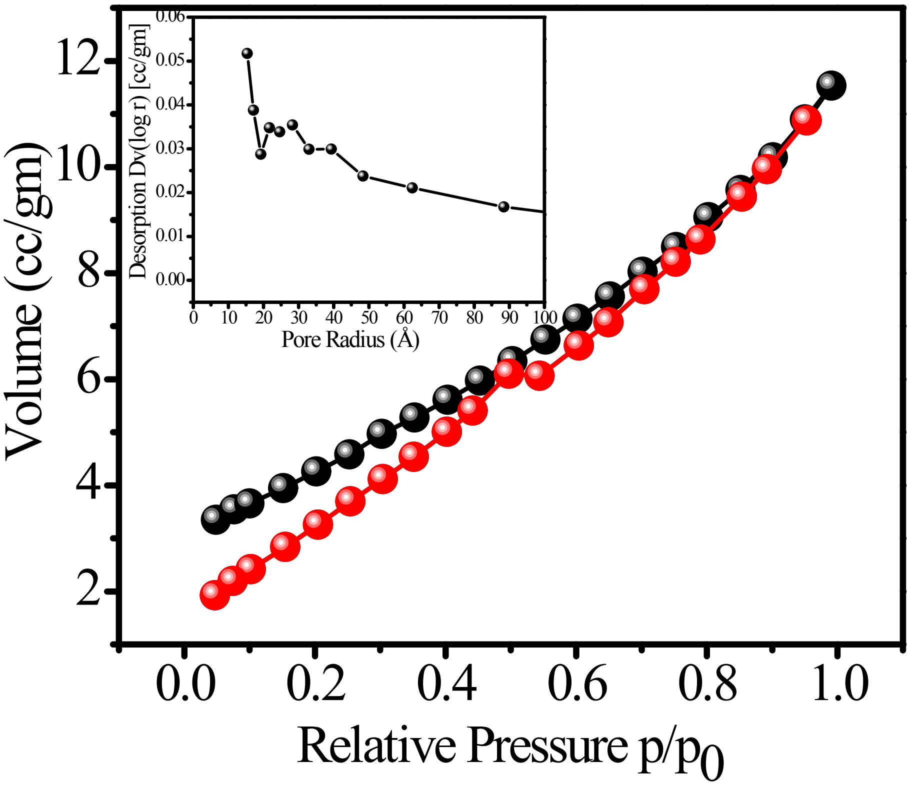

Figure S4: Nitrogen adsorption-desorption isotherm & inset Pore size distribution of g-C_3N_4.

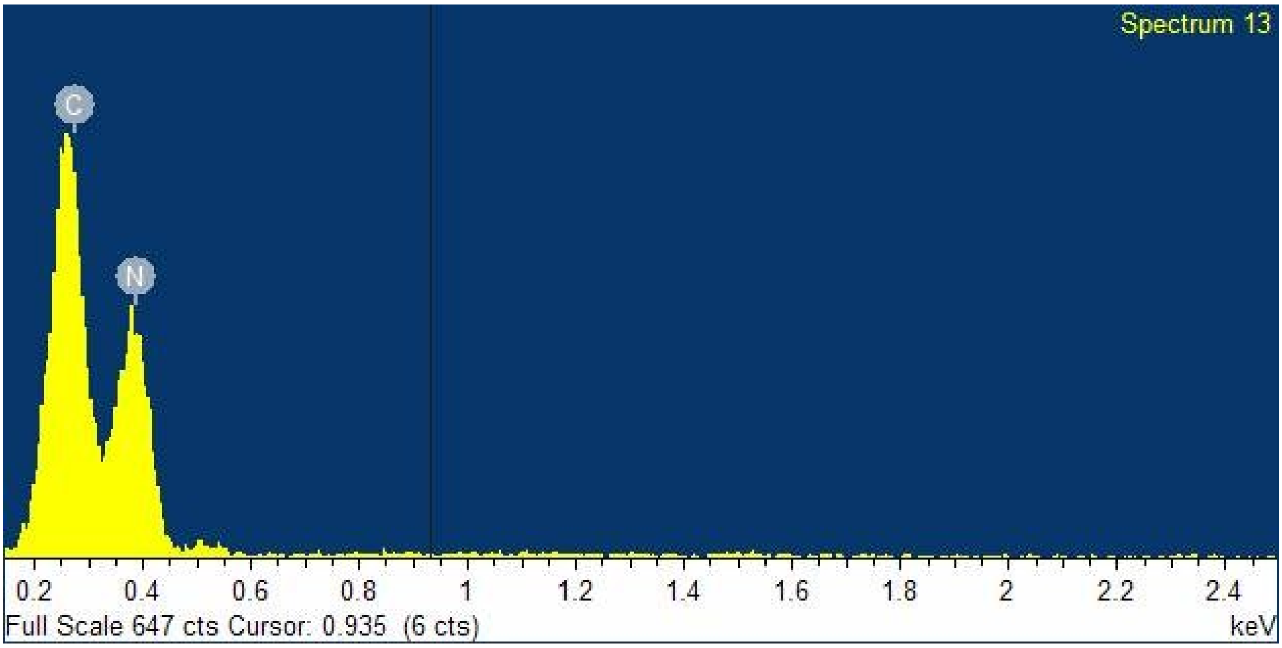

Figure S5: SEM-EDX images g-C_3N_4.

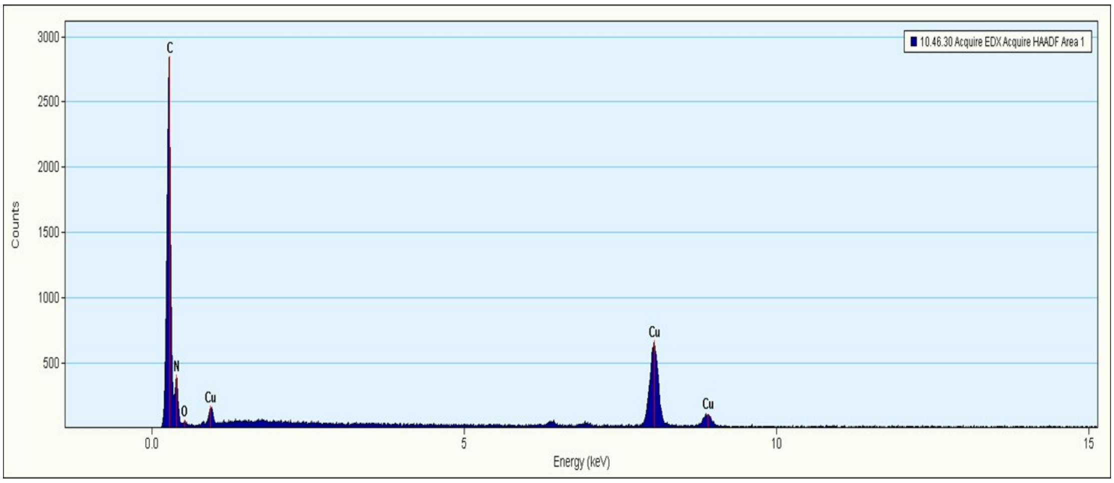

Figure S6: TEM-EDX images of g-C_3N_4.

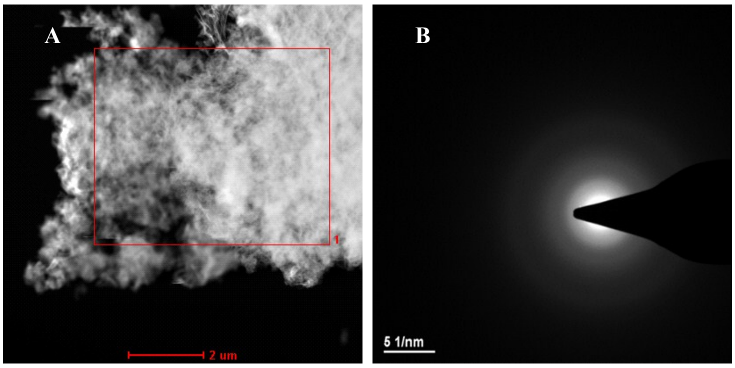

Figure S7: TEM images of g-C_3N_4 with different magnification (A) at 1µm scale, (B) g-C_3N_4 SAED pattern.

CHARACTERIZATION

XRD measurements were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Soller slits, and 0.2 mm receiving slit. A low background quartz sample holder was carefully filled with the powder samples. XRD patterns from 5° to 85° 2θ were recorded at room temperature using Cu Kα radiation (λ = 0.15418 nm) with the following measurement conditions: a tube voltage of 40 kV, a tube current of 40 mA, step scan mode with a step size of 0.02° 2θ and a counting time of 1 s per step for preliminary study and 12 s per step for structural refinement. The instrumental broadening was determined using LaB6 powder (NIST-660a). X-ray diffraction patterns were collected by using a Bruker AXS D8 Advance. UV/Vis absorption spectra were monitored by using a Carry 100 Bio and diffuse reflectance analysis was carried out by using an Integrating Sphere (JASCOV-650 Series ISV-722). XPS analysis was conducted using an XPS Kratos AXIs Ultra (Kratos Analytical Ltd, UK) high resolution photoelectron spectroscopy instrument. FTIR spectra were obtained by using a Bruker (Alpha-T). The surface area was determined by the N_2 Brunauer–Emmett– Teller (BET) method (NOVA-1200e). Sample morphology was observed by extra high-resolution scanning electron microscopy (Magellan™ 400 L).

EXPERIMENTAL

Synthetic procedures, Materials and methods Material: The materials used in the experiments such as urea, alcohols, aldehydes, and ketones tetrabutyl ammonium bromide (TBAB), tetrahexyl ammonium bromide (THAB), tetrabutyl ammonium

Iodide (THAB), (tetrahexyl ammonium Chloride (THAB), (tetraethyl ammonium Chloride (THAB), 18 Crown ether 6 were purchased from commercial firms (Sigma Aldrich and reliable resources) and used without further purification. GC analyses were performed using a Focus GC from Thermo Electron Corporation, equipped with a low polarity ZB-5 column. GC analyses were performed using a Trace 1300 Gas Chromatograph model from Thermo Scientific, equipped with an Rxi-1 ms (Crossbond 100% dimethyl polysiloxane) column. Conversion was based on the GC area.

Graphitic carbon nitride (g-C_3N_4) synthesis: Graphitic carbon nitride (g-C_3N_4) is synthesized by a known published method by *Wei Chen et. al.*[1] In a typical experiment, 5 g of urea (99%) was kept in a ceramic crucible, and loaded inside the central region of the furnace. The furnace was programmed upto 550 °C (10 °C min^{-1} rate) in air and kept at 550 °C for 3 h, and then allowed to cool to room temperature automatically. After the process completion a pale yellow colored g-C_3N_4 material was obtained for further characterization and use (Scheme 1).

Heterogeneous Study of catalyst g-C_3N_4

Owning the preferred advantages in heterogeneous catalyst *viz;* reusability ease, economically synthesis, reactors compatibility, and continuous product production processes; solid catalysts were selective choice since long compared to homogeneous catalysts.[2-3] The recycling test for g-C_3N_4 was carried out under the optimized Knoevenagel condensation conditions by using model reaction substrate 4-nitrotoluene (1 mmol) and benzaldehyde (1 mmol), at room temperature (25°C) with PTC (0.1 mmol), solvent toluene (5 mL) and g-C_3N_4 (30 mg) catalyst.

After the reaction completion, the heterogeneous g-C_3N_4 basic catalyst was recovered by simple filtration (using Whatmann filter paper), washed with acetone, dried (overnight in oven) and reused in other new fresh experiments for next five runs. The heterogeneous g-C_3N_4 catalyst is stable in nature and can be reused several times (Figure 5).

References

1. Liu, J.; Zhang, T.; Wang, Z.; Dawson, G.; Chen, W., Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity. *Journal of Materials Chemistry* **2011,** *21* (38), 14398-14401.
2. Sharma, P.; Singh, A. P., A covalently anchored 2,4,6-triallyloxy-1,3,5-triazine Pd(ii) complex over a modified surface of SBA-15: catalytic application in hydrogenation reaction. *RSC Advances* **2014,** *4* (102), 58467-58475.
3. Sharma, P.; Singh, A. P., Phosphine free SBA-15-EDTA-Pd highly active recyclable catalyst: synthesis characterization and application for Suzuki and Sonogashira reaction. *Catalysis Science & Technology* **2014,** *4* (9), 2978-2989.

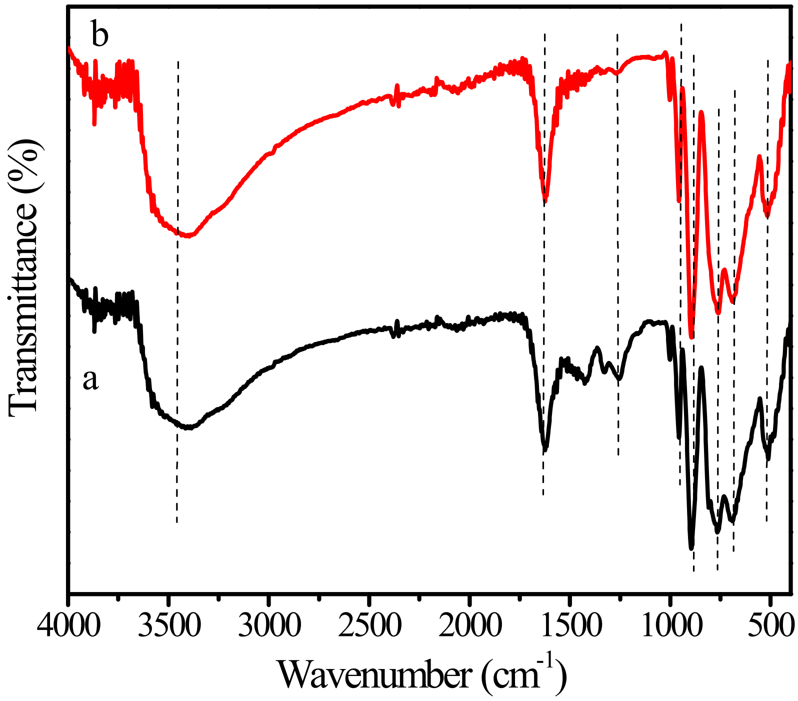

Figure S8: FT-IR analyses of (a) Fresh g-C_3N_4 (b) spent g-C_3N_4.

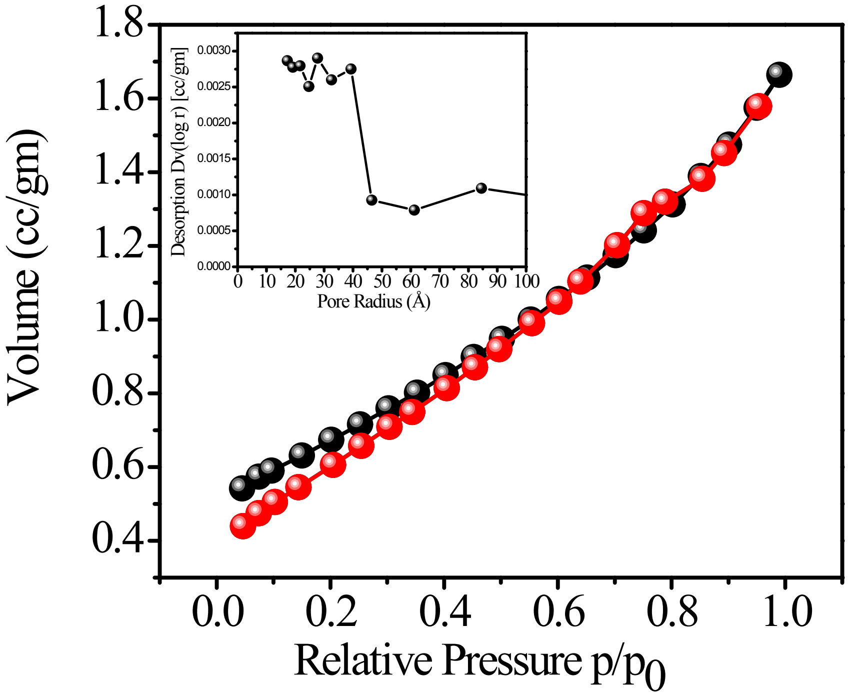

Figure S9: Nitrogen adsorption-desorption isotherm & inset Pore size distribution of reused g-C_3N_4.