

Green synthesis of zinc oxide nanoparticles by using Plant extract for catalysis applications

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Synthesis of ZnO nanoparticles

In a typical green synthesis method, peeled oranges are washed and dried. Placed in a dryer for 12 hours until completely dry, and then ground to a moderate fine powder with a mortar and pestle. 1 g of powder is placed in a RB flask, then add 50 ml of water and stirred for 3 h. The mixture is placed in a water bath at 60°C for 60 minutes. Finally, the mixtures were filtered. 2 g of zinc nitrate was added to the 45 ml of extract. The mixture was placed in a water bath at 60 °C for 60 min with continues stirring. White precipitate can be observed; the white precipitate was separated by centrifugation, and then washed with deionized water followed by ethanol respectively to make it free from impurities. The precipitate was then dried at 100 °C and then heat treated at 400 °C for 1 h.

Catalytic Reaction

The alkylation reaction was carried out in a round bottom reflux flask with a continuous flow of cold water and constant stirring. In a typical reaction study, 3 mmol of benzyl alcohol, 0.5 g of catalyst and 5 mL of acetonitrile are taken in a round bottom flask, and then 1 mmol of acetophenone is added drop wise. The temperature was increased to 100°C and this temperature was maintained for 4 hours. The reaction mass was then cooled to room temperature, after which the product was collected by filtration and analyzed by GC-MS.

General Characterizations

The powder X-ray diffraction (XRD) patterns of the materials were recorded using a Rigaku D/Max 2550 X-ray diffractometer operating with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The transmission electron microscope (TEM) images of the materials were obtained with a Topcon

002B TEM microscope operating at 200 kV. The scanning electron microscope (SEM) images of the materials were acquired using a Zeiss Sigma field emission SEM microscope (Model 8100).

The ex-situ FT-IR spectra of pyridine adsorbed samples were recorded on a ThermoElectron FTIR 560 spectrometer together with a MIRacle attenuated total reflectance (ATR) platform assembly and a Ge plate. The pyridine adsorption was carried out on an AutoChem 2920 II (Micromeritics). Prior to adsorption, the catalysts were heated in helium flow at 300 °C for 1 h to remove moisture.

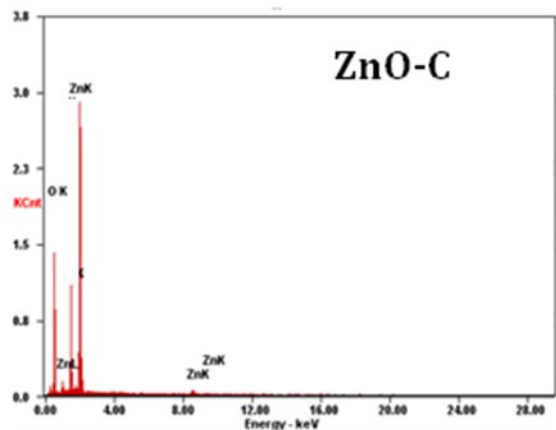


Fig. S1. EDX patterns of ZnO-C.

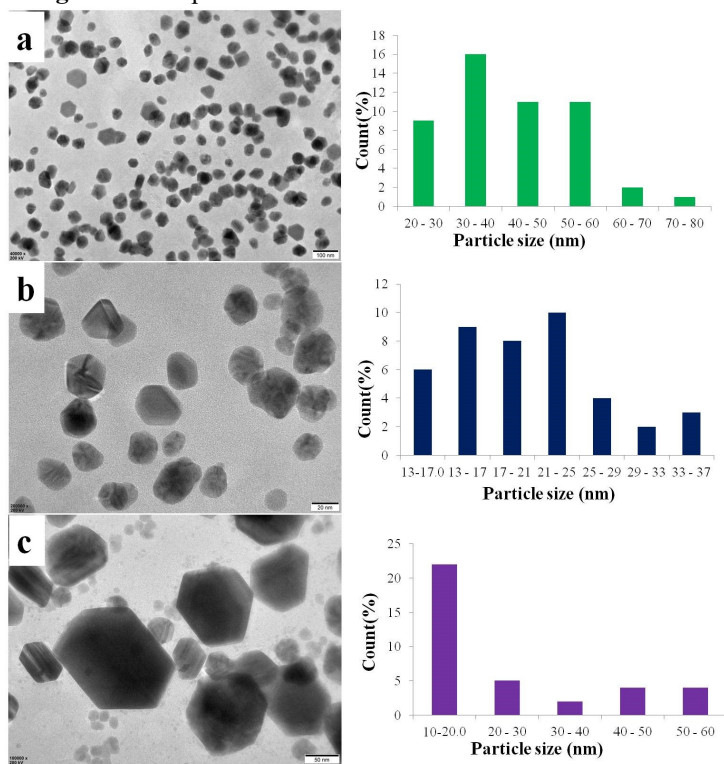


Fig. S2. a, b and c are the TEM images and particle size of ZnO-C, ZnO-H and ZnO-F materials

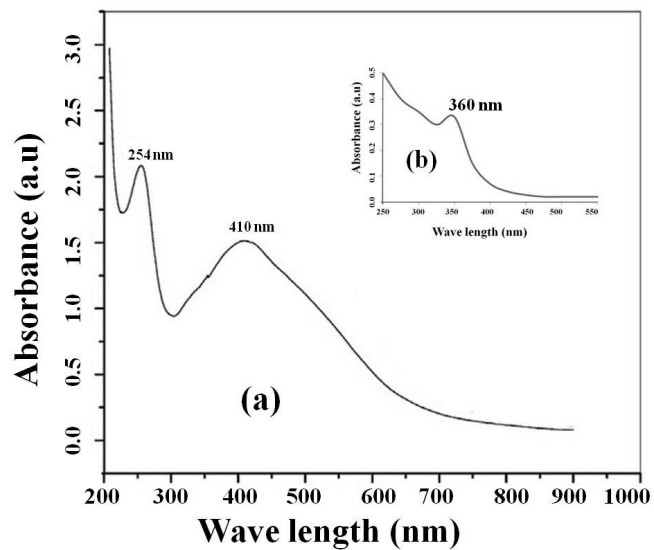


Fig. S3. UV-Vis graph of a) orange peel extract and b) ZnO-C

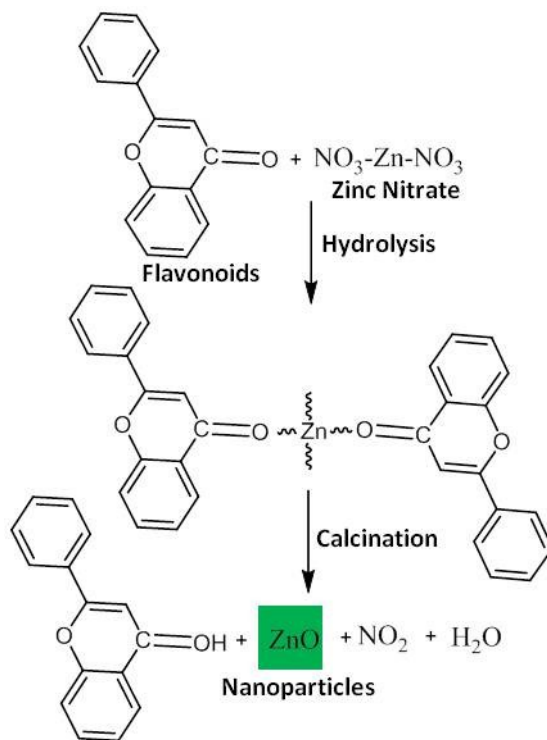


Fig. S4. The chemical mechanism of ZnO nanoparticle formation.

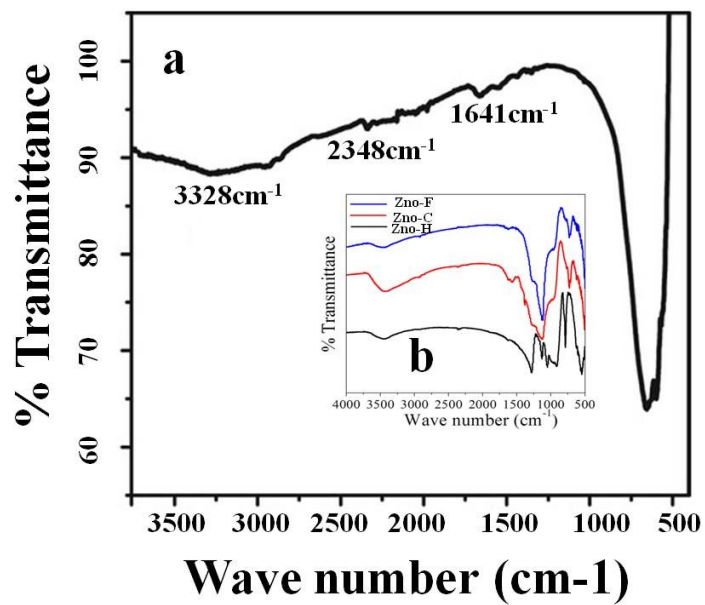


Fig. S5. FT-IR patterns of a) orange peel extract and b) ZnO-C

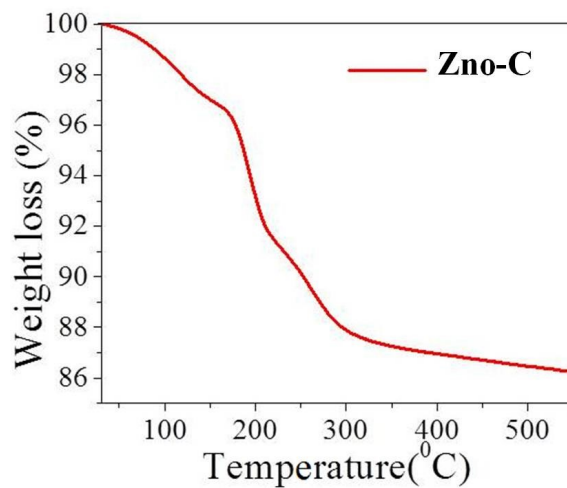


Fig. S6. Typical TGA pattern of Citrus Sinensis synthesized ZnO-C(Before calcination).

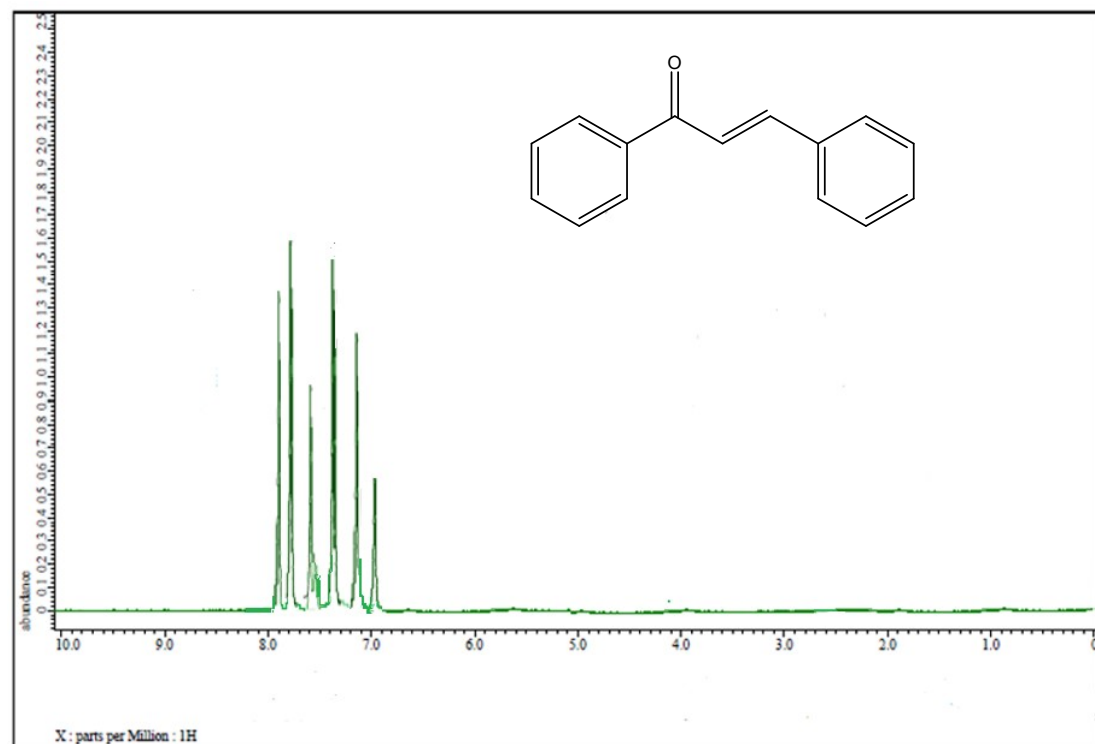
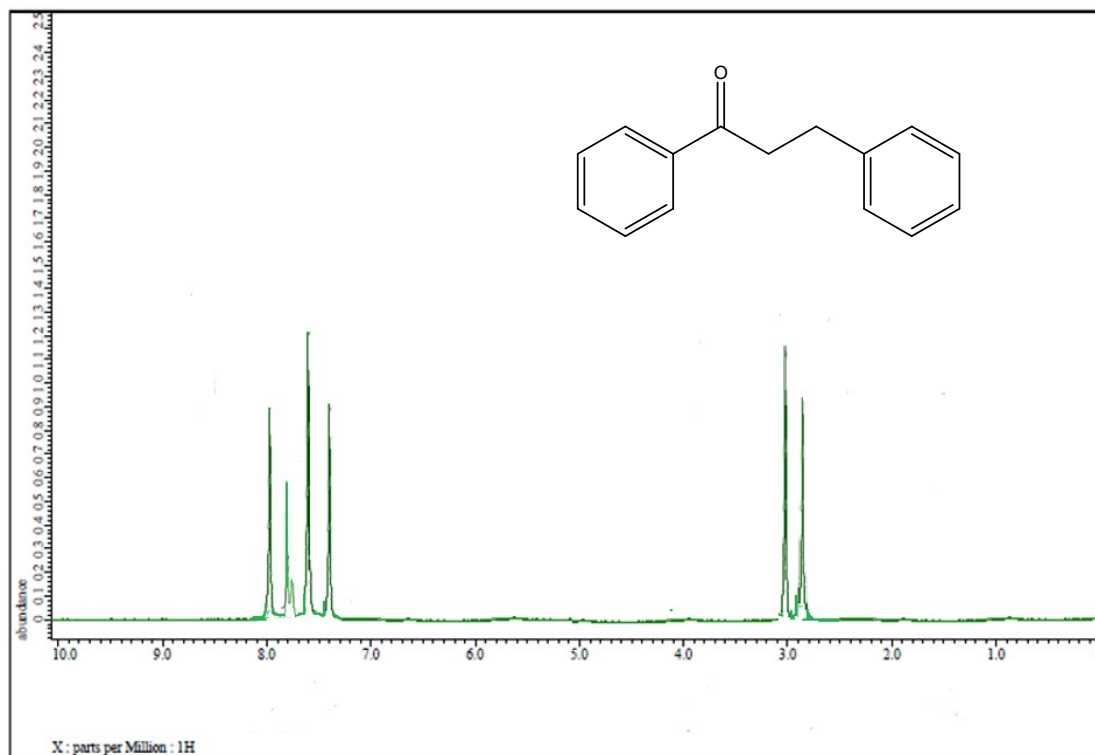


Fig. S7 NMR spectra of products

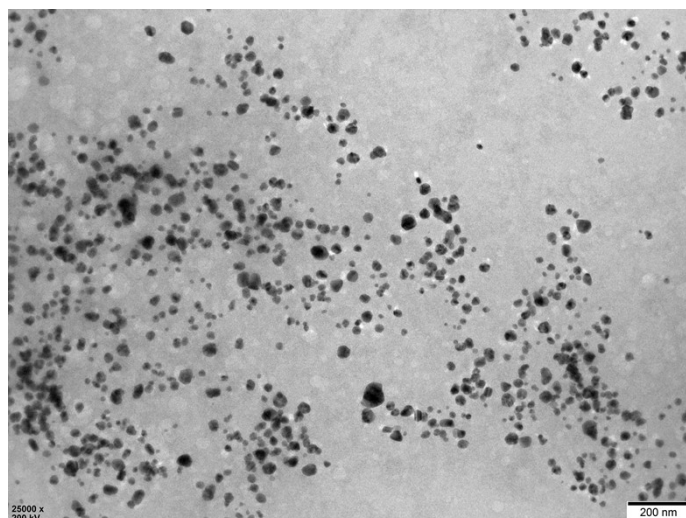


Fig. S8 TEM image of spent material of ZnO-C

Table S1. Comparison of the catalytic performances of ZnO catalysts in acetophenone alkylation with other reported catalysts for the same reaction.

S.No	Catalyst	Base	Temperature (°C)	Time(h)	Yield (%) ¹ , 3diphenyl prope-1one	Conversion based on	Ref
1	(iPr-PNP)Mn(H)(CO) ₂	tBuOK	125	18	98	Benzyl alcohol	S1
2	Ni/SiO ₂ -Al ₂ O ₃	K ₃ PO ₄	175	14.5	86	Benzyl alcohol	S2
3	Nano-Fe ₂ O ₃	t-ButOK	135	24	97	--	S3
4	Cu/CuOx 250	K ₃ PO ₄ (0.5)	170	12	93	Acetophenone	S4
5	CeO ₂	--	150	6	14	Acetophenone	S5
6	ZnO-C	----	100	4	80	Acetophenone	Present work
7	ZnO-C(used catalyst)	----	100	4	78	Acetophenone	Present work

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