Phenylacetylene hydrogenation on Au@Ni bimetallic core shell nanoparticles synthesized under mild conditions

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Experimental section:-

Syntheses of core shell bimetallic nanoparticles are always challenging and needs precise attention while carrying out the experiments. All the glass wares are cleaned thoroughly with aquaregia and dried properly. The reagents must be used without any contamination like moisture or heat. Hydrogen tetrachloroaurate tri hydrate $[\text{HAuCl}_4\cdot3\text{H}_2\text{O}]$ and Nickel acetylacetonate $[\text{Ni(acac)}_2]$ serves as metal precursors whereas NaBH$_4$, $\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O}$/ NaOH were used as the reducing agents and they were purchased from Sigma Aldrich [Germany] including reaction medium solvent Oleyl amine. Remaining compounds like Phenyl acetylene, TPP along with other solvents Methanol, DCM, THF, Ethanol and Hexane were purchased from Merck.

Synthesis of core shell Au@Ni Core shell Nanoparticles:-

In a modified synthesis strategy, followed by our previous reports\textsuperscript{38} we found that Au@Ni core shell nano particles can be synthesized through an energy efficient way without going for high temperature thermal reduction methods as mentioned before. In the first stage, gold nanoparticles were synthesised by a facile room temperature reduction of gold precursor by the addition of 30µL of .1M aqueous NaBH$_4$ solution in to 0.025 mmol gold precursor solution dissolved in 6ml oleyl amine. The solution is stirred well for 15 minutes for the complete reduction to gold nanoparticles. A gradual colour change occurs from a light yellow to wine red colour during the course of time. In the second stage, the gold seed solution is heated to 45 ºC, and then added 0.02 mmol of nickel precursor $[\text{Ni(acac)}_2]$. After the complete dissolution, the entire solution mixture is heated to 80 ºC with simultaneous addition of 0.015 mmol TPP. After reaching the desired temperature 500µL NH$_2$-$\text{NH}_2\cdot\text{H}_2\text{O}$/NaOH mixture was added drop wise very slowly [the mixture is prepared by mixing 5 ml hydrazine solution and 50 mg NaOH]. The solution is stirred well for 20 minutes to get a brownish black colloidal solution which in turn sticks to the magnetic bead inside the solution. The disappearance of wine red colour indicates the reduction of nickel ions on the surface of preformed gold nanoparticles and resulted in a black colloidal solution, since nickel does not possess any SPR like gold nanoparticles. Finally magnetic core shell nanoparticles are recovered with the help of an external magnet,
washed with hexane-ethanol mixture thoroughly to remove excess of capping agents and redispersed in hexane for further characterizations. For catalytic applications the Au@Ni core shell nano particles are washed thoroughly with the respective solvents before the reactions were conducted.

**Liquid phase hydrogenation of Phenylacetylene (P.A):-**

Hydrogenation of phenylacetylene under different reaction parameters were carried out in a Parr stirred tank reactor having a volume of 100ml capacity. In a typical hydrogenation reaction the stirred tank is charged with 5 mg of the Au@Ni catalyst dispersed in 50 ml solvent. After that 5 mmol of the substrate is added to the reaction vessel. The reaction vessel was closed and flushed with hydrogen 3 times to remove the air and other impurities from the vessel then it is pressurised to the desired condition. The reactions were done at required temperatures with continuous stirring. The samples were collected at specific time intervals and analysed with the help of a Gas chromatograph equipped with a flame ionization detector having a HP-1 capillary column.

**Characterization:--**

(i) **UV-Visible Spectroscopy:** Varian Cary 50 Conc UV–Vis spectrophotometer with a dual beam source has been used for obtaining the UV-vis spectra.

(ii) **X-ray Diffraction Analysis:** Powder X-ray diffraction (XRD) of Au@Ni core shell nanoparticles were measured on a PANalytical X’pert Pro dual goniometer diffractometer working under 40 kV and 30 mA. The Cu Kα (1.5418 Å) radiation was used with a Ni filter. The data collection was carried out using a flat holder in Bragg–Brentano geometry. An X’celerator solid-state detector with a scan speed of 0.012° min⁻¹ was employed in measuring wide angle X-ray diffractions.

(iii) **Transmission Electron Microscopy (TEM):** FEI Tecnai TF-30 electron microscope, operating at 300 kV, was used for High Resolution Transmission Electron Microscopy (HRTEM) images of core shell nanoparticles.

(iv) **Magnetic measurements** were done on a Quantum Design MPMS 7T SQUID-VSM.

(v) **X-ray photo electron spectroscopy (XPS):** XPS measurements were carried out under UHV (ultra high vacuum) conditions by using an ambient pressure X-ray photoelectron spectrometer from Prevac, Poland.

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![UV-Vis spectra of (a) gold seed solution and (b) Au@Ni core shell nanoparticles. (Inset shows the photograph of gold colloid).](image)
S.I Fig. 2 XRD spectra obtained for (a) Nickel nanoparticles, (b) Au nanoparticles and (c) Au@Ni nanoparticles. Pink and black dotted lines indicate the standard gold and nickel reflections respectively. Figure (II) is the enlarged area of figure (I) and the shaded region corresponds to the Ni (200) reflection.

S.I Fig. 3 TEM image and EDX analysis quantification result of Au@Ni core shell nanoparticles.
S.I Fig. 4 Wide scan XPS spectra of Au@Ni core shell nanoparticles. The shaded areas indicate the presence of typical binding energy values of Au, Ni, C and O elements.

S.I Fig. 5 Hysteresis loops obtained for Au@Ni core shell nanoparticles measured at room temperature in VSM. [Inset (down) shows the hysteresis width near to the origin and photograph (above) of bimetallic nanoparticles attracted towards external magnet].

S.I Fig. 6 Gas Chromatograph obtained for the analysis of reaction mixture during P.A hydrogenation in MeOH and DCM. (a) G.C result of P.A in MeOH at the initial point (0 Hrs), Green dotted line indicates the standard P.A peak position. (b) G.C result obtained after 4 Hrs of reaction in MeOH. Red dotted line indicates the peak position obtained for the standard sample of E.B. Absence of P.A peak corresponds to complete hydrogenation to E.B after 4 Hrs. (c) G.C result obtained after 10 Hrs of reaction in DCM. Blue and red dotted lines indicate the peak position obtained for the standard sample of Styrene and E.B respectively.