Supplementary material

One-Pot Synthesis Of Hantzsch Dihydropyridines Using Highly Efficient and Stable PdNiRu@GO Catalyst

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Chemicals and Equipments

The synthesis was carried out using standard airless procedures and commercially available reagents. PdCl₂, RuCl₃ and NiCl₂ used in the tandem reaction were purchased from Sigma-Aldrich and used as received. Water was purified using a Millipore water purification system (18 MΩ) analytical grade. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by washing with distilled water before drying. Tetrahydrofuran (THF; 99.5%), methanol (≥99.5%), ethanol (99.9%), 2-propanol and HClO₄ (60%) were purchased from Merck, superhydride, dimetilaminoborane (DMAB), NaBH₄ and all aldehyde compounds were bought from Aldrich and used as received. Graphite oxide, Sulfuric acid (H₂SO₄), Hydrochloric acid (HCl), Nitric acid (HNO₃), Acetonitrile (ACN), N,N-
Dimethylformamide (DMF), Lithium perchlorate (LiClO\textsubscript{4}), 3,4-Ethylenedioxythiophene (EDOT) were purchased from Sigma Aldrich.

UV–Vis analyses were taken by Perkin Elmer Lambda 750. 200–900 nm was selected to gather the data and 1 cm-long a quartz cell was employed. FT-IR analyses were taken by Perkin Elmer Spectrum 2. Raman spectrum was carried out using an in via Raman microprobe (Renishaw Instruments) with 514 nm laser excitation.

The samples were coated with gold by placing the stamp and they were analyzed and took micrographs in Field Emission Scanning Electron Microscopy (FESEM-Carl Zeiss, Supra 40 VP).

TEM images of Pd-Ru-Ni@GO NPs have been obtained by a JEOL 200 kV TEM instrument. Sample preparation was carried out through the suspension of ~0.5 mg catalyst in 3 ml of ethanol in an ultrasonic bath and then a drop of this solution was put on to a carbon covered 400-mesh copper grid. More than 300 particles were analyzed to get a particle size distrubition. Finally, evaporation of the solvent was done at room temperature.

X-ray diffraction (XRD) was performed using a Panalytical Empyrean diffractometer with Ultima + theta-theta high resolution goniometer, the X-ray generator (Cu K\textalpha{} radiation, \(\lambda = 1.54056\text{Å}\)) with an operation conditions at 45 kV and 40 mA.

A Specs spectrometer was used for X-ray photoelectron spectroscopy (XPS) measurements using K\textalpha{} lines of Mg (1253.6 eV, 10 mA) as an X-ray source. C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line.

The amount of metals in monodisperse Pd-Ru-Ni@GO NPs was determined by a Leeman Lab inductively coupled plasma spectroscopy (ICP). \textsuperscript{1}H NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer. BET analysis was performed at 77 K using a NOVA 4200e. Before the BET analysis, catalyst were degassed at 120 °C for 5 h.

The preparation of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer’s method. Briefly, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of KMnO\textsubscript{4} was added gradually to the above solution while keeping the temperature less than 20 °C to
prevent overheating and explosion. The mixture was stirred at 35 °C for 12 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H₂O₂ solution (5 ml). The resulting mixture was washed with HCl and H₂O respectively, followed by filtration and drying, graphene oxide sheets were thus obtained.

The characterization of GO

The prepared GO was characterized by Fourier Transform Infrared (FT–IR) and UV-Vis Spectrophotometer. FT–IR spectra of graphene oxide (Fig. S1) indicate that a broad absorption band between 3200-3600 cm⁻¹ correspond to the –OH stretching mode. Furthermore, carbonyl groups at around 1632 cm⁻¹ and the stretching vibration of C-O of carboxylic acid and C-OH of alcohol at around 1155-1032 cm⁻¹ indicate the formation of GO.

![FT–IR of Graphene Oxide](image)

**Fig. S1.** FT–IR of Graphene Oxide

Moreover, UV-Vis spectrum of graphene oxide also indicates the formation of GO as shown in Fig. S2. The peak at ~235 nm and shoulder peak at ~300 nm may be due to π-π* transition of the atomic C-C bonds and n-π* transitions of aromatic C-C bonds, respectively.
As shown in Figure S3a, the C1s XPS spectrum of the pristine GO exhibits four different peaks centered at 284.0, 284.8, 287.4 and 290.6 eV, corresponding to sp^3 C, C = O, C-O and O= C=O groups, respectively. Besides, in Fig. S3b, the O1s spectra of GO can be curve-fitted into two peaks, which are corresponding to C=O (carbonyl and carboxyl, 533.6 eV) and C-O (epoxy and hydroxyl, 532.7 eV).
Raman spectroscopy is also an effective method to distinguish the ordered and disordered structure of carbon in carbonaceous materials. The Raman spectrum of GO is shown in Fig. S4. The $I_D/I_G$ ratio for GO was found to be $\sim 1.01$.

**Fig. S4.** The Raman spectra of GO
Figure S5 SEM and EDX image of PdRuNi@GO before the reaction
Figure S6 SEM and EDX image of PdRuNi@GO after using five times of catalyst
$^1$H and $^{13}$C NMR spectra of 1,4-dihydropyridine compounds

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (1):
Diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2)
Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (3):
Diethyl 4-(3-nitrophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4):
Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5):
Diethyl 4-(4-(dimethylamino)phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (6):
Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7):
Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (8):
Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (9):
Ethyl 2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (10):
Ethyl 4-(2,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (11):
Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (12):
Ethyl 4-(4-(dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (13)
Ethyl 2,7,7-trimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (14)
Ethyl 4-cyclohexyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (15)
Ethyl 2,7,7-trimethyl-5-oxo-4-pentyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (16)
Ethyl 2,7,7-trimethyl-4-(naphthalen-2-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (17)
Ethyl 4-(furan-2-yl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (18)