

Mild bottom-up synthesis of indium(0) nanoparticles: characterization and application in the allylation of carbonyl compounds.

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Supporting Information

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General experimental details

All moisture sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents were treated prior to use by standard methods. All starting materials were of the best available grade (Aldrich, Fluka, Merck) and were used without further purification. Commercially available indium(III) chloride were kept in a dry desiccator after opening. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm , 240–400 mesh). Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in ethanol.

Instrumentation and analysis

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrometer using CDCl_3 as the solvent and tetramethylsilane (TMS) as internal reference.

Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector.

The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-14B instrument equipped with a flame-ionization detector and a 30 m column (HP-5MS, 0.25mm, 0.25 μm), using nitrogen as carrier gas.

The freshly prepared InNPs were characterized by Transmission Electron Microscopy (TEM) in a JEOL 100CX2 instrument, operated at an acceleration voltage of 100 kV. TEM images were obtained by dropping the THF solution of the InNPs on holey-carbon coated 300 mesh. Near one hundred metal particles were measured to perform the particle size distribution.

The UV/VIS absorption spectra were measured on a UV JASCO V-630 spectrophotometer.

The X-ray diffraction (XRD) study was carried out on a Philips PW 1710 X-ray diffractometer with $\text{CuK}\alpha$ irradiation ($\lambda = 1.5406 \text{ \AA}$), operating at 45 kV and 30 mA; and scanning from $2\theta = 20$ up to 80.

The X-ray photoelectron spectroscopy (XPS) spectra were measured with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatised $\text{MgK}\alpha$ (1253.6 eV) radiation source of 300 W and a hemispheric electron analyzer equipped with 9 channeltron electron multipliers. All the bond energies were referred to the line of the C1s to 284.8 eV.

Synthesis and characterization of the InNPs

Indium(III) chloride (221 mg, 1 mmol) was added to a suspension of lithium sand (24.5 mg, 3.5 mmol) and 4,4'-di-tert-butylbiphenyl (DTBB, 27 mg, 0.1 mmol) in THF (2 mL) at room temperature under nitrogen atmosphere. The formation of the indium nanoparticles (InNPs) is indicated by the color change of the solution from dark green to black. The InNPs were analyzed and characterized physical and morphologically by TEM, UV, XRD and XPS.

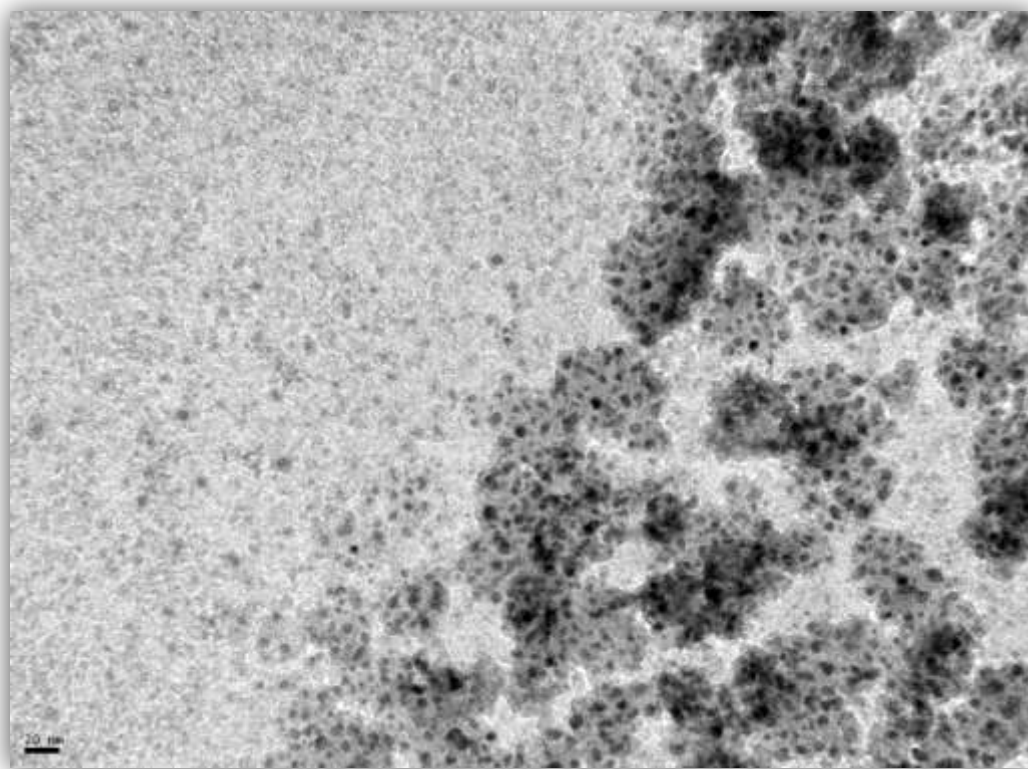


Figure 1. Representative TEM micrograph of the InNPs.

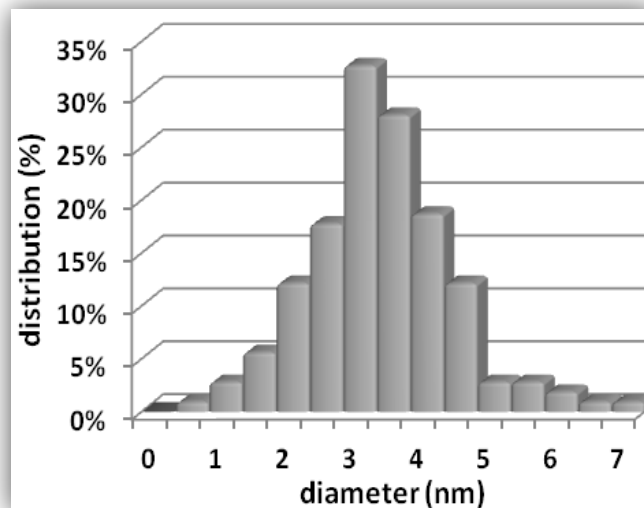


Figure 2. Size distribution determined for 100 nanoparticles selected at random.

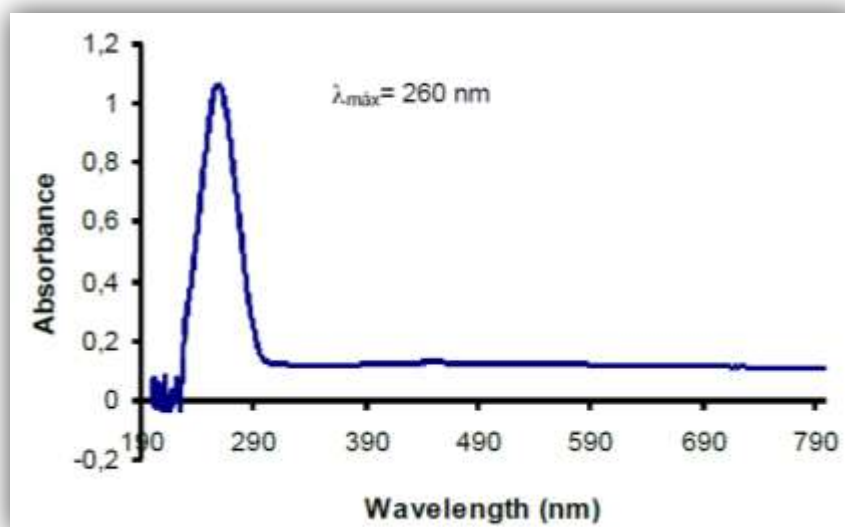


Figure 3. UV absorption spectrum of InNPS in CH_2Cl_2 .

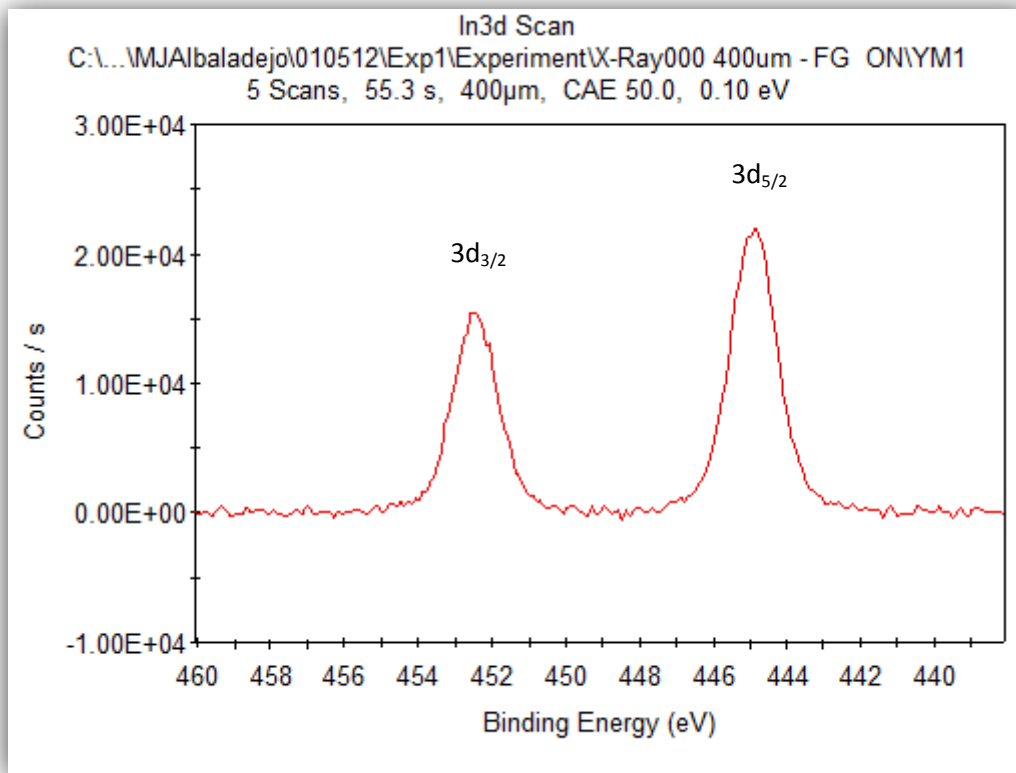


Figure 4. XPS spectra of InNPS (In_{3d}).

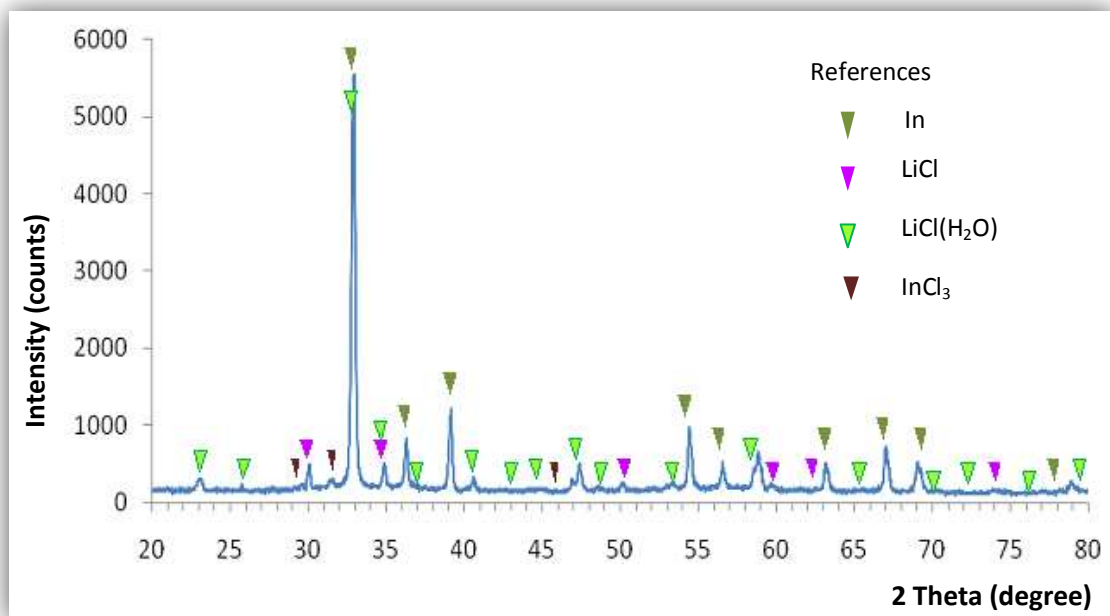


Figure 5. XRD diffractogram of the InNPs.

Representative procedure for the allylation of carbonyl compounds promoted by In powder. Synthesis of homoallylic alcohol 1a.

A suspension of indium powder (-300 mesh, 115 mg, 1 mmol) and allyl bromide (181.3 mg, 0.128 mL, 1.5 mmol) in THF (4 mL) was stirred at room temperature under nitrogen atmosphere for 30 minutes. Then, benzaldehyde (53 mg, 0.051 mL, 0.5 mmol) in THF (1 mL) was added by syringe. After 1 h reaction time, the resulting suspension was diluted with diethyl ether (10 mL) and treated with 10% HCl and water. The combined organic extracts were dried over anhydrous MgSO₄ and quantified by GC (**1a**, 74%).

Representative procedure for the allylation of carbonyl compounds promoted by InNPs. Synthesis of homoallylic alcohol 1a.

The allyl bromide (181.3 mg, 0.128 mL, 1.5 mmol) in THF (1 mL) was added by syringe over the InNPs suspension, and the solution was stirred at room temperature under nitrogen atmosphere for 30 minutes. Then, benzaldehyde (53 mg, 0.051 mL, 0.5 mmol) in THF (1 mL) was added by syringe and monitored by TLC and/or GLC until total conversion of the starting material (1 h). Then the resulting suspension was diluted with diethyl ether (10 mL) and treated with 10% HCl and water. The combined organic extracts were dried over anhydrous MgSO₄, and quantified by GC (**1a**, 98%). The solvent was removed in vacuo and the resulting residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate) to give the corresponding homoallylic alcohol **1a** in 87% isolated yield.

All the homoallylic alcohols obtained are known compounds and were characterized by comparison of their spectroscopic and/or chromatographic data with those described in the literature: 1-phenylbut-3-en-1-ol (**2a**),¹ 2-phenylpent-4-en-2-ol (**2b**),¹ 1-allylcyclohexanol (**2c**),² 1-phenyl-2-methylbut-3-en-1-ol (**2d**),¹ 1-phenyl-3-methylbut-3-en-1-ol (**2e**),¹ 1-phenyl-2,2-dimethylbut-3-en-1-ol (**2f**),¹ 1-allyl-2-isopropyl-5-methylcyclohexanol (**2g**),³ 3-ethylhex-5-en-3-ol (**2h**),⁴ 1-decen-4-ol (**2i**),⁵ 1-phenyl-4-penten-2-ol (**2j**),⁶ 6,10-dimethylundeca-1,9-dien-4-ol (**2k**),⁷ (*E*)-5-methyl-1,5-heptadien-4-

ol (**2l**),⁸ 1-(2-furfuryl)-3-buten-ol (**2m**),⁵ 1-(1-naphtalenyl)-3-buten-ol (**2n**),⁵ 1-(2-methoxyphenyl)-3-buten-1-ol (**2o**),⁵ 1-(2-chlorophenyl)but-3-en-1-ol (**2p**),¹ 1-(2-(trifluoromethyl)phenyl)-3-buten-1-ol (**2q**),⁹ 1-(2-nitrophenyl)-3-buten-1-ol (**2r**),¹⁰ 1-(4-methoxyphenyl)-3-buten-1-ol (**2s**),¹ 1-(4-methylphenyl)-3-buten-1-ol (**2t**),¹ 1-(4-chlorophenyl)-3-buten-1-ol (**2u**),¹ 1-(4-bromophenyl)-3-buten-1-ol (**2v**),⁵ 1,1'-(1,4-phenylene)bis(3-buten-1-ol) (**2z**),¹¹ 1-(4-cyanophenyl)-3-buten-1-ol (**2x**),¹ 1-(4-nitrophenyl)-3-buten-1-ol (**2y**).¹²

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