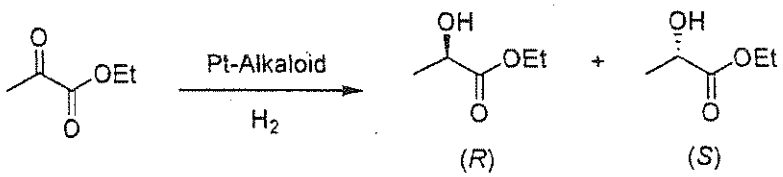
because of their selectivity for catalytic transformations. Small variations in the metal, the modifier and the substrate type can lead to significant changes in enantiodiscrimination.

Catalytic hydrogenation of activated ketones is extremely important because of its effectiveness in producing chiral secondary alcohols. Nanostructures are of particular interest in the asymmetric hydrogenation of α-ketoesters. Platinum nanoparticle catalysts supported on silica, alumina and titania are mainly used in the hydrogenation of activated β-ketoesters. The activity and selectivity of the platinum catalyst are influenced by the support and chiral modifiers, e.g. cinchona alkaloids. Cinchona alkaloids have gained industrial importance in the enantioselective heterogeneous catalytic hydrogenations. Platinum catalysts modified with cinchona alkaloids for the hydrogenation of activated ketones have demonstrated ligand acceleration with a heterogeneous catalyst system, the Orito's catalytic system, giving reasonably good yield and selectivity (Scheme 2). [(a) von Arx, M.; Mallat, T.; Baiker, A. *Top. Catal.* **2002**, *19*, 75. (b) Vayner, G.; Houk, K. N.; Sun, Y.-K. *J. Am. Chem. Soc.* **2004**, *126*, 199]. However, the reproducibility and mechanism of this reaction have remained a challenge for this catalytic system.

**Scheme 2**




Nanowires and nanorods have received tremendous attention in recent years due to their applications in solar cells and other energy applications. Even though metal nanowires are known for many years, their application in catalysis, especially asymmetric catalysis, has not been explored.

## Object of the Invention

It is the object of the present invention to substantially overcome or at least ameliorate one or more of the above disadvantages.

### Summary of the Disclosure~~Invention~~

In a first aspect of the disclosure there is provided a nanoparticulate material comprising long ultrathin metal nanowires, said nanowires having a chiral modifier associated therewith and said nanowires being catalytic for a hydrogenation reaction.

In an embodiment ~~first aspect~~ of the disclosure~~invention~~ there is provided a nanoparticulate material comprising (optionally consisting or consisting essential of) metal nanowires. The nanowires may be long ultrathin nanowires. The nanowires may have a diameter of less than about 2 nm. They may have a length of greater than about 40 nm, or greater than about 50 nm. Each nanowire may be a single crystal. The nanowires may be single crystal nanowires. The nanowires may be etched nanowires, optionally acid etched nanowires.

The disclosure~~invention~~ therefore provides, in an embodiment, a nanoparticulate material comprising (optionally consisting of, or consisting essential of) long ultrathin etched metal nanowires. It provides, in another embodiment, a nanoparticulate material comprising (optionally consisting of, or consisting essential of) long ultrathin single crystal metal nanowires.

The following options may be used in conjunction with the first aspect, either individually or in any suitable combination.

The nanowires may a length of about 40 to about 500 nm. They may have a length of 50 to about 500 nm. They may have a length of about 100 to about 500 nm. They may have a length greater than 500nm. They may have a length of about 1 to about 10 microns. They may have a diameter of less than or equal to about 1.5 nm. They may have a diameter of less than or equal to about 1 nm. They may have a length of about 50 to about 500nm and a diameter of less than about 2, optionally 1.5, nm.

The metal of the metal nanowires may be a Group 8 to Group 11 element, or may be a mixture of any two or more (e.g. 2, 3, 4 or 5) Group 8 to Group 11 elements. The metal may be for example platinum, palladium, rhodium, ruthenium or gold or a mixture of any two or more of these. In a particular embodiment the metal is platinum or is predominantly platinum.

The nanoparticulate material may be catalytic. It may be catalytic for a hydrogenation reaction.

The metal nanowires may have a chiral modifier associated therewith. The chiral modifier may be any suitable chiral compound for example an alkaloid (e.g. a Cinchona alkaloid), an optically active aminoalcohol, an optically active diamine, an optically active phosphine or an optically active aminophosphine or may be a mixture of any two or more of these. Examples of suitable chiral modifiers include 8*R*,9*S*-cinchonidine, 8*R*,9*S*-dihydrocinchonidine, 8*R*,9*S*-quinine, 8*R*,9*S*-dihydroquinine, 8*S*,9*R*-cinchonidine, 8*S*,9*R*-dihydrocinchonidine, 8*S*,9*R*-quinine and 8*S*,9*R*-dihydroquinine.

In an embodiment there is provided a catalytic nanoparticulate material comprising platinum nanowires having a diameter of less than about 2 nm and a length of about 50 to about 500 nm, optionally about 100 to about 500 nm. The nanowires may be straight nanowires. They may be nanorods.

In another embodiment there is provided a catalytic nanoparticulate material comprising platinum nanowires having a diameter of less than about 2 nm and a length of

about 50 to about 500 nm, optionally about 100 to about 500 nm, and having a chiral modifier associated therewith (e.g. adsorbed thereon).

In another embodiment there is provided a nanoparticulate material for use in asymmetric hydrogenation reactions, said material comprising platinum nanowires having a diameter of less than about 2 nm and a length of about 50 to about 500 nm, optionally about 100 to about 500 nm, and having a chiral modifier associated therewith, said chiral modifier being an alkaloid.

In a second aspect of the disclosure~~invention~~ there is provided a process for making a nanoparticulate material comprising:

a) preparing a mixture of a precursor and an amine solvent, said precursor being capable of being converted to a metal or a mixture of metals; and said mixture comprising no solvent other than the amine; and

b) exposing the mixture to a metal carbonyl at elevated temperature;

so as to produce the nanoparticulate material in the form of metal nanowires.

The process may produce the nanoparticulate material of the first aspect.

The following options may be used in conjunction with the second aspect, either individually or in any suitable combination.

The precursor may be a precursor to a metal selected from the Group 8 to Group 11 elements, or it may be a mixture of two or more such precursors. The precursor or, in the event that the more than one precursor is used, at least one of the precursors (or each independently) may be a metal complex. The complex may be for example an acetylacetone (acac) complex. In one embodiment, the complex is $Pt(acac)_2$.

The amine may be a C6 to C18 amine. It may be an alkenylamine. It may be for example oleylamine. The amine may function as a reducing agent. It may function as a surfactant. It may function as a reducing agent and as a surfactant. In the event that the amine is not capable of acting as a surfactant, a non-amine surfactant (e.g. a non-ionic surfactant) may be used in addition to the amine.

The process may be conducted under an inert atmosphere, e.g. a noble gas.

The metal carbonyl may be added in a trace amount (e.g. less than about 10% relative to the precursor on a molar basis with respect to the metals) or it may be added in a non-trace amount (e.g. greater than about 10%, optionally greater than about 100% relative to the precursor, on a molar basis with respect to the metals). The metal carbonyl may be for example iron pentacarbonyl.

The elevated temperature is between about 100 and about 300°C.

a) preparing a mixture of platinum complex, a C6 to C18 carboxylate salt and a C6 to C18 amine, said platinum complex being capable of being converted to a metal or a mixture of metals; and

b) exposing the mixture to iron pentacarbonyl at elevated temperature;

so as to produce the nanoparticulate material in the form of metal nanowires.

The disclosure~~invention~~ also provides a nanoparticulate material made by the process of the second aspect. Thus there is provided a nanoparticulate material made by:

a) preparing a mixture of a precursor and an amine, said precursor being capable of being converted to a metal or a mixture of metals; and

b) exposing the mixture to a metal carbonyl at elevated temperature;

so as to produce the nanoparticulate material in the form of metal nanowires.

In particular there is provided a nanoparticulate material made by:

a) preparing a mixture of a precursor, an amine and a carboxylate salt, said precursor being capable of being converted to a metal or a mixture of metals; and

b) exposing the mixture to a trace amount (e.g. less than 10% on a molar basis with respect to the metals of the precursor and the metal carbonyl) of metal carbonyl at elevated temperature;

so as to produce the nanoparticulate material in the form of metal nanowires.

There is also provided a nanoparticulate material made by:

a) preparing a mixture of a precursor and an amine, said precursor being capable of being converted to a metal or a mixture of metals;

b) exposing the mixture to a metal carbonyl at elevated temperature to form nanowires; and

c) treating the nanowires with an etchant capable of removing the metal of the metal carbonyl;

so as to produce the nanoparticulate material in the form of metal nanowires.

In a third aspect of the disclosure~~invention~~ there is provided a method for conducting a catalytic reduction comprising exposing a substrate to a nanoparticulate material according the first aspect, or made by the process of the second aspect, in the presence of a hydrogen source. The nanoparticulate material may function as a catalyst. It may be a catalytic nanoparticulate material.

The following options may be used in conjunction with the third aspect, either individually or in any suitable combination.

The method may be conducted in an aqueous solvent.

In another embodiment there is provided a method for conducting a catalytic reduction comprising exposing a substrate to a catalytic nanoparticulate material according the first aspect, or made by the process of the second aspect, in the presence of gaseous hydrogen at a pressure of less than about 750kPa.

In another embodiment there is provided a method for conducting a catalytic reduction comprising exposing a substrate to a catalytic nanoparticulate material according the first aspect, or made by the process of the second aspect, in the presence of ammonium formate or alkaline isopropanol.

The disclosure~~invention~~ also comprises a product, optionally an optically active product, made by the method of the third aspect.

In a fourth aspect of the disclosure~~invention~~ there is provided the use of a nanoparticulate substance as defined above. In an embodiment there is provided use of a catalytic nanoparticulate substance according to the first aspect, or made by the process of the second aspect, in catalysis.

The catalysis may be catalysis of a hydrogenation reaction. It may be catalysis of an enantioselective reaction, e.g. of an enantioselective hydrogenation reaction.

## Brief Description of the Drawings

A preferred embodiment of the present invention will now be described, by way of an example only, with reference to the accompanying drawings wherein:

Figure 1 shows TEM (transmission electron microscope) images and (inset) selected area electron diffraction (SAED) of (A, B) FePt and (C, D) Pt nanowires.

Figure 2 shows an EDX (energy-dispersive X-ray spectroscopy) analysis of (A) FePt and (B) Pt nanowires with Fe/Pt weight ratios of (A) 52:48 and (B) 5:95.

Figure 3 is an XRD (X-ray diffraction) pattern of the as-synthesized (— : upper trace) FePt and (--- : lower trace) Pt nanowires.

Figure 4 shows structures of some products of hydrogenation of activated ketones over 1 mol% of Pt nanowires.

Figure 5 shows (A–C) TEM and (D) high-resolution TEM images of Pt nanowires (A) before use, (B) after 2 runs, and (C, D) after 10 runs.

Figure 6 shows a proposed transition state model for the asymmetric hydrogenation of ethylpyruvate over alkaloid-modified Pt nanowires in water.

Figure 7 is a photograph of reaction mixtures after the asymmetric hydrogenation of ethyl pyruvate over alkaloid-modified Pt nanowires in water. The catalyst and the ligand were dispersed in the aqueous phase, and the product was extracted into the solvent, ethyl acetate.