(12) **UK Patent Application** (19) **GB** (11) **2 457 134** (13) **A**

(43) Date of A Publication   **12.08.2009**

(21) Application No: **0801123.1**

(22) Date of Filing: **22.01.2008**

(71) Applicant(s):
Westfälische Wilhelms-Universität Münster
(Incorporated in the Federal Republic of Germany)
Schlossplatz 2, 48149 Münster,
Federal Republic of Germany

(72) Inventor(s):
Taolei Sun
Kangjian Tang

(74) Agent and/or Address for Service:
24IP Law Group Sonnenberg Fortmann
Medius House LG, 2 Sheraton Street,
LONDON, W1F 8BH, United Kingdom

(51) INT CL:
C01G 23/053 (2006.01)   *C01G 25/02* (2006.01)

(56) Documents Cited:
CN 101070192 A   **CN 001821086 A**
CN 001524796 A   **US 6413489 B**
US 20060247322 A

(58) Field of Search:
INT CL **C01G**
Other: **WPI EPODOC**

(54) Abstract Title: **Synthesis of Metal Oxide Nanoparticles**

(57)   A method for the manufacture of metal oxide
nanoparticles via a two-phase interface hydrolysis
reaction under hydrothermal reaction conditions is
disclosed. The method comprises providing a water
phase and an organic phase where the organic
phase contains a metal oxide precursor such as
metal alkoxides or alkyls, placing the water and
organic phases in a chamber and providing heat to
reach hydrothermal reaction conditions thus
hydrolyzing the metal oxide precursor to form metal
oxide nanoparticles. The metal may be zirconium or
titanium. The organic phase may be toluene,
chloroform, iso-octane or ethyl acetate.
    The manufactured nanoparticles have good
monodispersity, high crystallinity, as well as further
advantageous properties such as strong
photoluminescence and excellent photocatalytic
properties. The nanoparticle size can be controlled
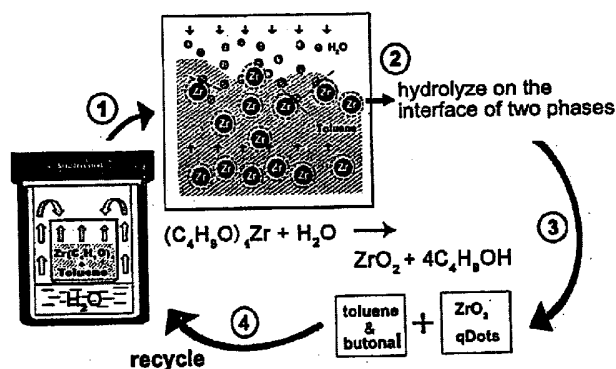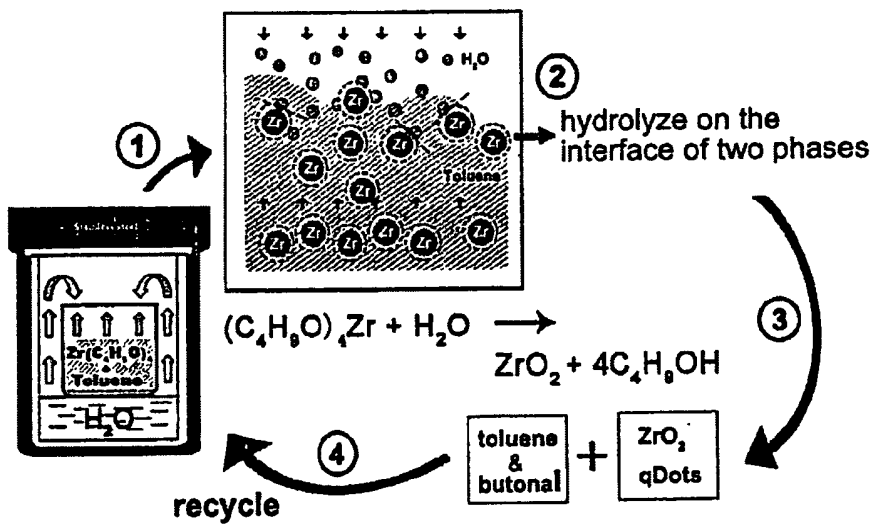by the manipulation of the hydrothermal reaction
temperature.

hydrolyze on the
interface of two phases

$(C_4H_9O)_4Zr + H_2O \longrightarrow ZrO_2 + 4C_4H_9OH$

toluene & butonal + ZrO₂ qDots

recycle

Figure 1

GB 2 457 134 A

① ② hydrolyze on the interface of two phases

$(C_4H_9O)_4Zr + H_2O \longrightarrow ZrO_2 + 4C_4H_9OH$

Zr(C₄H₉O)₄ Toluene

H₂O

③

④ recycle

toluene & butonal + ZrO₂ qDots

Figure 1

5

1|9

Start 200

Providing Phases 210

Hydrothermal Chamber 220

Hydrothermal Reaction Temperature 230

Hydrolysis 240

Nanopartilcles 250

Analysis 260

Finish 270

Figure 2

2\9

Figure 3

3\9
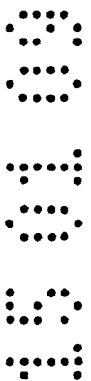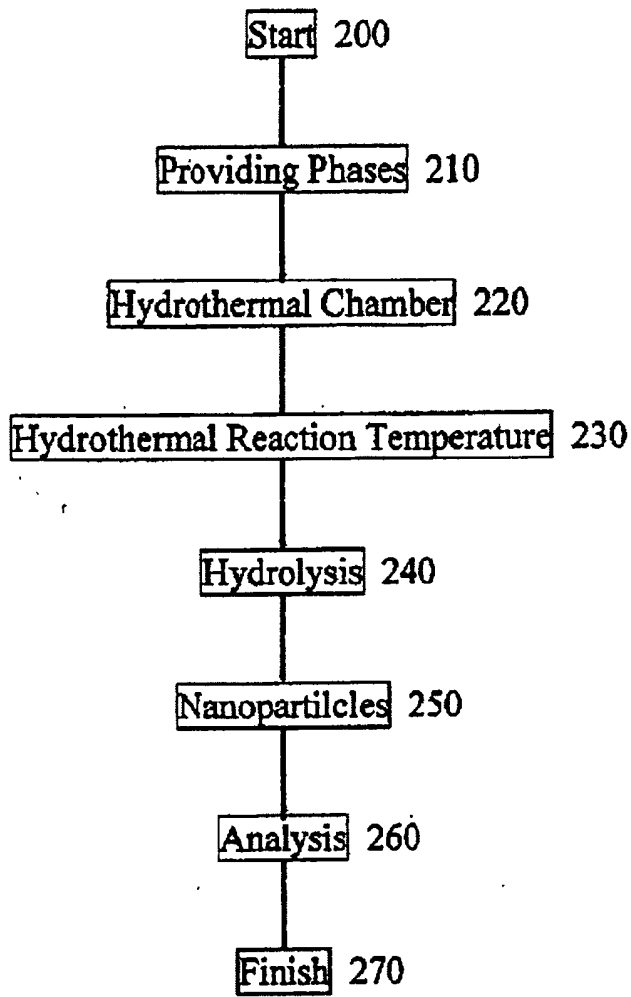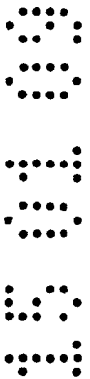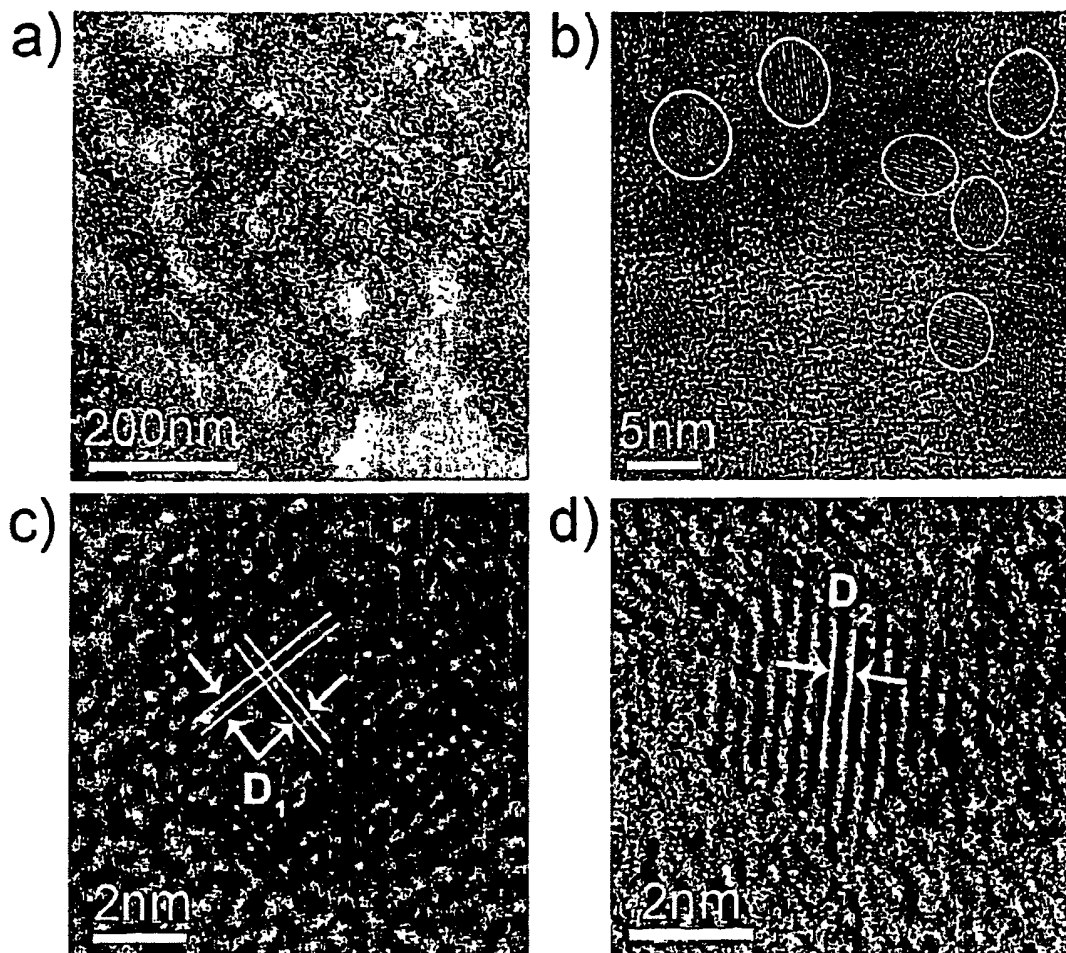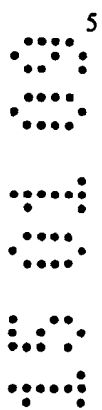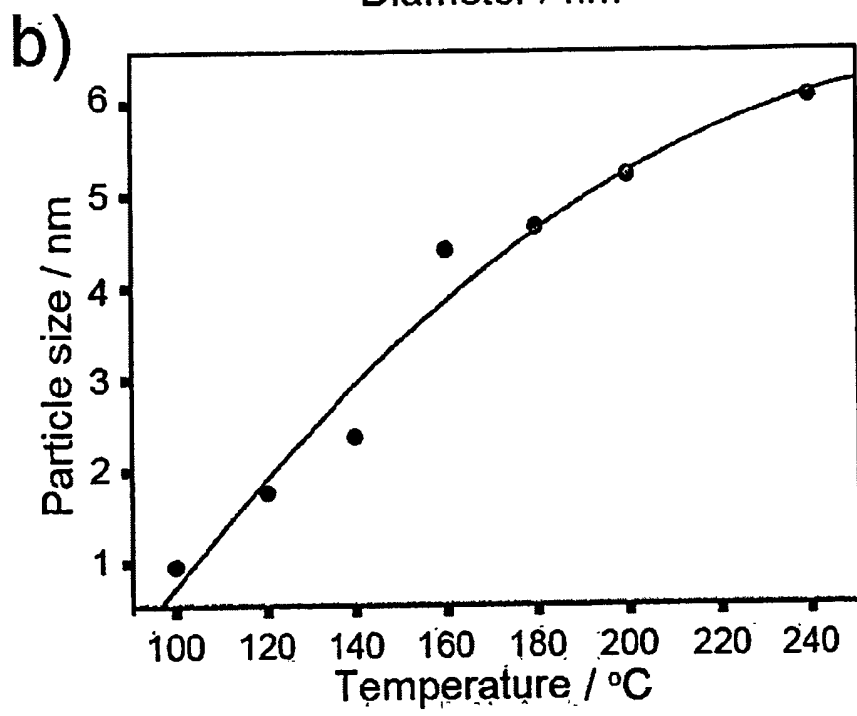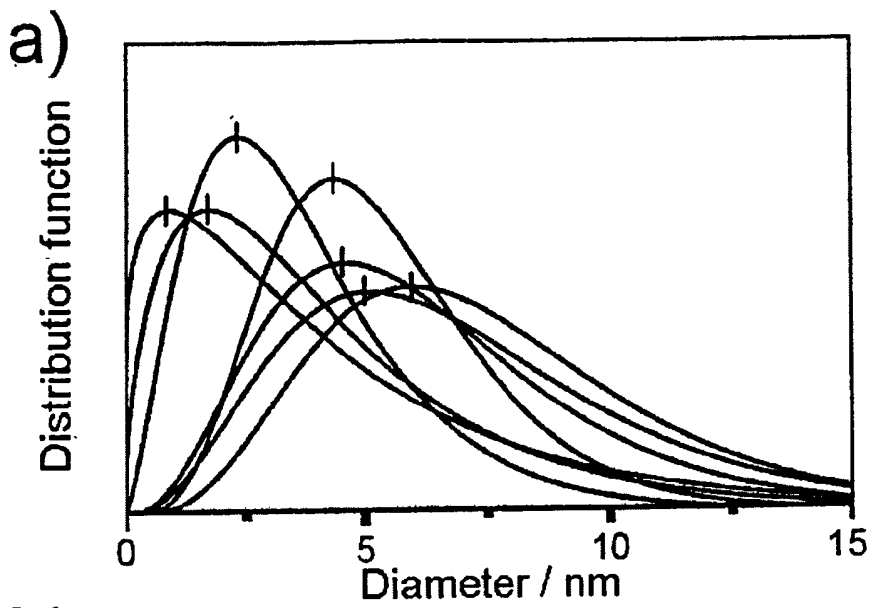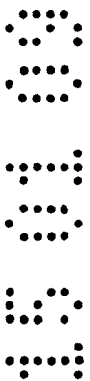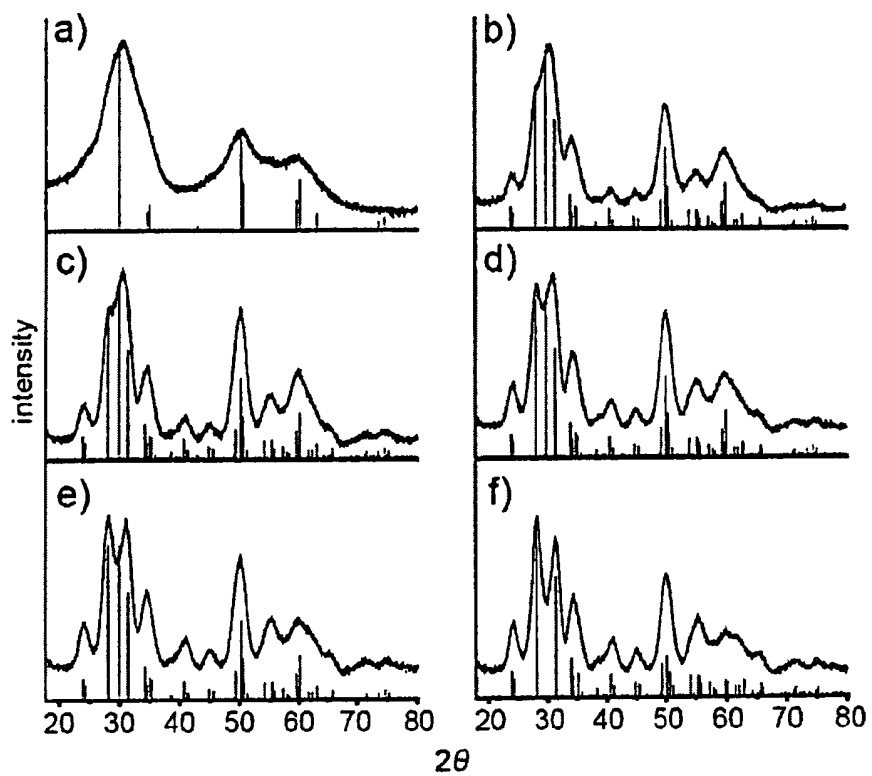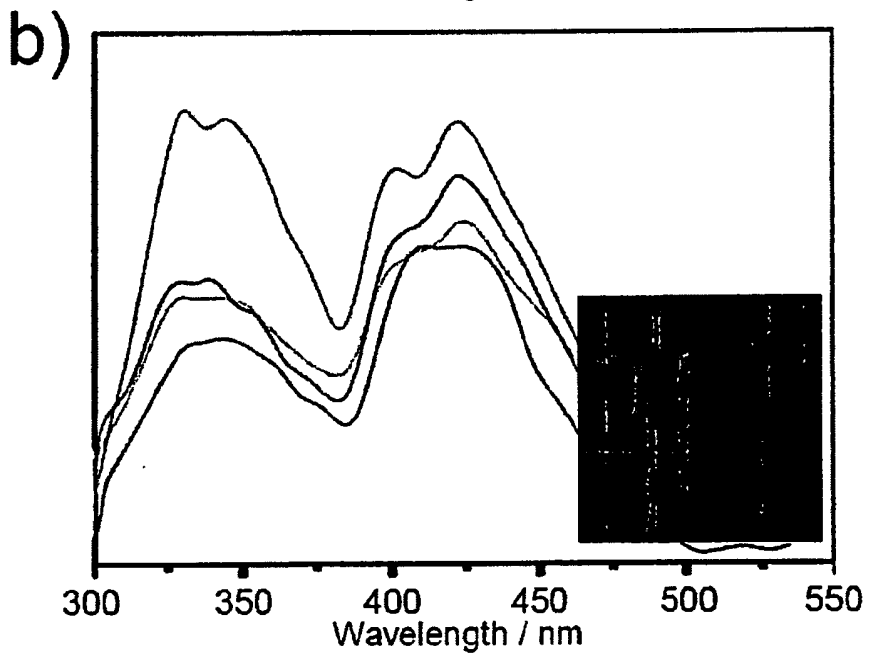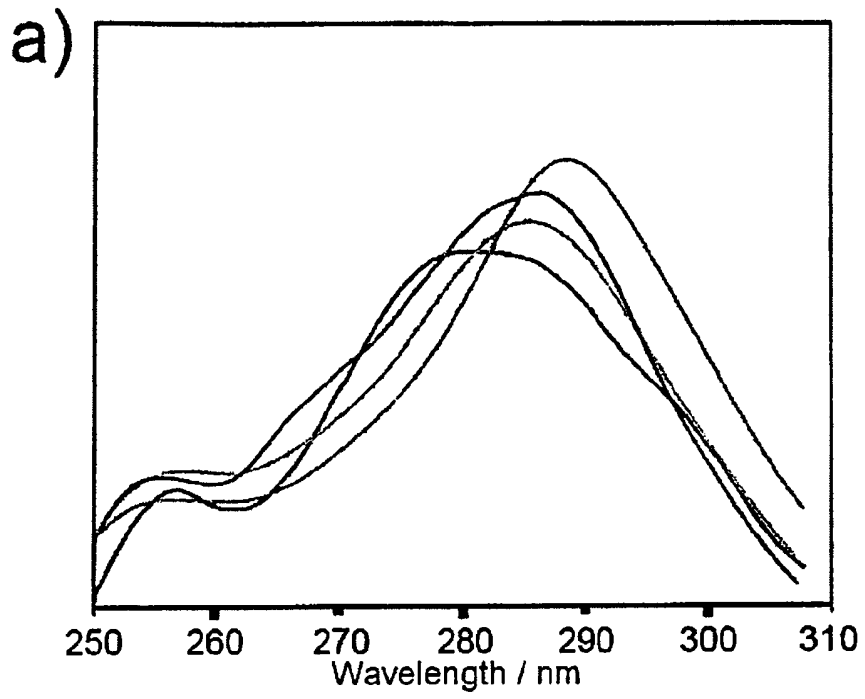
Figure 4

Figure 5

Figure 6
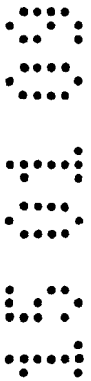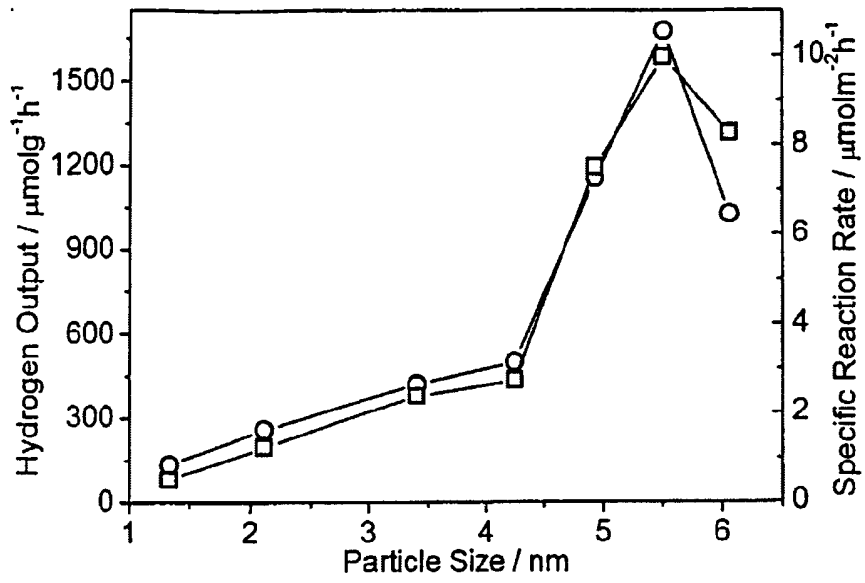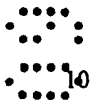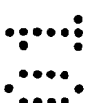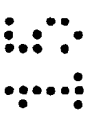
Figure 7

| Temp. | D^a [hkl] / nm | | | | Aver. Size |
/°C	[101]	[200]	[105]	[211]	/ nm
100	7.0	5.9	8.0	6.0	6.7
120	10.9	8.0	10.0	7.0	8.9
140	14.2	13.9	13.9	12.2	13.5
180	15.5	15.7	17.3	15.5	16.0
220	20.9	22.6	24.3	20.7	22.1

Table 1

5

10

15

20

25

30
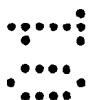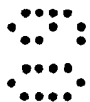
Temperature / °C	110	130	150	170	190	210	240
Average particle size / nm	1.3	2.1	3.4	4.3	4.9	5.5	6.1
Specific surface Area / m^2g^{-1}	273.3	209.1	177.3	182.8	153.8	168.3	124.1

Table 2
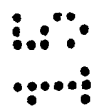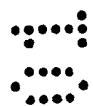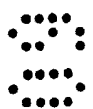
TITLE

5   [0001] Synthesis of Metal Oxide Nanoparticles.

CROSS RELATION TO OTHER APPLICATIONS

[0002] None.

10

FIELD OF INVENTION

[0003] The present invention is directed to the field of the manufacture of metal oxide nanoparticles.

15   ## PRIOR ART

[0004] Methods for the manufacture of metal comprising nanoparticles are known in the literature. For example *J. Phys Chem. B* 2006 110, 14262-14265, titled "Synthesis of FeNi$_3$ alloyed nanoaprticles by hydrothermal reduction" by Xun Wang *et al*, discloses the reduction of Ni(NO$_3$)$_2 \cdot$ 9H$_2$O with

20   hydrazine hydrate in strong alkaline media. Transmission electron microscope images show that the size of the nanoparticles increases with prolongation of the hydrothermal reaction time.

[0005] Furthermore, the paper in *Nature* 2005, 437. 121-124, titled "a general strategy for nanocrystal synthesis" by Qilong Liao *et al*, discloses the manufacture of nanocrystals through the reduction of

25   noble metal ions by ethanol at a temperature of 20 to 200 °C under hydrothermal or atmospheric conditions.

[0006] None of the prior art provides an enabling disclosure for the manufacture of metal oxide nanoparticles according to present invention.

30

35
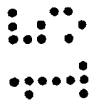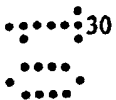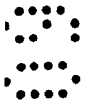
BACKGROUND OF THE INVENTION

[0007] Inorganic semiconductor nanoparticles have attracted great interest in recent decades due to their implementation in a wide variety of applications including photo catalysis, electronic devices, light-emitting devices, solar cells, bioimaging and biosensors. One of the most important factors regarding nanoparticles in these applications is that the size of the nanoparticles must be substantially uniform in order for the nanoparticles to function accordingly.

[0008] Although numerous methods for the manufacture of inorganic nanoparticles (also referred to as nanocrystals) have been developed, such as sol techniques, micelles or emulsion methods, sol-gel process, pyrolysis, chemical vapour deposition (CVD) and electrochemical methods, the prior art methods of manufacture suffer from complicated preparation and post-treatment procedures, problems of aggregation, size and poor monodispersity which greatly influence and hinder the desired properties of the nanoparticles and restrict their large-scale production and application in industry.

[0009] Currently simple methods that are suitable for the industrial production of monodispersed semiconductor nanoparticles with a tuneable size (especially under 10 nm), remain a challenge to the manufacturing industry.

SUMMARY OF INVENTION

[00010]The present invention teaches a method for the manufacture of metal oxide nanoparticles, preferably but is not limited to nanoparticles used in the semiconductor industry.

[00011] The method comprises providing at least one water phase and at least one organic phase in a chamber of a hydrothermal apparatus. The organic phase is a solution of a metal oxide precursor. The metal oxide precursor is soluble in the organic phase and not the water phase. Once heated to a hydrothermal reaction temperature, hydrolysis and nucleation of the metal oxide precursor occurs at the interface of the organic phase and the water phase resulting in the simultaneous nucleation of the insoluble metal oxide nanoparticles.

[00012] The method provides a simple yet novel method for the manufacture of metal oxide nanoparticles. The method further allows the controlling of the size of the metal oxide nanoparticles by altering the hydrothermal reaction temperature.

[00013] The present invention produces nanoparticles that have good monodispersity, are highly crystalline, and additionally possess strong photoluminescence and excellent photocatalytic activities.

[00014] The invention discloses a method for the manufacture of nanoparticles whereby the manipulation of the hydrothermal reaction temperature allows the manufacture of nanoparticles with a size below 10 nm.

5

[00015] Furthermore, the method also exhibits other distinct advantages, compared with other methods of manufacture reported previously. First, the preparation process is simple and cheap, and does not contain any complicated post-treatment procedure. Second, products (without coating) can be collected from the organic phase which effectively avoids grain aggregation induced by the capillary

10   condensation in water environment. Third, the production yield is very high (almost 100 %) and the organic and water phases after reaction can be easily recycled.

[00016] The present invention can be used for the industrial manufacture of nanoparticles and help to reduce the cost of manufacture.

15

DESCRIPTION OF DRAWINGS

Figure 1. Depicts the manufacture of metal oxide nanoparticles under the separate two-phase hydrothermal reaction conditions.

20
Figure 2. Depicts a flow diagram for the steps to manufacture metal oxide nanoparticles under the separate two-phase hydrothermal reaction conditions.

Figure 3. Shows low resolution TEM (a) and corresponding high resolution TEM images (b) of ZrO_2

25   nanoparticles prepared at 160 °C. Further magnified images show the coexistence of the tetragonal (c) and monoclinic ZrO_2 nanoparticles (d) in the samples.

Figure 4. Shows a) Size distribution function of ZrO_2 nanoparticles that calculated from the SAXS data. b) Relationship [AH1] between the particle size (max probability of diameter) and the

30   hydrothermal temperature.

Figure 5. Shows XRD patterns for ZrO_2 nanoparticles that prepared at different temperatures. a): 100 °C; b) 120 °C; c) 140 °C; d): 160 °C; e) 180 °C; f) 200 °C. Red lines: characteristic peaks for tetragonal phase; Blue lines: characteristic peaks for monoclinic phase.

35

Figure 6. Shows fluorescence spectra of the ZrO_2 nanoparticles prepared at different temperatures (T), which were [AH2] dispersed in chloroform. a) Excitation spectra, in which obvious red-shift of the absorption peaks can be observed. b) Emission spectra (excitation wavelength: 285nm). Four main

peaks located at 331, 344, 401 and 423 nm in blue-light region can be observed. Inset: blue-light emission of ZrO_2 nanoparticles dispersed in chloroform (recorded by a CCD camera in dark room, irradiated by a black-light lamp (365 nm), left tube: with ZrO_2 nanoarticles, right tube: without ZrO_2 nanoparticles).

5

Figure 7. Shows photocatalytic properties of the ZrO_2 nanoparticles with different particle sizes. hydrogen output efficiency; specific reaction rate considering the specific surface area of the nanoparticles.

10   **Fugure 8.** Shows average sizes of the TiO_2 nanoparticles prepared at different temperatures.

Figure 9. Shows average particle size and specific surface area (BET) of the ZrO_2 nanoparticles prepared at different temperatures.

15

DETAILED DESCRIPTION OF THE INVENTION

[00017] The present invention teaches a method for the manufacture of metal oxide nanoparticles 10. The invention is not limited to the use of the metal oxide nanoparticles 10 in a specific application, for

20   example in photo catalysis, electronic devices, light-emitting devices, solar cells, bioimaging and biosensors etc.

[00018]Under hydrothermal reaction temperatures an almost 1:1 ratio mixture of a water phase 20 and an organic phase 30 (which are immiscible at room temperature and pressure) will exhibit different

25   characteristics. These different characteristics are due to the pressure increase that occurs when the temperature of the mixture of the water phase and the organic phase exceeds both the boiling point of the water phase 20 and the boiling point of the organic phase 30. The mixture of the water phase and the organic phase exhibit a non-liquid and non-gaseous state and, consequently, the mixture of the organic phase 30 and water phase 20 exists as tiny droplets. These tiny droplets diffuse with each other to form an interface. The tiny droplets of the organic phase 30 and water phase 20 exist with substantially uniform sizes and can therefore be envisaged as a "nanoreactor".
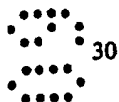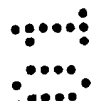
[00019]The nanoreactors, due to their substantially uniform size, provide an environment for the manufacture of the nanoparticles 10 of substantially uniform sizes. The size of the nanoreactors accordingly determines the size of the nanoparticles and will also consequently confine the further growth of nanoparticles.

[00020]Under these circumstances where the mixture of the organic phase 30 and the water phase 20 are subjected to hydrothermal reaction temperatures and where the organic phase 30 contains a chemical substance that comprises hydrolysable groups, hydrolysis of the hydrolysable groups will occur at the interface of the water phase 20 and the organic phase 30. This hydrolysis results in a hydrolysed chemical substance with a substantially uniform particle size.
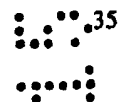
[00021] The process of diffusion at the interface of the droplets of the organic phase 30 by the water phase 20 is a dynamic process. The sizes of the tiny droplets (nanoreactors) and the diffusion at the interface of the organic phase 30 with the water phase 20 depends upon the hydrothermal reaction temperature. Therefore, if a hydrolysable chemical substance is present in the organic phase 30, a size of the nanoparticles can be controlled by altering the hydrothermal reaction temperature.

[00022] Where the chemical substances to be hydrolysed are metal oxide precursors 40, the metal oxide precursors 40 will be initially soluble in the organic phase 30. Once the metal oxide precursors 40 are hydrolysed to form a metal oxide nanoparticle 10, the metal oxide nanoparticle 10 will neither be soluble in the organic phase 30 or the water phase 20. The metal oxide nanoparticle 10 will crystallise from the mixture of the water phase 20 and the organic phase 30 during manufacture.

[00023] The hydrolysis reactions are carried out in a Teflon lined hydrothermal chamber 60 as shown in Fig 1.

[00024] In one aspect of the present invention shown in Fig. 2, the method for the preparation of nanoparticles commences as in step 200. The water phase 20 and the organic phase 30 are prepared as in step 210. The organic phase 30 contains a metal oxide precursor 40 dissolved in the organic phase 40 to form a solution. The solution is prepared in the open atmosphere and the ration of the organic phase to the water phase is 1:1.

[00025]The water phase 20 and the organic phase 30, which contains the metal oxide precursor 40 are then placed in the sealed hydrothermal chamber 60 of a hydrothermal apparatus as in step 220.

[00026] The mixture of the water phase 20 and the organic phase 30 is then heated to a hydrothermal reaction temperature as in step 230. As discussed above, the hydrothermal reaction temperature determines the size of the manufactured nanoparticles 10.

[00027] Once the hydrothermal reaction temperature has been reached, hydrolysis 240 of the metal oxide precursor 40 occurs almost instantaneously.
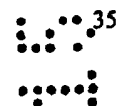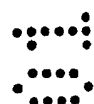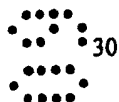
[00028] Upon hydrolysis 240 of the metal oxide precursor 40, the manufactured nanoparticles 10 fall from the solution as in step 250 as ultrafine, crystalline metal oxide nanoparticles 10.

[00029] The manufactured nanoparticles 10 are then collected and analysed as in step 260. The analysis is carried out by transmission electron microscopy (TEM), small angle X-Ray scattering (SAXS), X-Ray diffraction (XRD). Photoluminescent and photocatalytic activity of the manufactured nanoparticles are measured using a Perkinelmer ls55 luminescence spectrometer and photocatalytic hydrogen production experiments

[00030] Following the analysis 260 of the manufactured nanoparticles 10, the method is complete (step 270). The water phase 20 and the organic phase 30 may then be recycled by distillation.

Examples

[00031] The examples demonstrate the various aspects of the invention but are not intended to limit the invention when taken in conjunctions with the claims and the detailed description.

Example 1 Preparation of ZrO$_2$ nanoparticles

[00032] A water phase 20 and an organic phase 30 of toluene which contains the metal oxide precursor 40 Zr(OC$_4$H$_9$)$_4$ were placed in the hydrothermal chamber 60 and the hydrothermal reaction temperature set to 160 °C. The manufactured ZrO$_2$ nanoparticles 10 were prepared in 99.9 % yield.

[00033] Figure 3a shows a TEM of the manufactured ZrO$_2$ nanoparticle. The manufactured ZrO$_2$ nanoparticle shows excellent dispersity and no toluene coating as determined by proton NMR. Figure 3b displays a high resolution TEM depicting well crystallised quantum dots of the manufactured ZrO$_2$ nanoparticle and a particle size of approximately 4.4nm is observed.

[00034] The reaction of Example 1 was then carried out at different hydrothermal reaction temperatures and the manufactured nanoparticles 10 were investigated by SAXS. The curves of distribution function (Figure 4a) show good monodispersity for all samples prepared at different temperatures with the average size of the manufactured nanoparticles 10 increasing monotonously from 1.0nm to approximately 6.1nm when the temperature was increased from 110 °C to 240 °C (Figure 4b). The XRD patterns (Figure 5) show that the samples have very good crystallinity, which increases with the increase of preparation temperature.

[00035] Photoluminescent and photocatalytic activities of the manufactured ZrO_2 was measured. When the size of the manufactured ZrO_2 nanoparticle decreases to a value that is comparable to the Bohr exciton radius of the manufactured ZrO_2 nanoparticles, e.g. 10 nm or less, the manufactured ZrO_2 nanoparticles will exhibit some unique properties because of the nanosize effect, such as

5 photoluminescent properties. In order to verify the performance of the manufactured ZrO_2 nanoparticles 10, the luminescent properties and the photocatalytic properties were further investigated. As shown in the excitation spectra (Figure 6a), the absorption peaks for the ZrO_2 nanoparticles exhibit obvious red-shift from ~ 278.0 − 284.0 nm to ~ 288.5 nm when the size of the nanoparticles increases from ~ 1.0 nm (prepared at T = 110 °C) to ~ 6.1 nm (T = 240 °C), indicating a

10 distinct quantum size effect. The emission spectra (Figure 6b) show four emission peaks in blue light region for all the samples. As a result, strong blue light emission (inset of Figure 4b) when irradiated by a UV-light lamp (365 nm) can be clearly observed even at daytime. These features are related to the near band-edge transitions and a mid-gap trap state that results from incomplete surface passivation such as surface defects and oxygen vacancies, and the change of the corresponding band

15 gap with the decrease of the nanocrystal size.

[00036] The manufactured ZrO_2 nanoparticles also show excellent and size-dependent photocatalytic activity. Figure 7 shows the relationship between the nanoparticle size and the photocatalytic

20 efficiency of the ZrO_2 nanoparticles (as denoted by the hydrogen output in the photocatalytic hydrogen production experiment). It can be observed that the photocatalytic efficiency increases firstly with the increase of crystal size and reach a maximum value of 1676 $\mu mol \cdot g^{-1} \cdot h^{-1}$ at the size of ~ 5.5 nm (prepared at 210°C) and then decreases dramatically when the size increases further. Because the specific surface area (SSA) is an important factor influencing the photocatalytic efficiency, SSA

25 values were measured from the samples prepared at different temperatures. As shown in Figure 9, the SSA values increase significantly with the decrease of the reaction temperatures. The specific reaction rate of the photocatalytic reaction after considering the SSA values is also included in Figure 7. It can be observed that 5.5 nm also shows a highest specific reaction rate, which indicates that the crystallinity is another important factor influencing the photocatalytic efficiency of ZrO_2 30 nanoparticles. In order to make a comparison, a further investigateion into the photocatalytic activity of the commercial ZrO_2 (Beijing Chemical Plant, China) and TiO_2 (p25, Degussa) powders was performed, which show hydrogen output efficiencies of about 673 and 300 $\mu mol \cdot g^{-1} h^{-1}$, respectively. It indicates that the manufactured ZrO_2 nanoparticles have excellent photocatalytic activity that are superior to the commercially available metal oxide nanoaprticles.

35

Example 2 Preparation of TiO_2 nanoparticles

[00037] A water phase 20 and an organic phase 30 of toluene which contains the metal oxide precursor 40 $Ti(OC_4H_9)_4$ were placed in the hydrothermal chamber 60 and the hydrothermal reaction temperature varied stepwise from 100 °C to 200 °C.

5   [00038] The average size of the manufactured nanoparticle 10, shows an increase from approximately 1.0 nm to approximately 22 nm (Figure 8). Figure 8 also shows the dimensions of the particles indicating a spherical morphology of the manufactured nanoparticles 10.

10
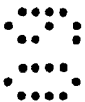
Claims

1. A method for the manufacture of metal oxide nanoparticles (10) comprising:

providing at least one water phase (20);

providing at least one organic phase (30), wherein the at least one organic phase (30) contains a metal oxide precursor (40);

placing the at least one water phase (20) and the at least one organic phase (30) in a same chamber (60)

providing heat to reach a hydrothermal temperature, thus hydrolysing the metal oxide precursor (40) to form the metal oxide nanoparticles (10).

2. The method according to claim 1, wherein the formation of the metal oxide nanoparticles (10) is at a two phase interface reached by heating the at least one water phase (20) and at least one organic phase (30 to the hydrothermal temperature.

3. The method according to any of the above claims, wherein the at least one water phase (20) and the at least one organic phase (30) are placed in a hydrothermal chamber (60).

4. The method according to any of the above claims wherein a ratio of organic phase (30) and water phase (20) is substantially a 1:1 ratio.

5. The method according to any of the above claims, wherein the organic phase is selected from a group comprising of toluene, chloroform, isooctane and ethyl acetate.

6. A method according to any of the above claims, wherein the metal oxide precursor (50) is selected from a group comprising a metal alkyl-oxides and metal alkyls.

7. A method according to any of the above claims, wherein a metal in the metal oxide precursor is selected from group two metal of the transition elements of the periodic table.

8. A method according to any of the above claims, wherein the hydrothermal temperature is selected to control the size of the metal oxide nanoparticles (10).

Application No:	GB0801123.1	**Examiner:**	Nicholas Mole
Claims searched:	1-8	**Date of search:**	4 June 2009

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-3, 5-8	US 6413489 B (YING) see esp. figure 1 and col. 5 lines 48-65
X	1, 2, 3, 5, 6, 7, 8	CN 1821086 A (CHANGCHUN APPLIED CHEMISTRY) see EPODOC abstract
X	1-3, 7-8	CN 1524796 A (INST PROCESS ENG CAS) see WPI abstract no. 2005-000201
X	1-3, 7-8	CN 101070192 A (UNIV TIANJIN) see WPI abstract no. 2008-H94033
X	1-3, 5, 7	US 2006/0247322 A (LI) see examples

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C01G

The following online and other databases have been used in the preparation of this search report

WPI EPODOC

International Classification:

Subclass	Subgroup	Valid From
C01G	0023/053	01/01/2006

INTELLECTUAL
PROPERTY OFFICE

Subclass	Subgroup	Valid From
C01G	0025/02	01/01/2006