

Inorganic nanomaterials: current status and future prospects†

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The article highlights recent developments in inorganic nanomaterials based on the literature of the last 18 months. The article covers various aspects of synthesis and characterization of inorganic nanocrystals, nanowires and nanotubes as well as the properties and phenomena associated with these materials. Applications based on these materials have also been indicated.

1. Introduction

Chemistry plays a major part in the science of nanomaterials. The three important classes of nanomaterials are zero-dimensional nanocrystals, one-dimensional nanotubes and nanowires.^{1–4} In addition, there are two-dimensional nanowalls and nanofilms. A variety of chemical methods have been employed for the synthesis of inorganic nanoparticles, nanotubes and nanowires. These materials have been characterized by electron microscopy, spectroscopic techniques and diffraction methods. Chemical modification, surface functionalization as well as self-assembly constitute an important area of the chemistry of nanomaterials. Nanomaterials exhibit properties related to their size and shape. Besides such quantum properties, several other features of these materials are of academic and technological interest. Typical of these are field emission, gas sensing, medical diagnostics, transistor action, lasing behavior, photovoltaic properties and catalytic properties. In this article, we present the important findings on inorganic nanocrystals, nanowires and nanotubes based on the literature of the last one-year. In doing so, we have had some difficulty because nearly 1000 papers were published on inorganic nanomaterials during the last year leaving out the literature on carbon nanotubes. We have done our best to describe the present status of the subject by making a choice of the papers. We would like to apologize for any omissions or errors in our judgment.

2. Nanocrystals

Synthesis

Metal nanoparticles are generally prepared by the reduction of metal salts in the presence of suitable capping agents such as poly(vinylpyrrolidone) (PVP). Solvothermal and other reaction conditions are employed for the synthesis, to exercise control over their size and shape.^{1–3} One of the steps in the synthesis generally involves the use of phase transfer reagents. A method of producing gold nanoparticles free from

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† The HTML version of this article has been enhanced with colour images.

surfactants has been recently reported.⁵ The method involves the reduction of HAuCl₄ by sodium naphthalenide in diglyme. The shape and colour of Au nanoparticles have been altered by NAD(P)H-mediated growth in the presence of ascorbic acid.⁶ The method yields dipods, tripods and tetrapods. The morphology of gold nanoparticles has also been changed by varying the ratio of the competing reagents, more specifically, alkanethiols and tetralkylammonium salts.⁷ Branched gold nanocrystals have been prepared by the seed-mediated growth in the presence of a surfactant.⁸ The method yields highly faceted nanoparticles that transform into branched nanocrystals. Gold nanoparticles have been incorporated in SiO₂-TiO₂ films.⁹ By varying the composition of the matrix, the refractive index has been changed to tune the position of the Au plasmon band between 542 and 600 nm. Dumb-bell shaped Au-Fe₂O₃ nanoparticles have been synthesized by the decomposition of Fe(CO)₅ on the surface of Au nanoparticles, followed by oxidation.¹⁰

Cobalt nanoparticles of ~3 nm diameter have been prepared by the reduction of cobalt precursors.¹¹ Ruthenium nanoparticles, stabilized by oligoethyleneoxythiol, are found to be soluble in both aqueous and organic media.¹² While rhodium multipods are obtained through the seeded-growth mechanism on reducing RhCl₃ in ethylene glycol in the presence of PVP,¹³ iridium nanocrystals have been prepared by the reduction of an organometallic precursor in the presence of hexadecanediol and different capping agents.¹⁴ Monodisperse Pt nanocrystals with cubic, cuboctahedral and octahedral shapes with diameters of ~9 nm have been obtained by the polyol process.¹⁵ The polyol process has also been employed to obtain PtBi nanoparticles.¹⁶ AuPt nanoparticles have been successfully incorporated in SiO₂ films.¹⁷

Nanocrystals of semiconductors such as CdS and CdSe are generally prepared by the reaction of the metal salts with an appropriate sulfiding or seleniding agent in high boiling solvents. Several new procedures for the synthesis of semiconductor nanocrystals have recently been reported. For example, a spray-based method has been developed for the synthesis of CdS nanocrystals with diameters ranging between 3 and 6 nm.^{18a} In this method, a spray containing the metal salts in monodisperse droplets yields nanocrystals with a narrow diameter distribution on evaporation of the solvent. An aerosol flow synthesis of CdSe nanocrystals making use of a solution of low and high boiling solvents has been reported starting with different Cd precursors and trioctylphosphine selenide.^{18b} It has been found that the size of CdS nanocrystals can be controlled photochemically in the reaction of CdSO₄ with Na₂S₂O₃.¹⁹ Nanocrystals of Ni₃S₄ and Cu_{1-x}S have been prepared by adding elemental sulfur to metal precursors dissolved in dichlorobenzene or oleylamine at relatively high temperatures.²⁰ CdSe and CdTe nanocrystals can be prepared without precursor injection.²¹ The method involves refluxing the cadmium precursor with Se or Te in octadecene. CdSe nanocrystals have also been synthesized using elemental selenium dispersed in octadecene without the use of trioctylphosphine.²² CdSe nanocrystals have been obtained by a microwave-assisted route.²³ By varying the quantity as well as the nature of the organic surfactant, the synthesis of hyperbranched CdSe and CdTe nanocrystals with a fair degree of control over the length as well as branching has been reported.²⁴ High-temperature synthesis of CdSe nanocrystals in nanolitre-volume droplets flowing in a perfluorinated carrier fluid through a microfabricated reactor has been described.²⁵ This method could be useful for providing a precise control in chemical or biochemical reactions. The kinetics of formation of CdSe nanocrystals in trioctylphosphine oxide and stearic acid has been studied by following the changes in the emission band.²⁶ The nanocrystal growth was found to be controlled by the diffusion and depletion of reactants before the

onset of Ostwald ripening. ZnSe nanocrystals have been prepared in a hot mixture of a long chain alkylamine and alkylphosphines.²⁷

New methods have been developed for the synthesis of group 13 nitrides, AlN, GaN and InN.²⁸ One method involves the solvothermal reaction between 1,1,1,3,3,3-hexamethyldisilazane (HMDS) with the metal cupferronate or with the metal trichloride in toluene. The cupferron precursor under solvothermal conditions first decomposes to give an active oxide species $MO_{1.5}$, which reacts with HMDS to form the metal nitride and hexamethyldisiloxane. The reaction of the metal trichloride with HMDS yields the metal nitride and gaseous Me_3SiCl . These procedures yield nanocrystals with average diameter of ~ 10 nm for AlN, ~ 15 nm for InN and as low as 4 nm for GaN. By the decomposition of simple metal trichloride-urea precursors nanocrystals and other nanostructures of AlN, GaN and InN have been synthesized.²⁹ InAs nanocrystals can also be prepared by the decomposition of an organometallic precursor.³⁰ A sonochemical method for the synthesis of hollow MoS_2 nanocrystals has been described.³¹

The synthesis and characterization of a variety of metal oxide nanoparticles have been described in the literature, but there is continued interest in finding new methods. Thus, ZnO nanoparticles have been prepared from zinc acetate in 2-propanol by the reaction with water.³² Hexagonal pyramid-shaped ZnO nanoparticles have been obtained by the thermolysis of the Zn-oleate complex.³³ ZnO nanoparticles with cone, hexagonal cone and rod shapes are obtained by the non-hydrolytic ester elimination sol-gel reactions.³⁴ In this process, ZnO nanocrystals with various shapes were obtained by the reaction of zinc acetate with 1,12-dodecanediol in the presence of different surfactants. The reaction of metal acetylacetonates under solvothermal conditions produces nanocrystals of metal oxides such as Ga_2O_3 , ZnO and cubic In_2O_3 .³⁵ The kinetics of the growth of ZnO nanocrystals has been investigated by using UV-absorption spectroscopy.³⁶ The growth does not follow Ostwald ripening kinetics.

Nearly monodisperse In_2O_3 nanocrystals (Fig. 1) have been obtained by starting with indium acetate, oleylamine and oleic acid.³⁷ The nanocrystals are highly crystalline and they self-assemble into to 2-D and 3-D superlattices as shown in Fig. 1. TiO_2 nanoparticles can be prepared by the low-temperature reaction of low-valent organometallic precursors.³⁸ Highly pure anatase nanocrystals have been prepared by the hydrolysis of $TiCl_4$ with ethanol at 273 K followed by calcination at 360 K for 3 days.³⁹ The growth kinetics and the surface hydration chemistry has also been investigated. Nanoparticles of MnO and NiO are obtained from cupferronate precursors under solvothermal conditions. The nanoparticles exhibit superparamagnetism accompanied by magnetic hysteresis below a blocking temperature.⁴⁰ CoO nanoparticles with diameters in 4.5–18 nm range have been prepared by the decomposition of cobalt cupferronate in decalin at 543 K under solvothermal conditions. Magnetic measurements indicate the presence of ferromagnetic interactions in the small CoO nanoparticles.⁴¹ Cubic and hexagonal CoO nanocrystals have also been obtained starting from $Co(acac)_3$.⁴² Metallic ReO_3 nanoparticles with diameters in the 8.5–32.5 nm range are obtained by the decomposition of the Re_2O_7 -dioxane complex under solvothermal conditions.⁴³ The nanoparticles exhibit a surface plasmon band around 520 nm which undergoes blue-shifts with decreasing size.

Core-shell nanoparticles and nanocomposites

Core-shell particles involving metal, semiconductor or oxide nanocrystals in the core and having shells composed of different materials have been widely investigated.⁴⁴

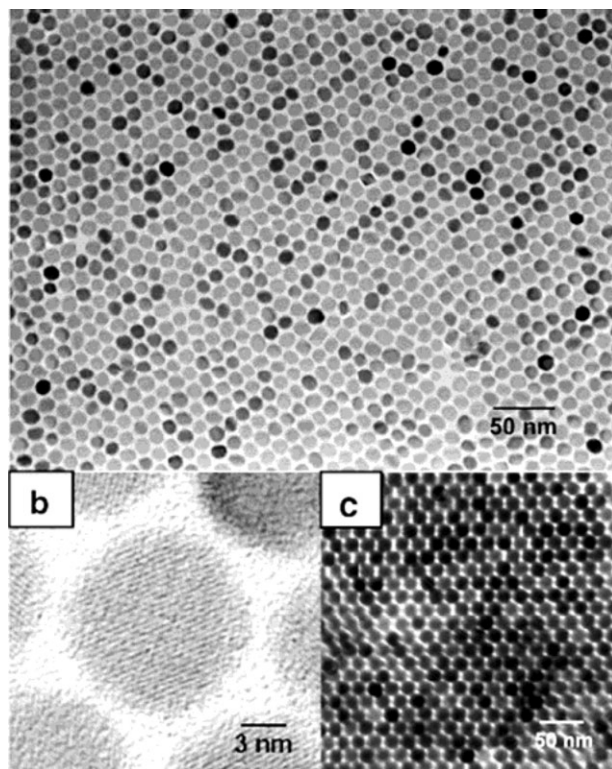


Fig. 1 (a) TEM image of 11.5 nm In_2O_3 nanocrystals (monolayer assembly), (b) HRTEM of a single 13.5 nm In_2O_3 nanocrystal and (c) TEM image of a 3-D superlattice of 20.0 nm In_2O_3 nanocrystals (from ref. 37).

ZnO nanorods have been coated with CdS nanoparticles by using a sonochemical route.⁴⁵ CdSe/CdS core-shell nanoparticles with a core diameter of ~ 1.5 nm have been prepared at the liquid–liquid interface starting with cadmium myristate and oleic acid in toluene and selenourea/thiourea in the aqueous medium.⁴⁶ Luminescent multi-shell nanocrystals of composition CdSe-core CdS/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ /ZnS-shell have been prepared by successive ion layer adhesion and reaction technique.⁴⁷ The growth of the shell was carried out one monolayer at a time by alternately injecting cationic and anionic precursors into the reaction mixture with core nanocrystals.

Core-shell nanoparticles with a ferrimagnetic CoFe_2O_4 core and an antiferromagnetic MnO shell have been obtained by a high-temperature decomposition route with seed mediated growth.⁴⁸ Pt-Cu core-shell nanoparticles showing high activity for NO_x reduction have been reported.⁴⁹ Silica-coated nanocomposites containing magnetic nanoparticles such as $\gamma\text{-Fe}_2\text{O}_3$ and quantum dots such as CdSe have been prepared by encapsulation.⁵⁰ Attachment of colloidal gold nanograins onto magnetic nanocrystals has been accomplished by the surface modification of individual Fe_3O_4 nanospheres with an amine-terminated silane, followed by the addition of negatively charged gold nanograins.⁵¹ Core-shell nanoparticles can be prepared in aqueous media by the addition of a solution of an amphiphilic organic polymer and a metal oxide precursor. The precursor is then converted to a metal oxide by the sol–gel reaction giving rise to hybrid nanoparticles.⁵² Hybrid thermosensitive

particles consisting of core-shell polymer particles containing gold nanoparticles on their surface have been prepared. The polymer core-shell particle consists of a poly(glycidyl methacrylate) core while the shell consists of a poly(N-isopropylacrylamide).⁵³

Self-assembly of nanocrystals

Mono-functionalized nanoparticles can be used as molecular building blocks to react with other chemicals such as polymers, to give rise to nanomaterials linked with covalent bonds.⁵⁴ Gold nanoparticles have been assembled into one-dimensional chains by the controlled ligand exchange of citrate ions with 2-mercaptoethanol.⁵⁵ Nanoparticles encapsulated within cross-linked polymers undergo a sphere to chain transition induced by the micelle transition.⁵⁶ Ordered self-assembly of gold nanocrystals and Fe_2MnO_4 nanocubes into two- and three-dimensional (2-D and 3-D) arrays from water soluble nanocrystalline micelles have been observed (Fig. 2).⁵⁷ The method involves drying water soluble gold nanocrystalline micelles synthesized by a surfactant encapsulation technique. A spontaneous formation of nanoparticle strip patterns has been observed on de-wetting a dilute film of polymer coated nanoparticles floating on a water surface.⁵⁸ Gold nanoparticle monolayers and multilayers have been constructed on a gold surface using the coordination chemistry of metal ions.⁵⁹ Gold nanoparticle networks can be prepared by functionalizing them with azobenzene derivatives.⁶⁰ Gold nanocrystals produced electrochemically in the presence of PVP spontaneously order into 1D or 2D arrays.⁶¹ Hybridization of branched DNA trimers and gold nanoparticle DNA conjugates have been employed to produce discrete self-assembled nanoparticle dendrimers.⁶² The effect of disorder on the phase behavior of DNA-linked gold nanoparticle assemblies has been studied.⁶³ Variation in the length of the DNA linker results in different melting temperatures of the DNA-linked nanoparticle assemblies.

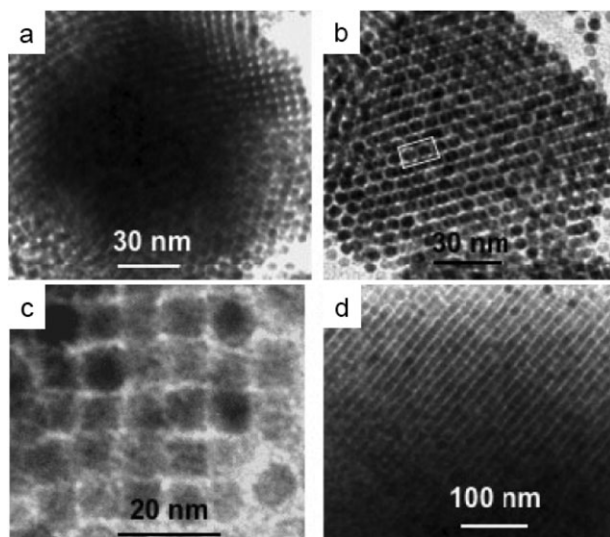


Fig. 2 TEM micrographs of ordered nanocrystal-micelle superlattices. (a) [100] orientation of 3D Au nanocrystal arrays, (b) [110] orientation of 3D Au-nanocrystal arrays, (c) 2D Fe_2MnO_4 -nanocube arrays and (d) [100] orientation of 3D ordered Fe_2MnO_4 -nanocube arrays (from ref. 57).

By controlling the size distribution of magnetic cobalt nanocrystals, mesoscopic patterns with columnar and labyrinth structures are achieved.⁶⁴ Self-assembly of triangular and hexagonal CdS nanocrystals into complex structures such as rods and arrows has been observed.⁶⁵ Ring-like structures of semiconductors are found to occur by the self-assembly of nanocrystals in aqueous media.⁶⁶ Heterostructures of γ -Fe₂O₃ and ZnS nanocrystals have been synthesized.⁶⁷ Nanoscale assembly of carbon nanotubes and quantum dots to produce hybrid structures has been achieved using viruses.⁶⁸

Nanoparticles have a tendency to self-assemble at liquid–liquid interfaces.⁶⁹ This property has been used for the synthesis of nanocrystals as well as single crystalline thin films of metals, metal oxides and semiconductors.⁷⁰ Self-directed self-assembly of CdSe nanoparticle-copolymer mixtures has been observed wherein the copolymers assemble into cylindrical domains that dictate the distribution of the nanoparticles.⁷¹ Multimillimeter large superlattices of FeCo nanoparticles have been fabricated.⁷²

Properties of nanocrystals

The properties as well as the stability of Si nanoparticles in aqueous solution are of importance for applications in bio-systems. Small Si nanoparticles prepared by anodic etching and ultrasonic fractionation have been characterized using photoluminescence spectroscopy.⁷³ The study suggests that properties of these nanoparticles can be controlled by surface chemistry. Small gold nanoparticles exhibit high photoluminescence upon irradiation with sub-100-fs pulses of 790-nm light indicating that the metal nanoparticles are alternatives to fluorophores or semiconductor nanoparticles for biological labeling and imaging.⁷⁴ Third harmonic signals can be generated from gold colloids with diameters of 40 nm, showing a potential use for tracking of single-biomolecules.⁷⁵ Surface plasmons of gold nanoparticle arrays can be imaged by far-field Raman spectroscopy.⁷⁶ Magnetotransport measurements on cobalt nanoparticles in the single-electron tunneling regime show features of spin accumulation.⁷⁷

Ordered CdS nanoparticles can be fabricated on Si substrates using alumina membranes.⁷⁸ Planar clusters of CdSe nanocrystals emit linearly polarized light in the plane of the cluster.⁷⁹ The ability to manipulate the direction and polarization of the photoemission of these nanoparticles by self-assembly is of interest for application in advanced optical devices. Magic-sized CdSe nanocrystals emit white light, a property of technological relevance.⁸⁰ CdSe–CdZnS core-shell nanocrystals prepared by wet-chemical methods exhibit multiphoton emission.⁸¹ CdSe–ZnO nanoparticle clusters are directional photoemitters with tunable wavelength.⁸² Optical properties of tetrapod shaped CdTe nanocrystals have been investigated in detail by a variety of methods.⁸³ The band gap of CdTe nanocrystals can be engineered through surface modification by thiolate ligands under ambient conditions.⁸⁴

Absorption spectra of PbS nanocrystals are modified on the application of electric fields.⁸⁵ Charge carrier transport in PbS nanocrystal-polymer composites has been examined and the results suggest potential use in photovoltaic devices.⁸⁶ Tunable transport phenomena in arrays of PbSe nanocrystals have been investigated.⁸⁷ The system evolves from an insulating regime dominated by coulomb blockade to a semiconducting regime, where the dominant transport mechanism is by hopping conduction. Colloidal semiconductor nanocrystals can be used as colour selectable chromophores by using GaN injection layers.⁸⁸

Nanoparticle assemblies connected by polymers act as molecular springs and nanothermometers. Surface plasmon resonance and exciton-plasmon interaction are responsible for the nanothermometer function.⁸⁹ A single molecule switch, based on two palladium nanocrystals linked by a conjugated dithiol, has been fabricated. The device exhibits negative differential resistance at ~ 0.67 and 1.93 V, respectively at 300 K and 90 K.⁹⁰ The super-shock ability and mechanism of failure of MoS_2 and WS_2 inorganic fullerenes (IF) have been investigated. IF- WS_2 survives pressures up to 25 GPa and temperatures up to 1273 K without a significant structural degradation or phase change.⁹¹

Fluorescence quenching of gold nanoparticles by heavy metal ions can be used to detect Cu^{2+} ions.⁹² Optical properties of suitably modified gold nanoparticles can be used for colourimetric assay of protein–protein interactions in solution.⁹³ Emission of CdSe quantum dots linked to the 5'-end of a DNA sequence is efficiently quenched by hybridization using a complementary DNA strand with a gold nanoparticle attached at the 3'-end.⁹⁴ Colourimetric sensors have been fabricated by using cationic conjugated polymers which form complexes of different colours with aptamers in the presence or absence of a target analyte. Colourimetric sensing of adenosine and cocaine has been achieved using this approach.⁹⁵ A nanoparticle-based polymerase chain reaction has been described.⁹⁶ A novel three-layer composite magnetic nanoparticle probe for DNA has been reported.⁹⁷ The composite probe consists of a gold surface, a silica core and a magnetic inner layer. The three-layer magnetic particles can be functionalized with DNA and reversibly assembled into macroscopic aggregates using complementary linking oligonucleotides. Inhibition assays based on fluorescence resonance energy transfer (FRET) between streptavidin-conjugated quantum dots and biotin related Au nanoparticles has been described.⁹⁸ Cation exchange reactions of ionic crystals have been investigated and the exchange found to be complete and fully reversible.⁹⁹ A novel nanoparticle based sensor for nerve gases has been demonstrated.¹⁰⁰

Nanoparticles are employed as catalysts for various chemical as well as biochemical reactions. Thus, Au–Pd nanocrystals supported on TiO_2 have a high turnover frequency for the oxidation of alcohols.¹⁰¹ The nanocrystals consist of Au-rich cores and Pd-rich shells indicating that gold electronically influences the catalytic properties of palladium. The effect of the nanoparticle shape on the catalytic properties has been investigated. Tetrahedral platinum nanoparticles are better catalysts than spherical platinum nanoparticles for the Suzuki reaction between phenylboronic acid and iodobenzene.¹⁰² Switching of directions of bioelectrocatalytic and photoelectrochemically generated currents at electrode surfaces using hydrophobic magnetic nanoparticles has been demonstrated.¹⁰³ Au-nanoparticle/polyaniline composite assemblies have been used for the bioelectrocatalytic activation of glucose oxidase towards the oxidation of glucose.¹⁰⁴

Potential applications

Nanocrystals are commercially used as catalysts for various chemical reactions and as fluorophores in biological imaging. Apart from these applications, several potential applications have been proposed in the recent literature. Semiconductor nanocrystals-based blue lasers have been fabricated using CdS–ZnS core-shell nanocrystals stabilized in a sol–gel matrix.¹⁰⁵ Electroluminescence from a single CdSe nanocrystal transistor has been observed. The light emission occurs when the bias voltage exceeds the band gap of CdSe.¹⁰⁶ Memory effects in the electronic

transport are observed in the CdSe nanocrystalline array.¹⁰⁷ An electrical transition induced by high electrical fields has been observed in a device consisting of a 2-naphthalenethiol-capped gold nanoparticle/polystyrene composite sandwiched between two aluminium electrodes, an observation with potential application in memory devices.¹⁰⁸ Memory effects have also been observed in polyaniline nanofibre/gold nanoparticle composites.¹⁰⁹

Organic solar cells have been fabricated with an efficiency of 1.5% using porphyrins and fullerene units along with gold nanoparticles deposited on nanostructured SnO₂ electrodes.¹¹⁰ Solution-processed infrared photovoltaic devices with monochromatic internal quantum efficiencies exceeding 10% have been reported.¹¹¹ The active layer in this device consists of PbS nanoparticles and poly(3-octylthiophene). Efficient photodetectors based on poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] and PbSe nanocrystals composite have been fabricated.¹¹² The observed photocurrent gain is attributed to carrier multiplication in PbSe nanocrystals *via* multiple exciton generation and efficient charge transport through the polymer matrix.

Drug delivery using pH-triggered thermally responsive polymer core-shell nanoparticles has been achieved.¹¹³ A magnetic nanoprobe consisting of superparamagnetic nanoparticles coated with a specific molecule of interest has been used to study molecular interactions in live cells.¹¹⁴ A nanocrystal-based nanomotor consisting of a single metal nanocrystal sandwiched between mechanical arms has been fabricated.¹¹⁵

3. Nanowires

Synthesis

Silicon nanowires (SiNWs) with diameters in the 5–20 nm range have been prepared along with nanoparticles of ~4 nm diameter by arc-discharge in water.¹¹⁶ SiNWs have also been synthesized in solution by using gold nanocrystals as seeds and silanes as precursors.^{117a} A vapor-liquid-solid (VLS) type nanowire growth has been accomplished by increasing the pressure on the solvent and employing a reaction temperature above the Au/Si eutectic temperature (640 K). Vertically aligned SiNWs have been obtained by the chemical vapor deposition (CVD) of SiCl₄ on a gold colloid deposited Si (111) substrate.^{117b} Gold colloids have been used for nanowire synthesis by the VLS growth mechanism. By manipulating the colloidal deposition of gold on the substrate, controlled growth of aligned silicon nanowires was achieved. Solution-liquid-solid synthesis of germanium nanowires (GeNWs) gives high yields.¹¹⁸ In this work, bismuth nanocrystals were used as seeds for promoting nanowire growth in trioctylphosphine (TOP), by the decomposition of GeI₂ at ~623 K. A solid-phase seeded growth with nickel nanocrystals has been employed to obtain GeNWs by the thermal decomposition of diphenylgermane in supercritical toluene.¹¹⁹ A patterned growth of freestanding single-crystalline GeNWs with uniform distribution and vertical projection has been accomplished recently.¹²⁰ A low temperature CVD has been employed to obtain high yields of GeNWs and nanowire arrays by using gold nanoseeds and patterned nanoseeds, respectively.¹²¹

A seed-mediated surfactant method using a cationic surfactant has been developed to obtain pentagonal silver nanorods.¹²² Linear Au–Ag nanoparticle chains are obtained by templated galvanostatic electrodeposition in the pores of anodic alumina membranes.¹²³ For particle-chain preparation, sacrificial nickel segments are included between the segments of noble metals (Au, Ag). During

electrodeposition, the template pore diameter fixes the nanowire width, and the length of each metal segment is independently controlled by the amount of current passed before switching to the next plating solution for deposition of the subsequent segments. Nanowires are released by dissolution of the template, and subsequently coated in SiO₂. Gold nanorods obtained by seed-mediated growth approach employ ~4 nm gold nanospheres as seeds, which react with the metal salt along with the weak reducing agent such as ascorbic acid in the presence of a directing surfactant.¹²⁴ The various reaction parameters can be used to control the shape. Addition of nitric acid significantly enhances the production of gold nanorods with high aspect ratios (~20) in seed-mediated synthesis.¹²⁵ A layer-by-layer deposition approach has been employed to produce polyelectrolyte-coated gold nanorods.¹²⁶ Depending on the surface chemical functionality of the coated gold nanorods, they can be selectively immobilized onto cationic or anionic surfaces. Micellar solutions of nonionic surfactants are employed to obtain nanowires and nanobelts of *t*-Se, which are single crystalline.¹²⁷

A nanoribbon multicomponent precursor has been used to produce nanoparticle nanoribbons of ZnO.¹²⁸ The 1-D porous structured nanoribbons are self-assembled by textured ZnO nanoparticles. Nanobelts of ZnO can be converted into superlattice-structured nanohelices due to a rigid lattice rotation or twisting.¹²⁹ Well-aligned crystalline ZnO nanorods along with nanotubes can be grown from aqueous solution on Si wafers, poly(ethylene terephthalate) and sapphire.¹³⁰ Atomic layer deposition was first used to grow a uniform ZnO film on the substrate of choice and to serve as a templating seed layer for the subsequent growth of nanorods and nanotubes. On this ZnO layer, highly oriented 2-D ZnO nanorod arrays were obtained by solution growth using zinc nitrate and hexamethylenetetramine in aqueous solution. A seed-assisted chemical reaction at 368 K is found to yield uniform, straight, thin single-crystalline ZnO nanorods on a hectogram scale.¹³¹ Controlled growth of well-aligned ZnO nanorod arrays has also been accomplished by an aqueous ammonia solution method.¹³² In this method, an aqueous ammonia solution of Zn(NO₃)₂ is allowed to react with a zinc-coated silicon substrate at a growth temperature 333–363 K. 3-D interconnected networks of ZnO nanowires and nanorods have been synthesized by a high temperature solid-vapour deposition process.¹³³

MgO nanowires and related nanostructures have been produced by carbothermal synthesis, starting with polycrystalline MgO or Mg with or without the use of metal catalysts.¹³⁴ This study has been carried out with different sources of carbon, all of them yielding interesting nanostructures such as nanosheets, nanobelts, nanotrees and aligned nanowires. Orthogonally branched single-crystalline MgO nanostructures have been obtained through a simple chemical vapour transport and condensation process in a flowing Ar/O₂ atmosphere.¹³⁵

Catalyst-assisted VLS growth of single-crystal Ga₂O₃ nanobelts has been accomplished through by graphite-assisted thermal reduction of a mixture of Ga₂O₃ and SnO₂ powders under controlled conditions.¹³⁶ Zigzag and helical β-Ga₂O₃ one-dimensional nanostructures have been produced by the thermal evaporation of Ga₂O₃ in the presence of GaN.¹³⁷ TiO₂ nanorods can be obtained on a large scale by the nonhydrolytic sol-gel ester elimination reaction.¹³⁸ Here, the reaction is carried out between titanium (iv) isopropoxide and oleic acid at 543 K to generate 3.4 nm diameter crystalline TiO₂ nanorods. Single-crystalline and well faceted VO₂ nanowires with rectangular cross sections have been prepared by the vapour transport method, starting with bulk VO₂ powder.¹³⁹ Copious quantities of single-crystalline

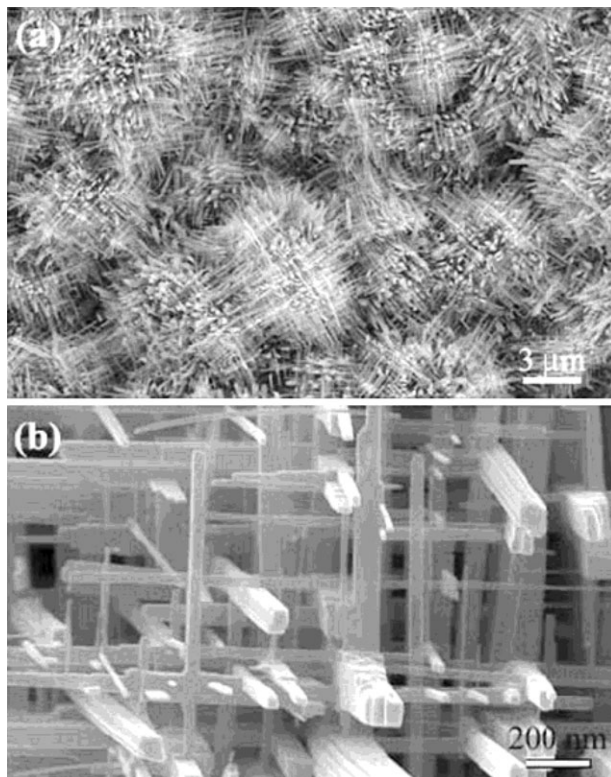


Fig. 3 (a) Low-magnification and (b) high-magnification SEM images of tungsten oxide nanowires (from ref. 142).

and optically transparent Sn-doped In_2O_3 (ITO) nanowires have been grown on gold-sputtered Si substrates by carbon-assisted synthesis, starting with a powdered mixture of the metal nitrates or with a citric acid gel formed by the metal nitrates.¹⁴⁰

Bicrystalline nanowires of hematite ($\alpha\text{-Fe}_2\text{O}_3$) have been synthesized by the oxidation of pure iron.¹⁴¹ Networks of WO_{3-x} nanowires shown in Fig. 3 are produced by the thermal evaporation of tungsten powder in the presence of oxygen.¹⁴² The growth mechanism involves ordered oxygen vacancies in the (100) and (001) planes which are parallel to the (010) growth direction. A general and highly effective one-pot synthetic protocol for producing one-dimensional nanostructures of transition metal oxides such as $\text{W}_{18}\text{O}_{49}$, TiO_2 , Mn_3O_4 and V_2O_5 through a thermally induced crystal growth process starting from mixtures of metal chlorides and surfactants has been described.¹⁴³ A polymer-assisted hydrothermal synthesis of single crystalline tetragonal perovskite PZT ($\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$) nanowires has been carried out.¹⁴⁴

Oriented attachment of nanocrystals can be used to make one-dimensional as well as complex nanostructures. Thus, nanotubes and nanowires of II–VI semiconductors have been synthesized using surfactants.¹⁴⁵ The nanorods or nanotubes of CdS and other materials produced in this manner actually consist of nanocrystals. The synthesis of SnO_2 nanowires from nanoparticles has been investigated.¹⁴⁶ Nanorods of V_2O_5 prepared by a polyol process self-assemble into microspheres.¹⁴⁷ Cubic ZnS nanorods are obtained by the oriented attachment mechanism starting with diethylzinc, sulfur and amine.¹⁴⁸ ZnS nanowires and nanoribbons with wurtzite structure

can be prepared by the thermal evaporation of ZnS powder onto silicon substrates, sputter-coated with a thin ($\sim 25 \text{ \AA}$) layer of gold film.¹⁴⁹ Thermal evaporation of a mixture of ZnSe and activated carbon powders in the presence of a tin-oxide based catalyst yields tetrapod-branched ZnSe nanorod architectures.¹⁵⁰ Nanorods of luminescent cubic CdS are obtained by injecting solutions of anhydrous cadmium acetate and sulfur in octylamine into hexadecylamine.¹⁵¹ CdSe nanowires have been produced by the cation-exchange route.¹⁵² By employing the cation-exchange reaction between Ag^{2+} and Cd^{2+} Ag_2Se nanowires are transformed into single-crystal CdSe nanowires. A single-source molecular precursor has been used to obtain blue-emitting, cubic CdSe nanorods ($\sim 2.5 \text{ nm}$ diameter and 12 nm length) at low temperatures.¹⁵³ An organometallic preparation of CdTe nanowires with high aspect ratios in the wurtzite structure has been described.¹⁵⁴ Thermal decomposition of copper diethyldithiocarbamate ($\text{CuS}_2\text{CNET}_2$) in a mixed binary surfactant solvent of dodecanethiol and oleic acid at 433 K gives rise to single-crystal line high aspect ratio ultrathin nanowires of hexagonal Cu_2S .¹⁵⁵

Atmospheric pressure CVD is employed to obtain arrays and networks of uniform PbS nanowires,¹⁵⁶ while PbSe nanowires are obtained in solution through oriented attachment of PbSe nanocrystals.¹⁵⁷ Monodispersed PbTe nanorods of sub- 10 nm diameter are obtained by sonoelectrochemical means by starting with a lead salt and TeO_2 along with nitrilotriacetic acid.¹⁵⁸ Using bismuth citrate and thiourea as the precursor material in DMF, well-segregated, crystalline Bi_2S_3 nanorods have been synthesized by a reflux process.¹⁵⁹ Single-crystalline Bi_2S_3 nanowires have also been obtained by using lysozyme which controls the morphology and directs the formation of the 1D inorganic material.¹⁶⁰ In this method, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, thiourea and lysozyme are reacted together at 433 K under hydrothermal conditions. A solventless synthesis of orthorhombic Bi_2S_3 nanorods and nanowires with high aspect ratios (> 100) has been accomplished by the thermal decomposition of bismuth alkylthiolate precursors in air at $\sim 500 \text{ K}$ in the presence of a capping ligand species, octanoate.¹⁶¹

Single crystalline AlN, GaN and InN nanowires can be deposited on Si substrates covered with gold islands by using urea complexes formed with the trichlorides of Al, Ga and In as the precursors.²⁹ Single crystalline GaN nanowires have been obtained by the thermal evaporation/decomposition of Ga_2O_3 powders with ammonia at 1423 K directly onto a Si substrate coated with a Au film.¹⁶² InN nanowires with uniform diameters has been obtained in large quantities by the reaction of In_2O_3 powders in ammonia.¹⁶³ A general method for the synthesis of Mn-doped nanowires of CdS, ZnS and GaN based on metal nanocluster-catalyzed chemical vapour deposition has been described.¹⁶⁴ Vertically aligned, catalyst-free InP nanowires have been grown on InP(III)B substrates by CVD of trimethylindium and phosphine at $623\text{--}723$.¹⁶⁵ Single-crystalline nanowires of LaB_6 , CeB_6 and GdB_6 have been prepared and deposited on a Si substrate by the reaction of the rare-earth chlorides with BCl_3 in the presence of hydrogen.¹⁶⁶ Nanowires and nanoribbons of NbSe_3 have been obtained by the direct reaction of Nb and Se powders.¹⁶⁷ A one-pot metal-organic synthesis of single-crystalline CoP nanowires with uniform diameters has been reported.¹⁶⁸ The method involves the thermal decomposition of cobalt(II) acetylacetonate and tetradecylphosphonic acid in a mixture of TOPO and hexadecylamine. CoNi nanowires have been prepared by heterogeneous nucleation in a liquid polyol.¹⁶⁹

Self assembly

Surfactant-protected gold nanorods self-assemble into ordered structures in the presence of adipic acid.¹⁷⁰ Gold nanorods can be linked to each other in an

end-to-end fashion by using cysteine as the molecular bridge.¹⁷¹ End-to-end assembly of gold nanorods and nanospheres is also accomplished by oligonucleotide hybridization.¹⁷² The rationale behind the selection of the mercaptoalkyloligonucleotide molecule is based on the fact that the thiol group binds to the ends of the nanorods, which assemble in an end-to-end fashion through hybridization with the target oligonucleotide. Multi-walled carbon nanotubes (MWNTs) can be effectively used as templates for aligning gold nanorods as seen in Fig. 4(a).¹⁷³ The longitudinal absorption band of the gold nanorods shifts to higher wavelengths as observed in Fig. 4(b), indicating a preference for preferential stringlike alignment on the surface of the MWNTs. Alignment of gold nanorods in polymer composites and on polymer surfaces has been examined.¹⁷⁴ By employing the stretch-film method, it was found that as the polymer was stretched in a direction, the nanorods got oriented with their long axis along the direction.

For the formation of a linear/oriented assembly of gold nanorods, antigens specifically binding to antibodies appears to be a feasible approach.¹⁷⁵ Anti-mouse IgG was immobilized on the {111} end faces of gold nanorods through a thioctic acid containing a terminal carboxyl group. The biofunctionalized nanorods are assembled using mouse IgG for biorecognition and binding. Nanowires and other nanostructures can be assembled utilizing highly engineered M13 bacteriophage as

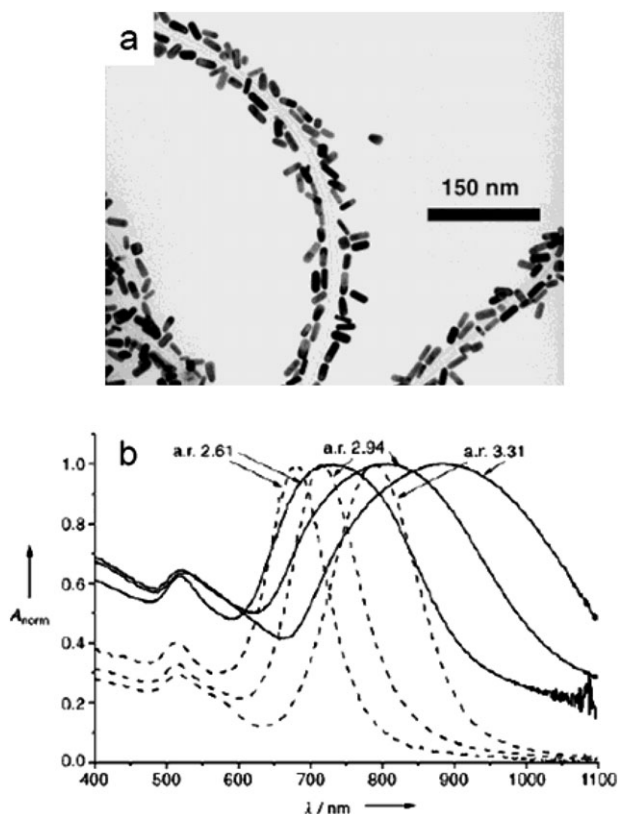


Fig. 4 (a) TEM image of Au nanorods assembled on MWNTs surface and (b) UV-Visible spectra of Au nanorods (dashed lines) and nanorods attached on MWNTs (solid lines) (from ref. 173).

templates.¹⁷⁶ The phage clones with gold-binding motifs on the capsid and streptavidin-binding motifs at one end are used to assemble Au and CdSe nanocrystals into ordered one-dimensional arrays and more complex geometries.

Silica nanowires can be assembled on silica aerogel substrates by employing a scanning tunneling microscope.¹⁷⁷ GeNWs prepared by CVD and chemically functionalized with alkanethiols are found to be soluble in organic solvents and to readily assemble into close-packed Langmuir–Blodgett films.¹⁷⁸

Crystalline WO_3 nanowires formed by the decomposition of tungsten isopropoxide in a solution of benzyl alcohol self-assemble into bundles with diameters in the 20–100 nm range and lengths in the 300–1000 nm range.¹⁷⁹ WO_3 nanostructures grow and assemble in the presence of deferoxamine mesylate under different reaction conditions.¹⁸⁰ Using a facile solution method, arrays of SnO_2 nanorods can be assembled on the surface of $\alpha\text{-Fe}_2\text{O}_3$ nanotubes.¹⁸¹

Functionalization of nanowires

Silicon nanowires can be covalently modified with DNA oligonucleotides and such nanowires show biomolecular recognition properties.¹⁸² Gold nanorods are stabilized and conjugated to antibodies for biological applications.¹⁸³ In_2O_3 nanowires have been selectively functionalized for biosensing applications by a simple and mild self-assembling process, making use of 4-(1,4-dihydroxybenzene)butyl phosphonic acid (HQ-PA) (Fig. 5).¹⁸⁴ Cyclic voltammetry and fluorescence have been used to study the DNA binding to the functionalized nanowire.

Coaxial nanowires and coatings on nanowires

SiC nanowires can be coated with Ni and Pt nanoparticles (~ 3 nm) by plasma enhanced CVD.¹⁸⁵ Single and double-shelled coaxial core-shell nanocables of GaP with SiO_x and carbon (GaP/SiO_x , GaP/C , $\text{GaP}/\text{SiO}_x/\text{C}$), with selective morphology and structure, have been synthesized by the thermal CVD.¹⁸⁶ Silica-sheathed $3\text{C-Fe}_7\text{S}_8$ has been prepared on silicon substrates with FeCl_2 and sulfur precursors at 873–1073 K.¹⁸⁷ A general procedure has been proposed for producing chemically bonded ceramic oxide coatings on carbon nanotubes and inorganic nanowires.¹⁸⁸ The ceramic oxide-coated structures are obtained by the reaction of reactive metal chlorides with acid-treated carbon nanotubes or metal oxide nanowires, followed by hydrolysis with water. On repeating the above process several times followed by calcination, ceramic coatings of the desired thickness are obtained. Core-sheath CdS and polyaniline (PANI) coaxial nanocables with enhanced photoluminescence have been fabricated by an electrochemical method using a porous anodic alumina membrane as the template.¹⁸⁹

Optical properties

The dependence of the fluorescence intensity of gold nanorods on the aspect ratio has been examined in detail.¹⁹⁰ It appears that non-radiative processes dominate the relaxation mechanism of the excited state. Photoluminescence of $\text{CdS}_x\text{Se}_{1-x}$ nanobelts can be tuned affording emission varying from 500 nm to 700 nm.¹⁹¹ In the $\text{CdS}_{1-x}\text{Se}_x$ nanowires, the band-gap is engineered by controlling the composition.¹⁹² Single-crystal ZnO nanowires can be used as ultraviolet photodetectors.¹⁹³ Quantum efficiency and other aspects of ZnO nanowire nanolasers have been investigated.¹⁹⁴ The nanowires were prepared on sapphire and Si using PLD and the differential

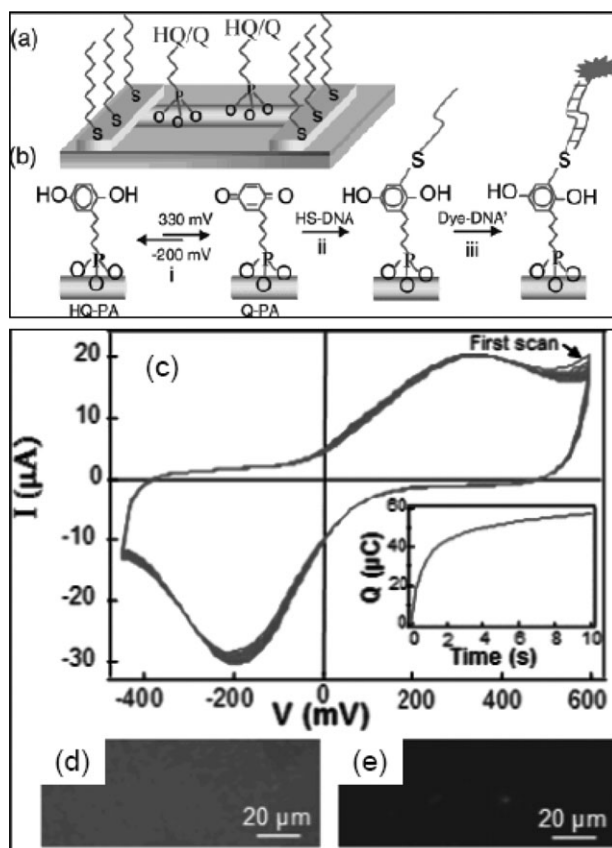


Fig. 5 (a) Schematic representation of an In_2O_3 nanowire mat device. The NW is functionalized with a SAM of HQ-PA and is placed between two gold electrodes protected by a SAM of dodecane-1-thiol. (b) (i) The monolayer of HQ-PA, deposited on the In_2O_3 nanowire or ITO, can be reversibly oxidized to Q-PA in an electrochemical cell. (ii) Addition of the probe, thiol-terminated DNA (HS-DNA) to Q-PA. (iii) Attachment of complementary DNA strand (dye-DNA) to the probe DNA. (c) Fifteen consecutive CVs showing the reversible oxidation/reduction of a SAM of HQ-PA on an ITO glass sheet. (Inset) Chronoamperometry shows the amount of charge necessary to oxidize a predefined area of HQ-PA: an average of $56.8 \mu\text{C}$. (d) A fluorescence image of ITO surface that was oxidized to Q-PA, reacted with SH-DNA, and the DNA paired to its complementary DNA strand labeled with a fluorescence dye. (e) A fluorescence image of ITO with the HQ-PA monolayer went through the same DNA attachment procedure as that of the ITO sheet in (d), showing little or no DNA binding (from ref. 184).

external quantum efficiency was as high as 60% (Fig. 6). Aligned CdS nanowires are shown to exhibit optical waveguide behaviour on continuous-wave laser excitation.¹⁹⁵ The mechanism of lasing action in single CdS nanowire cavities has been elucidated by temperature-dependent and time-resolved photoluminescence measurements.¹⁹⁶ Electric-field modulation of the visible and ultraviolet nanoscale lasers composed of single CdS and GaN nanowires has been achieved using integrated, microfabricated electrodes.¹⁹⁷ Optically pumped room-temperature lasing in GaN nanowires with low lasing thresholds has been reported.¹⁹⁸ Nanoscale light-emitting diodes with colours ranging from ultraviolet to near-infrared have been prepared

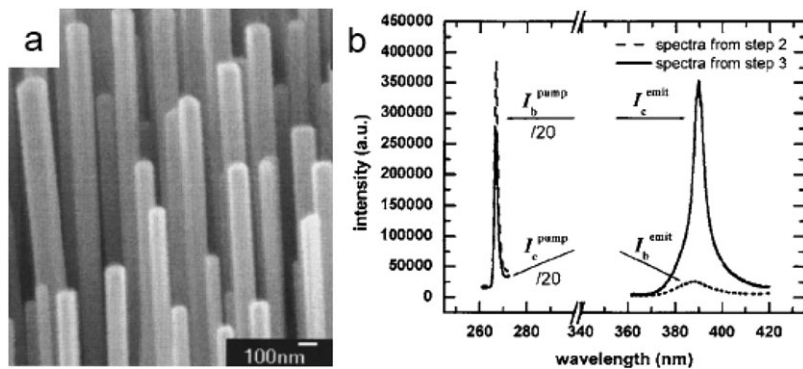


Fig. 6 (a) SEM image of ZnO nanowires grown by femtosecond PLD. and (b) Spectra of scattered pump laser light and emission from nanowires (from ref. 194).

using a solution-based approach in which electron-doped semiconductors are assembled with hole-doped silicon nanowires in a crossed nanowire architecture.¹⁹⁹

Electrical properties

Individual SiNWs exhibit coulomb blockade features, with coherent charge transport through discrete single particle quantum levels extending across the whole device.²⁰⁰ Electrical properties of single GaN nanowires have been characterized.²⁰¹ Gate-dependent one-dimensional transport in a single-crystal In_2O_3 nanowire field-effect transistor has been studied at low temperatures.²⁰² Field-effect transistors of ZnO nanowires have been fabricated and studied in vacuum and in a variety of ambient gases (Fig. 7).²⁰³ Field-effect transistors based on the self-assembly of colloidal ZnO nanorods have also been examined.²⁰⁴ ZnO nanowire field-effect transistors composed of individual ZnO nanowires can be made using a self-assembled superlattice as the gate insulator, a device of possible use in flexible display and logic technologies.²⁰⁵ Top-gated field-effect transistors of core-shell structured GaP nanowires have been fabricated.²⁰⁶ Storage of electrons in semiconductor nanowires (InAs/InP) epitaxially grown from gold nanoparticles have been demonstrated.²⁰⁷ Electrical properties of inorganic nanowire-polymer composites such as ZnO, RuO_2 and Ag with polyaniline (PANI) as well as with polypyrrole (PPY) have been examined.²⁰⁸ Thermoelectric properties of electrodeposited bismuth telluride nanowires have been reported.²⁰⁹

Field-emission properties of P-doped GaN nanowires synthesized, *via* a simple thermal evaporation process, has been examined.²¹⁰ Large-area nanowires of organic charge-transfer complexes such as Ag-TCNQ and Cu-TCNQ show field-emission properties.²¹¹

Superconductivity is suppressed in Zn nanowires.²¹² Photovoltaic applications of aligned silicon nanowire arrays have been explored.²¹³ Dye-sensitized solar cells incorporating ZnO nanowires have been assembled.^{214,215} Dye-sensitized solar cells using TiO_2 single-crystalline nanorod electrodes provide efficient photocurrent generation in a quasi-solid-state, with a conversion efficiency of 6.2% under 100 mW/cm^2 .²¹⁶ Self-powered synthetic nanorotors have been prepared from bar-coded gold-nickel nanorods having the gold end anchored to the surface of a silicon wafer. Constant velocity circular movements are observed when hydrogen peroxide is

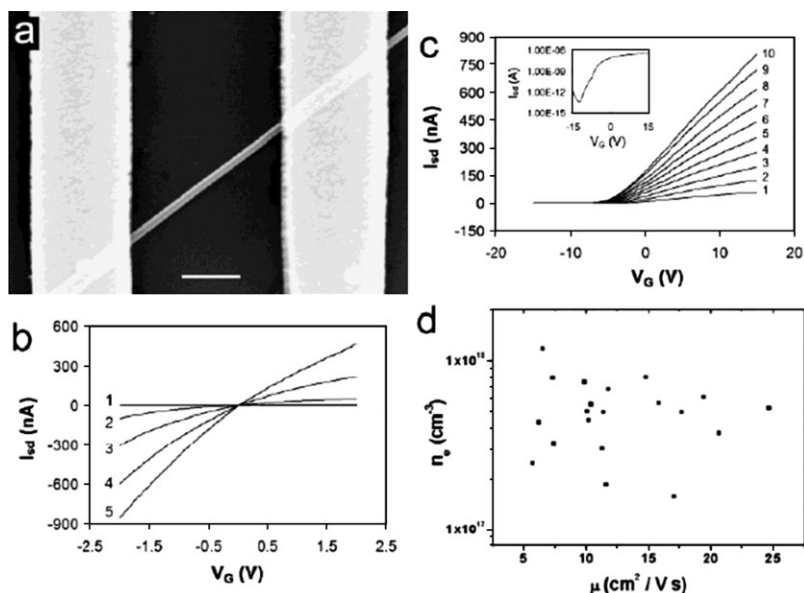


Fig. 7 (a) SEM micrograph of a 101 nm diameter ZnO nanowire device (b) Current (I_{sd}) vs. voltage (V_{sd}) curves recorded at different gate voltages for the device shown in (a). Curves 1–5 correspond to gate voltages of -10 , -5 , 0 , $+5$, and $+10$ V, respectively. (c) Current (I_{sd}) vs. gate voltage (V_G) of the same device measured at bias voltages from 0.1 to 1.0 V. Curves 1–10 correspond to bias voltages of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 V, respectively. The inset plots the current (I_{sd}) vs. gate voltage (V_G) measured at a bias voltage of $0.5V_{sd}$ on a logarithmic scale. (d) Carrier concentration (n_c) vs. mobility (μ) for all transistor devices fabricated (from ref. 203).

catalytically decomposed to oxygen at the unattached nickel end of the nanorod.²¹⁷ A high-throughput procedure is reported for lithographically processing one-dimensional nanowires.²¹⁸ This procedure has been called on-wire lithography.

Magnetic properties

Dynamics of field-driven domain-wall propagation in ferromagnetic nanowires ($\text{Ni}_{80}\text{Fe}_{20}$) have been investigated.²¹⁹ Magnetoresistive properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ nanowires have been reported.²²⁰ Mn doped GaP nanowires appear to exhibit ferromagnetism with a Curie temperature higher than room temperature.²²¹

Some chemical aspects and sensor applications

Intercalation of lithium ions in TiO_2 -B nanowires has been performed without any structural degradation or loss of nanowire morphology.²²² Arrayed gold nanowires provide a useful platform for the electrochemical detection of DNA.²²³ Remote-controlled autonomous movement of stripped metallic nanorods (catalytic nanomotors) has been reported.²²⁴ ZnO nanorods integrated with a microchannel show a sensitivity (change in conductance) to the pH of the medium, suggesting that they

can be used in sensor applications.²²⁵ Hydrogen and ethanol sensing characteristics of pure and Pt-impregnated ZnO nanorods and nanowires have been investigated.²²⁶ Both nanorods and nanowires exhibit good sensing characteristics for 1000 ppm of ethanol at or below 423 K, where as Pt impregnated nanorods and nanowires show better sensitivity for both hydrogen and ethanol as shown in Fig. 8. Field-effect transistors fabricated with ZnO nanowires have been used for sensing NO₂ and ammonia at room temperature.²²⁷ LiMo₃Se₃ nanowire films show variation of conductivity in the presence of various chemical vapors suggesting possible use as chemical sensors.²²⁸

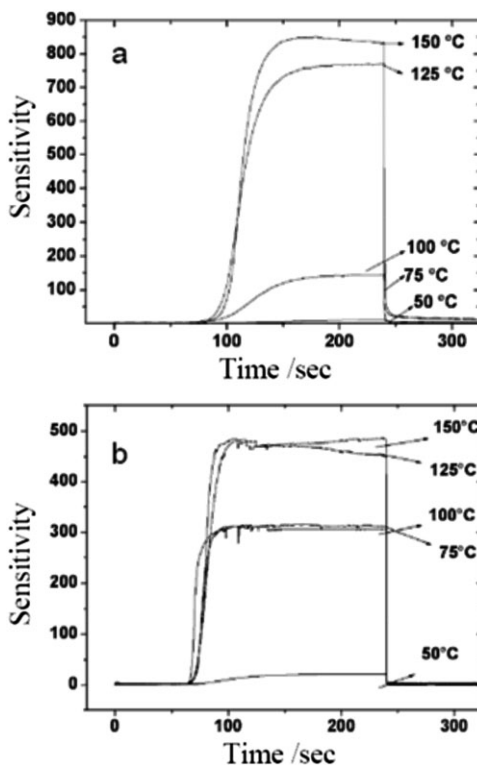


Fig. 8 Sensitivity of Pt-impregnated ZnO nanowires for (a) 1000 ppm H₂ and (b) 1000 ppm ethanol (from ref. 226).

In₂O₃ nanowires along with carbon nanotubes can be usefully employed for the complementary detection of prostate-specific antigen biomolecules.²²⁹ SnO₂ nanobelts have been integrated with microsystems for nerve agent detection.²³⁰ Using silicon nanowire field-effect devices, multiplexed electrical detection of cancer markers has been achieved.²³¹

Mechanical properties

Gold nanowires show a Young's modulus which is essentially independent of diameter whereas the yield strength is largest for the smallest diameter nanowires.²³²

The elastic modulus of (0001) ZnO nanowires grown on a sapphire surface has been measured (29 ± 8 GPa) using atomic force microscopy.²³³ ZnS nanobelts exhibit 79% increase in hardness and 52% decrease in elastic modulus compared to bulk ZnS.²³⁴ A large increase in the elastic strength ($\sim 90\%$) and tensile strength ($\sim 70\%$) has been observed on incorporation of inorganic nanowires of SiC and Al₂O₃ in poly(vinyl alcohol).²³⁵

4. Inorganic nanotubes

Synthesis

The synthesis and characterization of nanotubes of inorganic materials including elements, oxides and chalcogenides have been widely reported in the recent literature.²³⁶ Several inorganic nanotubes have been synthesized during the last year by different strategies. Thus, a low-temperature route for synthesizing highly oriented ZnO nanotubes/nanorod arrays has been reported.²³⁷ In this work, a radio frequency magnetron-sputtering technique was used to prepare ZnO-film-coated substrates for subsequent growth of the oriented nanostructures. High aspect-ratio, self-organized nanotubes of TiO₂ are obtained by anodization of titanium.^{238a} These self-organized regular porous structures consist of pore arrays with a uniform pore diameter of ~ 100 nm and an average spacing of 150 nm. The pore mouths are open on the top of the layer while on the bottom of the structure the tubes are closed by the presence of a ca 50 nm thick barrier of TiO₂. Electrochemical etching of titanium under potentiostatic conditions in fluorinated dimethyl sulfoxide and ethanol (1 : 1) under a range of anodizing conditions gives rise to ordered TiO₂ nanotube arrays.^{238b} TiO₂-B nanotubes can be prepared by hydrothermal methods.²³⁹ Lithium is readily intercalated into the TiO₂-B nanotubes up to a composition of Li_{0.98}TiO₂ compared with Li_{0.91}TiO₂ for the corresponding nanowires. Intercalation of alkali metals into titanate nanotubes has also been investigated.²⁴⁰

Transition metal oxide nanotubes have been prepared in water using iced lipid nanotubes as the template.²⁴¹ Self-assembled cholesterol derivatives act as a template as well as a catalyst for the sol-gel polymerization of inorganic precursors to give rise to double-walled tubular structures of transition metal oxides.²⁴² Hydrothermal synthesis of single-crystalline α -Fe₂O₃ nanotubes has been accomplished.²⁴³ Nanotubes of single crystalline Fe₃O₄ have been prepared by wet-etching of MgO inner cores of MgO/Fe₃O₄ core-shell nanowires.²⁴⁴ Cerium oxide nanotubes can be prepared by the controlled annealing of the as-formed Ce(OH)₃ nanotubes.²⁴⁵

Boron nitride nanotubes can be grown directly on substrates at 873 K by a plasma-enhanced laser-deposition technique.²⁴⁶ Nanotubes and onions of GaS and GaSe have been generated through laser and thermally induced exfoliation of the bulk powders.²⁴⁷ GaP nanotubes with zinc blend structure have been prepared by the VLS mechanism.²⁴⁸ Open-ended gold nanotube arrays have been obtained by the electrochemical deposition of Au onto arrays of nickel nanorod templates followed by selective removal of the templates.²⁴⁹ Free-standing, electro-conductive nanotubular sheets of indium tin oxide with different In/Sn ratios have been fabricated by using cellulose as the template.²⁵⁰

Solubilization and functionalization

Boron nitride nanotubes can be dissolved in organic solvents by wrapping them with a polymer.²⁵¹ Such a solution does not destroy the intrinsic properties due to the

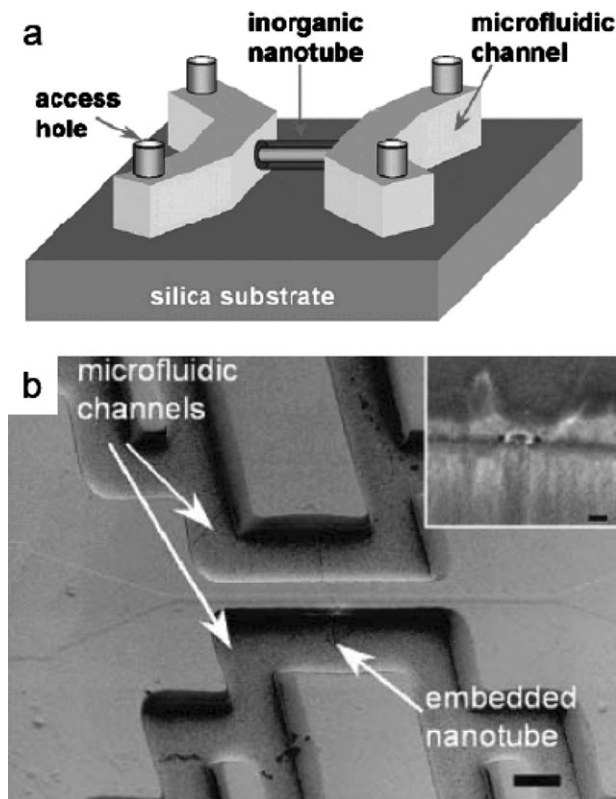


Fig. 9 Inorganic nanotube nanofluidic device: (a) Schematic of device structure features a single nanotube bridging two microfluidic channels to form a nanofluidic system. (b) Scanning electron micrograph of the nanofluidic device before cover bonding. Scale bar represents 10 μm . Inset shows cross-section view of the nanotube embedded between two silicon dioxide layers. Scale bar represents 100 nm (from ref. 255).

noncovalent functionalization of the BN nanotubes. Functionalization and solubilization of BN nanotubes have been carried out based on the interactions of the amino groups with the boron atoms of the nanotube surface.²⁵² Solubilization here is based on the interactions of the amino groups in oligomeric diamine-terminated poly(ethyleneglycol) with the BN nanotube surface. Covalent functionalization of BN nanotubes has been accomplished by a reaction between the COCl group of stearoylchloride and the amino groups on the BN nanotubes.²⁵³ BN nanotubes have been fluorinated through the introduction of F atoms at the stage of the nanotube growth for possible applications in nanoelectronics.²⁵⁴ Inorganic nanotubes have been integrated with microfluidic systems to create devices for single DNA molecule sensing.²⁵⁵ A schematic diagram and a SEM image of the microfluidic devices are shown in Fig. 9. Hybrid nanotubes with concentric organic and inorganic layers are obtained by the self-assembly of glycolipids on silica nanotubes.²⁵⁶

Properties and applications

BN nanotubes have been shown to chemisorb hydrogen.²⁵⁷ Fluorescent silica nanotubes are suggested to be useful in gene delivery.²⁵⁸ Protein biosensors based

on biofunctionalized conical gold nanotubes have been fabricated.²⁵⁹ Ferroelectric phase transitions in template-synthesized BaTiO₃ nanotubes and nanofibres have been examined.²⁶⁰ Ferroelectric and piezoelectric properties of biferroic BiFeO₃ nanotube arrays have been studied.²⁶¹ Highly efficient α -Fe₂O₃ nanotube chemical sensors based on chemiluminescence have been fabricated to detect H₂S gas, using carbon nanotubes as templates.²⁶² The α -Fe₂O₃ nanotubes have a high specific area and exhibit excellent sensitivity to reductive vapors and gases such as alcohol and hydrogen and superior electrochemical activity of 1415 mA_{hg}⁻¹ at 100 mA_g⁻¹ (293 K).²⁶³ LiCoO₂, LiMn₂O₄ and LiNi_{0.8}Co_{0.2}O₂ nanotubes, synthesized by the thermal decomposition of sol-gel precursors inside porous alumina templates have been examined as cathode materials for lithium ion batteries.²⁶⁴ Inorganic nanotubes have been integrated into metal-oxide-solution field-effect transistors which exhibit rapid field effect modulation of ionic conductance.²⁶⁵ Halloysite nanotubes can be employed as hollow enzymatic nanoreactors.²⁶⁶

5. Concluding remarks

The highlights of inorganic nanocrystals, nanowires and nanotubes provided in the previous sections indicate the vitality of the subject. Clearly, the subject is exploding considering the number of papers published in the last year. There is no doubt that the subject has come of age with many useful properties of inorganic nanomaterials being constantly discovered, many of them having potential applications. There is little doubt that the subject will grow during the next decade with the discovery of new materials as well as properties and phenomena of importance.

References

- 1 The Chemistry of Nanomaterials, eds. C. N. R. Rao, A. Muller and A. K. Cheetham, Wiley-VCH Verlag, Weinheim, 2004, Vol. 1 & 2.
- 2 G. Schmid, *Clusters and Colloids From Theory to Applications*, VCH, Weinheim, 1994.
- 3 (a) C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025; (b) M. Rajamathi and R. Seshadri, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 337.
- 4 Nanotubes and Nanowires, C. N. R. Rao and A. Govindaraj, *RSC Nanoscience and Nanotechnology*, Cambridge, 2005.
- 5 M. Schulz-Dobrick, K. V. Sarathy and M. Jansen, *J. Am. Chem. Soc.*, 2005, **127**, 12816.
- 6 Y. Xiao, B. Shyloshovskiy, I. Popov, V. Pavlov and I. Wilner, *Langmuir*, 2005, **21**, 5659.
- 7 S. I. Stoeva, V. Zaikoski, B. L. V. Prasad, P. K. Stoimenov, C. M. Sorensen and K. J. Klabunde, *Langmuir*, 2005, **21**, 10280.
- 8 C.-H. Kuo and M. H. Huang, *Langmuir*, 2005, **21**, 1012.
- 9 G. De and C. N. R. Rao, *J. Mater. Chem.*, 2005, **15**, 3278.
- 10 H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. Sun, *Nano Lett.*, 2005, **5**, 379.
- 11 O. Margeat, C. Amiens, B. Chaudret, P. Lecante and R. E. Banfield, *Chem. Mater.*, 2005, **17**, 107.
- 12 T. Tsukatani and H. Fujihara, *Langmuir*, 2005, **21**, 12093.
- 13 J. D. Hoefelmeyer, K. Niesz, G. A. Somarjai and T. D. Tilley, *Nano Lett.*, 2005, **5**, 435.
- 14 C. A. Stowell and B. A. Korgel, *Nano Lett.*, 2005, **5**, 1203.
- 15 H. Song, F. Kim, S. Connor, G. A. Somarjai and P. Yang, *J. Phys. Chem. B*, 2005, **109**, 188.
- 16 C. Roychowdhury, F. Matsumoto, P. F. Mutolo, H. A. Abruna and F. J. DiSalvo, *Chem. Mater.*, 2005, **17**, 5871.
- 17 G. De and C. N. R. Rao, *J. Mater. Chem.*, 2005, **15**, 891.
- 18 (a) L. Amirav, A. Amirav and E. Lifshitz, *J. Phys. Chem. B*, 2005, **109**, 9857; (b) Y. T. Didenko and K. S. Suslick, *J. Am. Chem. Soc.*, 2005, **127**, 12196.
- 19 M. Marandi, N. Taghavinia, A. I. Zad and S. M. Mahdavi, *Nanotechnology*, 2005, **16**, 334.
- 20 A. Ghezlbash and B. A. Korgel, *Langmuir*, 2005, **21**, 9451.

- 21 Y. A. Yang, H. Wu, K. R. Williams and Y. J. Cao, *Angew. Chem., Int. Ed.*, 2005, **44**, 6712.
- 22 J. Jasieniak, C. Bullen, J. V. Embden and P. Mulvaney, *J. Phys. Chem. B*, 2005, **109**, 20665.
- 23 A. V. Firth, Y. Tao, D. wang, J. Ding and F. Bensebaa, *J. Mater. Chem.*, 2005, **15**, 4367.
- 24 A. G. Kanaras, C. Sonnichsen, H. Liu and A. P. Alivisatos, *Nano Lett.*, 2005, **5**, 2164.
- 25 E. M. Chan, A. P. Alivisatos and R. A. Mathies, *J. Am. Chem. Soc.*, 2005, **127**, 13854.
- 26 B. D. Dickerson, D. M. Irving, E. Herz, R. O. Claus, W. B. Spillman, Jr and K. E. Meissner, *Appl. Phys. Lett.*, 2005, **86**, 171915.
- 27 P. D. Cozzoli, L. Manna, M. L. Curri, S. Kudera, C. Giannini, M. Striccoli and A. Agostiano, *Chem. Mater.*, 2005, **17**, 1296.
- 28 U. K. Gautam, K. Sardar, F. L. Deepak and C. N. R. Rao, *Pramana*, 2005, **65**, 549.
- 29 K. Sardar, M. Dan, B. Schwenzer and C. N. R. Rao, *J. Mater. Chem.*, 2005, **15**, 2175.
- 30 M. A. Malik, P. O'Brien and M. Helliwell, *J. Mater. Chem.*, 2005, **15**, 1463.
- 31 N. A. Dhas and K. S. Suslick, *J. Am. Chem. Soc.*, 2005, **127**, 2368.
- 32 Z. Hu, D. J. E. Ramirez, B. E. H. Cervera, G. Oskam and P. C. Searson, *J. Phys. Chem. B*, 2005, **109**, 11209.
- 33 S.-H. Choi, E.-G. Kim, J. Park, K. An, N. Lee, A. C. Kim and T. Hyeon, *J. Phys. Chem. B*, 2005, **109**, 14792.
- 34 J. Joo, S. G. Kwon, J. H. Yu and T. Hyeon, *Adv. Mater.*, 2005, **17**, 1873.
- 35 N. Pinna, G. Garweitner, M. Antonietti and M. Niederberger, *J. Am. Chem. Soc.*, 2005, **127**, 5608.
- 36 R. Viswanatha and D. D. Sharma, *Chem.–Eur. J.*, 2006, **12**, 180.
- 37 Q. Liu, W. Lu, A. Ma, J. Tang, J. Lin and J. Fang, *J. Am. Chem. Soc.*, 2005, **127**, 5267.
- 38 J. Tang, F. Redl, Y. Zhu, T. Siegrist, L. E. Brus and M. L. Steigerwald, *Nano Lett.*, 2005, **5**, 543.
- 39 G. Li, L. Li, J. B. Goated and B. F. Woodfield, *J. Am. Chem. Soc.*, 2005, **127**, 8659.
- 40 M. Ghosh, K. Biswas, A. Sundaresan and C. N. R. Rao, *J. Mater. Chem.*, 2006, **16**, 106.
- 41 M. Ghosh, E. V. Sampathkumaran and C. N. R. Rao, *Chem. Mater.*, 2005, **17**, 2348.
- 42 W. S. Seo, J. H. Shim, S. J. Oh, E. K. Lee, N. H. Hur and J. T. Park, *J. Am. Chem. Soc.*, 2005, **127**, 6188.
- 43 K. Biswas and C. N. R. Rao, *J. Phys. Chem. B*, 2006, **110**, 842.
- 44 W. Schartl, *Adv. Mater.*, 2000, **12**, 1899.
- 45 T. Gao, Q. Li and T. Wang, *Chem. Mater.*, 2005, **17**, 887.
- 46 D. Pan, Q. Wang, S. Jiang, X. Ji and L. An, *Adv. Mater.*, 2005, **17**, 176.
- 47 R. Xie, U. Kolb, J. Li, T. Basche and A. Mews, *J. Am. Chem. Soc.*, 2005, **127**, 7480.
- 48 O. Masala and R. Seshadri, *J. Am. Chem. Soc.*, 2005, **127**, 9354.
- 49 S. Zhou, B. Varughese, B. Eichhorn, G. Jackson and K. McIlwarth, *Angew. Chem., Int. Ed.*, 2005, **44**, 4539.
- 50 D. K. Yi, S. T. Selvan, S. S. Lee, G. C. Papaefthymiou, D. Kundaliya and J. Y. Ying, *J. Am. Chem. Soc.*, 2005, **127**, 4990.
- 51 D. Caruntu, B. L. Cushing, G. Caruntu and C. J. O'Connor, *Chem. Mater.*, 2005, **17**, 3398.
- 52 K. H. See, M. E. Mullins, O. P. Mills and P. A. Heiden, *Nanotechnology*, 2005, **16**, 1950.
- 53 D. Suzuki and H. Kawaguchi, *Langmuir*, 2005, **21**, 8175.
- 54 Q. Dai, J. G. Worden, J. Trullinger and Q. Huo, *J. Am. Chem. Soc.*, 2005, **127**, 8008.
- 55 S. Lin, M. Li, E. Dujardin, C. Girard and S. Mann, *Adv. Mater.*, 2005, **17**, 2553.
- 56 Y. Kang, K. J. Erickson and T. A. Taton, *J. Am. Chem. Soc.*, 2005, **127**, 13800.
- 57 H. Fan, E. Leve, J. Gabaldon, A. Wright, R. E. Haddad and C. J. Brinker, *Adv. Mater.*, 2005, **17**, 2587.
- 58 J. Huang, F. Kim, A. R. Tao, S. Connor and P. Yang, *Nat. Mater.*, 2005, **4**, 896.
- 59 M. Wanunu, R. P. Biro, H. Cohen, A. Vaskevich and I. Rubinstein, *J. Am. Chem. Soc.*, 2005, **127**, 9207.
- 60 D. S. Sidhaye, S. Kashyap, M. Sastry, S. Hotha and B. L. V. Prasad, *Langmuir*, 2005, **21**, 7979.
- 61 S. Huang, H. Ma, X. Zhang, F. Yong, X. Feng, W. Pan, X. Wang, Y. Wang and S. Chen, *J. Phys. Chem. B*, 2005, **109**, 19823.
- 62 S. A. Claridge, S. L. Goh, J. M. J. Frechet, S. C. Williams, C. M. Micheel and A. P. Alivisatos, *Chem. Mater.*, 2005, **17**, 1628.
- 63 N. C. Harris and C.-H. Kiang, *Phys. Rev. Lett.*, 2005, **95**, 046101.
- 64 V. Germain and M.-P. Pileni, *Adv. Mater.*, 2005, **17**, 1424.
- 65 J. H. Warner and R. D. Tilley, *Adv. Mater.*, 2005, **17**, 2997.

- 66 B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2005, **127**, 18262.
- 67 K.-W. Kwon and M. Shim, *J. Am. Chem. Soc.*, 2005, **127**, 10269.
- 68 N. G. Portney, K. Singh, S. Chaudhary, G. Destito, A. Schneemann, M. Manchester and M. Ozkan, *Langmuir*, 2005, **21**, 2098.
- 69 L. L. Dai, R. Sharma and C.-Y. Wu, *Langmuir*, 2005, **21**, 2641.
- 70 C. N. R. Rao, G. U. Kulkarni, V. V. Agrawal, U. K. Gautam, M. Ghosh and U. Tumkurkar, *J. Colloid Interface Sci.*, 2005, **289**, 305.
- 71 Y. Lin, A. Boker, J. He, K. Sill, H. Xiang, C. Abetz, X. Li, J. Wang, T. Emrick, S. Long, Q. Wang, A. Balazs and T. P. Russell, *Nature*, 2005, **434**, 55.
- 72 C. Desvieux, C. Amiens, P. Fejes, P. Renaud, M. Respaud, P. Lecante, E. Snoeck and B. Chaudret, *Nat. Mater.*, 2005, **4**, 750.
- 73 D. E. Eckhoff, J. D. B. Sutin, R. M. Clegg, E. Gratton, E. V. Rogozhina and P. V. Braun, *J. Phys. Chem. B*, 2005, **109**, 19786.
- 74 R. A. Farrer, F. L. Butterfield, V. W. Chen and J. T. Fourkas, *Nano Lett.*, 2005, **5**, 1139.
- 75 M. Lippitz, M. A. van Dijk and M. Orrit, *Nano Lett.*, 2005, **5**, 799.
- 76 G. Laurent, N. Felidj, S. L. Truong, J. Aubard, G. Levi, J. R. Krenn, A. Hohenau, A. Leitner and F. R. Aussenegg, *Nano Lett.*, 2005, **5**, 253.
- 77 K. Yakushiji, F. Ernult, H. Imamura, K. Yamane, S. Mitani, K. Takahashi, S. Takahashi, S. Maekawa and H. Fujimori, *Nat. Mater.*, 2005, **4**, 57.
- 78 Y. Lei, W. K. Chim, H. P. Sun and G. Wilde, *Appl. Phys. Lett.*, 2005, **86**, 103106.
- 79 J. Y. Kim, H. Hiramatsu and F. E. Osterloh, *J. Am. Chem. Soc.*, 2005, **127**, 15556.
- 80 M. J. Bowers II, J. R. McBride and S. J. Rosenthal, *J. Am. Chem. Soc.*, 2005, **127**, 15378.
- 81 B. Fisher, J. M. Caruge, D. Zehnder and M. G. Bawendi, *Phys. Rev. Lett.*, 2005, **94**, 087403.
- 82 J. Y. Kim and F. E. Osterloh, *J. Am. Chem. Soc.*, 2005, **127**, 10152.
- 83 D. Tari, M. D. giorgi, F. D. Sala, L. Carbone, R. Krahne, L. Manna, R. Cingolani, S. Kudera and W. J. Parak, *Appl. Phys. Lett.*, 2005, **87**, 224101.
- 84 K. Akamatsu, T. Tsuruoka and H. Nawafune, *J. Am. Chem. Soc.*, 2005, **127**, 1634.
- 85 E. J. D. Klem, L. Levina and E. H. Sargent, *Appl. Phys. Lett.*, 2005, **87**, 053101.
- 86 A. Watt, T. Eichmann, H. R. Dunlop and P. Meredith, *Appl. Phys. Lett.*, 2005, **87**, 253109.
- 87 H. E. Romero and M. Drndic, *Phys. Rev. Lett.*, 2005, **95**, 156801.
- 88 A. H. Mueller, M. A. Petruska, M. Ackermann, D. J. Werder, E. A. Akhadov, D. D. Koleske, M. A. Hoffbauer and W. I. Klimov, *Nano Lett.*, 2005, **5**, 1039.
- 89 J. Lee, A. O. Govorov and N. A. Kotov, *Angew. Chem., Int. Ed.*, 2005, **44**, 7439.
- 90 V. V. Agrawal, R. Thomas, G. U. Kulkarni and C. N. R. Rao, *Pramana*, 2005, **65**, 769.
- 91 Y. Q. Zhu, T. Sekine, Y. H. Li, M. W. Fay, Y. M. Zhao, C. H. P. Poa, W. X. Wang, M. J. Roe, P. D. Brown, N. Fleischer and R. Tenne, *J. Am. Chem. Soc.*, 2005, **127**, 16263.
- 92 X. He, H. Liu, Y. Li, S. Wang, Y. Li, N. Wang, J. Xiao, X. Xu and D. Zhu, *Adv. Mater.*, 2005, **17**, 2811.
- 93 C.-S. Tsai, T.-B. Yu and C.-T. Chen, *Chem. Commun.*, 2005, 4273.
- 94 L. Dyadyusha, H. Yin, S. Jaiswal, T. Brown, J. J. Baumberg and F. P. Booy, *Chem. Commun.*, 2005, 3201.
- 95 J. Liu and Y. Lu, *Angew. Chem., Int. Ed.*, 2005, **45**, 90.
- 96 H. Li, J. Huang, J. Lv, H. An, X. Zhang, Z. Zhang, C. Fan and J. Hu, *Angew. Chem., Int. Ed.*, 2005, **44**, 5100.
- 97 S. I. Stoeva, F. Huo, J.-S. Lee and C. A. Mirkin, *J. Am. Chem. Soc.*, 2005, **127**, 15362.
- 98 E. Oh, M.-Y. Hong, D. Lee, S.-H. Nam, H. C. Yoon and H. Sung Kim, *J. Am. Chem. Soc.*, 2005, **127**, 3270.
- 99 D. H. Son, S. M. Hughes, Y. Yin and A. P. Alivisatos, *Nano Lett.*, 2005, **5**, 1009.
- 100 V. Pavlov, Y. Xiao and I. Wilner, *Nano Lett.*, 2005, **5**, 649.
- 101 D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzog, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362.
- 102 R. Narayanan and M. A. El-Sayed, *Langmuir*, 2005, **21**, 2027.
- 103 E. Katz and I. Wilner, *Angew. Chem., Int. Ed.*, 2005, **44**, 4791.
- 104 E. Granot, E. Katz, B. Basnar and I. Wilner, *Chem. Mater.*, 2005, **17**, 4600.
- 105 Y. Chan, J. S. Steckel, P. T. Snee, J.-M. Caruge, J. M. Hodgkiss, D. G. Nocera and M. G. Bawendi, *Appl. Phys. Lett.*, 2005, **86**, 073102.
- 106 M. S. Gudiksen, K. N. Maher, L. Ouyang and H. Park, *Nano Lett.*, 2005, **5**, 2257.
- 107 M. D. Fischbein and M. Drndic, *Appl. Phys. Lett.*, 2005, **86**, 193106.
- 108 J. Ouyang, C.-W. Chu, D. Sieves and Y. Yang, *Appl. Phys. Lett.*, 2005, **86**, 123507.
- 109 R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner and Y. Yang, *Nano Lett.*, 2005, **5**, 1077.

- 110 T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2005, **127**, 1216.
- 111 A. Maria, P. W. Cyr, E. J. D. Lem, L. Levina and E. H. Sargent, *Appl. Phys. Lett.*, 2005, **87**, 213112.
- 112 D. Qi, M. Fischbein, M. Drndic and S. Selmic, *Appl. Phys. Lett.*, 2005, **86**, 093103.
- 113 K. S. Soppimath, D. C.-W. Tan and Y.-Y. Yang, *Adv. Mater.*, 2005, **17**, 318.
- 114 J. Won, M. Kim, Y.-W. Yi, Y. H. Kim, N. Jung and T. K. Kim, *Science*, 2005, **309**, 121.
- 115 B. C. Regan, S. Aloni, K. Jensen, R. O. Ritchie and A. Zettl, *Nano Lett.*, 2005, **5**, 1730.
- 116 S.-M. Liu, M. Kobayashi, S. Sato and K. Kimura, *Chem. Commun.*, 2005, 4690.
- 117 (a) D. C. Lee, T. Hanrath and B. A. Korgel, *Angew. Chem., Int. Ed.*, 2005, **44**, 3573; (b) A. I. Hochbaum, R. Fan, R. He and P. Yang, *Nano Lett.*, 2005, **5**, 457.
- 118 X. Lu, D. D. Fanfair, K. P. Johnston and B. A. Korgel, *J. Am. Chem. Soc.*, 2005, **127**, 15718.
- 119 H.-Y. Tuan, D. C. Lee, T. Hanrath and B. A. Korgel, *Chem. Mater.*, 2005, **17**, 5705.
- 120 P. Nguyen, H. T. Ng and M. Meyyappan, *Adv. Mater.*, 2005, **17**, 549.
- 121 D. Wang, R. Tu, L. Zhang and H. Dai, *Angew. Chem., Int. Ed.*, 2005, **44**, 2925.
- 122 C. Ni, P. A. Hassan and E. W. Kaler, *Langmuir*, 2005, **21**, 3334.
- 123 J. A. Sioss and C. D. Keating, *Nano Lett.*, 2005, **5**, 1779.
- 124 L. Gou and C. J. Murphy, *Chem. Mater.*, 2005, **17**, 3668.
- 125 H.-Y. Wu, H.-C. Chu, T.-J. Kuo, C.-L. Kuo and M. L. H. Huang, *Chem. Mater.*, 2005, **17**, 6447.
- 126 A. Gole and C. J. Murphy, *Chem. Mater.*, 2005, **17**, 1325.
- 127 Y. Ma, L. Qi, W. Shen and J. Ma, *Langmuir*, 2005, **21**, 6161.
- 128 Z. Gui, J. Liu, Z. Wang, L. Song, Y. Hu, W. Fan and D. Chen, *J. Phys. Chem. B*, 2005, **109**, 1113.
- 129 P. X. Gao, Y. Ding, W. Mai, W. L. Hughes, C. Lao and Z. L. Wang, *Science*, 2005, **309**, 1700.
- 130 Q. Li, V. Kumar, Y. Li, H. Zhang, T. J. Marks and R. P. H. Chang, *Chem. Mater.*, 2005, **17**, 1001.
- 131 H. Zhang, D. Yang, X. Ma, N. Du, J. Wu and D. Gue, *J. Phys. Chem. B*, 2006, **110**, 827.
- 132 Y. Tak and K. Yong, *J. Phys. Chem. B*, 2005, **109**, 19263.
- 133 P. X. Gao, C. S. Lao, W. L. Hughes and Z. L. Wang, *Chem. Phys. Lett.*, 2005, **408**, 174.
- 134 K. P. Kalyanikutty, F. L. Deepak, C. Edem, A. Govindaraj and C. N. R. Rao, *Mater. Res. Bull.*, 2005, **40**, 831.
- 135 Y. Hao, G. Meng, C. Ye, X. Zhang and L. Zhang, *J. Phys. Chem. B*, 2005, **109**, 11204.
- 136 J. Zhang, F. Jiang, Y. Yang and J. Li, *J. Phys. Chem. B*, 2005, **109**, 13143.
- 137 J. Zhan, Y. Bando, J. Hu, F. Xu and D. Goldberg, *Small*, 2005, **1**, 883.
- 138 J. Joo, S. G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon and T. Hyeon, *J. Phys. Chem. B*, 2005, **109**, 15297.
- 139 B. S. Gupton, Q. Gu, A. L. Prieto, M. S. Gudixsen and H. Park, *J. Am. Chem. Soc.*, 2005, **127**, 498.
- 140 K. P. Kalyanikutty, G. Gundiah, C. Edem, A. Govindaraj and C. N. R. Rao, *Chem. Phys. Lett.*, 2005, **408**, 389.
- 141 R. Wang, Y. Chen, Y. Fu, H. Zhang and C. Kisielowski, *J. Phys. Chem. B*, 2005, **109**, 12245.
- 142 J. Zhou, Y. Ding, S. Z. Deng, L. Gong, N. S. Xu and Z. L. Wang, *Adv. Mater.*, 2005, **17**, 2107.
- 143 J.-W. Seo, Y.-W. Jun, S. J. Ko and J. Cheon, *J. Phys. Chem. B*, 2005, **109**, 5389.
- 144 G. Xu, Z. Ren, P. Du, W. Weng, G. Shen and G. Han, *Adv. Mater.*, 2005, **17**, 907.
- 145 C. N. R. Rao, A. Govindaraj, F. L. Deepak, N. A. Gunari and M. Nath, *Appl. Phys. Lett.*, 2001, **78**, 1853.
- 146 E. J. H. Lee, C. Ribeiro, E. Longo and E. R. Leite, *J. Phys. Chem. B*, 2005, **109**, 20842.
- 147 A.-M. Cao, J.-S. Hu, H.-P. Liang and L.-J. Wan, *Angew. Chem., Int. Ed.*, 2005, **44**, 4391.
- 148 J. H. Yu, J. Joo, H. M. Park, S.-II. Baik, Y. W. Kim, S. C. Kim and T. Hyeon, *J. Am. Chem. Soc.*, 2005, **127**, 5662.
- 149 S. Kar and S. Chaudhuri, *J. Phys. Chem. B*, 2005, **109**, 3298.
- 150 J. Hu, Y. Bando and D. Goldberg, *Small*, 2005, **1**, 95.
- 151 P. Christian and P. O'Brien, *Chem. Commun.*, 2005, 2817.
- 152 Y. Jeong, Y. Xia and Y. Yin, *Chem. Phys. Lett.*, 2005, **416**, 246.
- 153 S. G. Thoma, A. Sanchez, P. Provencio, B. L. Abrams and J. P. Wilcoxon, *J. Am. Chem. Soc.*, 2005, **127**, 7611.
- 154 S. Kumar, M. Ade and T. Nann, *Chem.-Eur. J.*, 2005, **11**, 2220.

- 155 Z. Liu, D. Xu, J. Liang, J. Shen, S. Zhang and Y. Qian, *J. Phys. Chem. B*, 2005, **109**, 10699.
- 156 J.-P. Ge, J. Wang, H.-X. Zhang, X. Wang, Q. Peng and Y. Li, *Chem.-Eur. J.*, 2005, **11**, 1889.
- 157 K.-S. Cho, D. V. Talapin, W. Gaschler and C. B. Murray, *J. Am. Chem. Soc.*, 2005, **127**, 7140.
- 158 X. Giu, Y. Lou, A. C. S. Samia, A. Devadoss, J. D. Burgess, S. Dayal and C. Burda, *Angew. Chem., Int. Ed.*, 2005, **44**, 5855.
- 159 R. Chen, M. H. So, C.-M. Che and H. Sun, *J. Mater. Chem.*, 2005, **15**, 4540.
- 160 F. Gao, Q. Lu and S. Komarneni, *Chem. Commun.*, 2005, 531.
- 161 M. B. Sigman and B. A. Korgel, *Chem. Mater.*, 2005, **17**, 1655.
- 162 B. Liu, Y. Bando, C. Tang, F. Xu, J. Hu and D. Goldberg, *J. Phys. Chem. B*, 2005, **109**, 17082.
- 163 S. Luo, W. Zhou, Z. Zhang, L. Liu, X. Dou, J. Wang, X. Zhao, D. Liu, Y. Gao, L. Song, Y. Xiang, J. Zhou and S. Xie, *Small*, 2005, **1**, 1004.
- 164 P. V. Radonanic, C. J. Barrelet, S. Gradecak, F. Qian and C. M. Lieber, *Nano Lett.*, 2005, **5**, 1407.
- 165 C. J. Novotny and P. K. L. Yu, *Appl. Phys. Lett.*, 2005, **87**, 203111.
- 166 H. Zhang, Q. Zhang, G. Zhao, J. Tang, O. Zhou and L.-C. Qin, *J. Am. Chem. Soc.*, 2005, **127**, 13120.
- 167 Y. S. Hor, Z. L. Xiao, U. Welp, Y. Ito, J. F. Mitchell, R. E. Cook, W. K. Kwok and G. W. Crabtree, *Nano Lett.*, 2005, **5**, 397.
- 168 Y. Li, M. A. Malik and P. O'Brien, *J. Am. Chem. Soc.*, 2005, **127**, 16020.
- 169 D. Ung, G. Viau, C. Ricolleau, F. Warmont, P. Gredin and F. Fievet, *Adv. Mater.*, 2005, **17**, 338.
- 170 C. J. Orendorff, P. L. Hankins and C. J. Murphy, *Langmuir*, 2005, **21**, 2022.
- 171 X. Hu, W. Cheng, T. Wang, E. Wang and S. Dong, *Nanotechnology*, 2005, **16**, 2164.
- 172 B. Pan, L. Ao, F. Gao, H. Tian, R. He and D. Cui, *Nanotechnology*, 2005, **16**, 1776.
- 173 M. A. C-Duarte, J. P-Juste, A. S-Iglesias, M. Giersig and L. M. L-Marzan, *Angew. Chem., Int. Ed.*, 2005, **44**, 4375.
- 174 C. J. Murphy and C. J. Orendorff, *Adv. Mater.*, 2005, **17**, 2173.
- 175 J.-Y. Chang, H. Wu, H. Chen, Y.-C. Ling and W. Tan, *Chem. Commun.*, 2005, 1092.
- 176 Y. Huang, C.-Y. Chiang, S. K. Lee, Y. Gao, E. L. Hu, J. D. Yoreo and A. M. Belcher, *Nano Lett.*, 2005, **5**, 1429.
- 177 L. Tong, J. Lou, R. R. Gattass, S. He, X. Chen, L. Liu and E. Mazur, *Nano Lett.*, 2005, **5**, 259.
- 178 D. Wang, Y.-L. Chang, Z. Liu and H. Dai, *J. Am. Chem. Soc.*, 2005, **127**, 11871.
- 179 J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti and M. Niederberger, *Angew. Chem., Int. Ed.*, 2005, **44**, 261.
- 180 D.-F. Zhang, L.-D. Sun, C.-J. Jia, Z.-G. Yan, L.-P. You and C.-H. Yan, *J. Am. Chem. Soc.*, 2005, **127**, 13492.
- 181 J. Polleux, N. Pinna, M. Antonietti and M. Niederberger, *J. Am. Chem. Soc.*, 2005, **127**, 13492.
- 182 J. A. Streifer, H. Kim, B. M. Nichols and R. J. Hammers, *Nanotechnology*, 2005, **16**, 1868.
- 183 H. Liao and J. H. Hafner, *Chem. Mater.*, 2005, **17**, 4636.
- 184 M. Curreli, C. Li, Y. Sun, B. Lei, M. A. Gundersen, M. E. Thompson and C. Zhou, *J. Am. Chem. Soc.*, 2005, **127**, 6922.
- 185 A. D. LaLonde, M. G. Norton, D. N. McIlroy, D. Zhang, R. Padmanabhan, A. Alkhateeb, H. Man, N. Lane and Z. Holman, *J. Mater. Res.*, 2005, **20**, 549.
- 186 S. Y. Bae, H. W. Seo, H. C. Choi, D. S. Han and J. Park, *J. Phys. Chem. B*, 2005, **109**, 8496.
- 187 H.-X. Zhang, J.-P. Ge, J. Wang, Z. Wang, D.-P. Yu and Y.-D. Li, *J. Phys. Chem. B*, 2005, **109**, 11585.
- 188 A. Gomathi, S. R. C. Vivekchand, A. Govindaraj and C. N. R. Rao, *Adv. Mater.*, 2005, **17**, 2757.
- 189 Y. Xi, J. Zhou, H. Guo, C. Cai and Z. Lin, *Chem. Phys. Lett.*, 2005, **412**, 60.
- 190 S. Eustis and M. El-Sayed, *J. Phys. Chem. B*, 2005, **109**, 16350.
- 191 A. Pan, H. Yang, R. Liu, R. Yu, B. Zou and Z. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 15692.
- 192 Y. Liang, L. Zhai, X. Zhao and D. Xu, *J. Phys. Chem. B*, 2005, **109**, 7120.
- 193 C.-L. Hsu, S.-J. Chang, Y.-R. Lin, P.-C. Li, T.-S. Lin, S.-Y. Tsai, T.-H. Lu and I.-C. Chen, *Chem. Phys. Lett.*, 2005, **416**, 75.

- 194 Y. Zhang, R. E. Russo and S. S. Mao, *Appl. Phys. Lett.*, 2005, **87**, 043106.
- 195 A. Pan, R. Liu, Q. Yang, Y. Zhu, G. Yang, B. Zou and K. Chen, *J. Phys. Chem. B*, 2005, **109**, 24268.
- 196 R. Agarwal, C. J. Barrelet and C. M. Lieber, *Nano Lett.*, 2005, **5**, 917.
- 197 A. B. Greytak, C. J. Barrelet, Y. Li and C. M. Lieber, *Appl. Phys. Lett.*, 2005, **87**, 151103.
- 198 S. Gradecak, F. Qian, Y. Li, H.-G. Park and C. M. Lieber, *Appl. Phys. Lett.*, 2005, **87**, 173111.
- 199 Y. Huang, X. Duan and C. M. Lieber, *Small*, 2005, **1**, 142.
- 200 Z. Zhong, Y. Fang, W. Lu and C. M. Lieber, *Nano Lett.*, 2005, **5**, 1143.
- 201 E. Stern, G. Cheng, E. Cimpoiasu, R. Klie, S. Guthrie, J. Klemic, I. Kretzschmar, E. Steinlauf, D. T. Evans, E. Broomfield, J. Hyland, R. Koudelka, T. Boone, M. Young, A. Sanders, R. Munden, T. Lee, D. Routenberg and M. A. Reed, *Nanotechnology*, 2005, **16**, 2941.
- 202 F. Liu, M. Bao, K. L. Wang, C. Li, B. Lei and C. Zhou, *Appl. Phys. Lett.*, 2005, **86**, 213101.
- 203 J. Goldberger, D. J. Sirbuly, M. Law and P. Yang, *J. Phys. Chem. B*, 2005, **109**, 9.
- 204 B. Sun and H. Sirringhaus, *Nano Lett.*, 2005, **5**, 2408.
- 205 S. Ju, K. Lee, D. B. Janes, M.-H. Yoon, A. Facchetti and T. J. Marks, *Nano Lett.*, 2005, **5**, 2281.
- 206 B.-K. Kim, J.-J. Kim, J.-O. Lee, K.-j. Kong, H. J. Seo and C. J. Lee, *Phys. Rev. B*, 2005, **71**, 153313.
- 207 C. Thelander, H. A. Nilsson, L. E. Jensen and L. Samuelson, *Nano Lett.*, 2005, **5**, 635.
- 208 S. R. C. Vivekchand, K. C. Kam, G. Gundiah, A. Govindaraj, A. K. Cheetham and C. N. R. Rao, *J. Mater. Chem.*, 2005, **15**, 4922.
- 209 J. Zhou, C. Jin, J. H. Seol, X. Li and L. Shi, *Appl. Phys. Lett.*, 2005, **87**, 133109.
- 210 B. D. Liu, Y. Bando, C. C. Tang, F. F. Xu and D. Goldberg, *J. Phys. Chem. B*, 2005, **109**, 21521.
- 211 H. Liu, Q. Zhao, Y. Li, Y. Liu, F. Lu, J. Zhuang, S. Wang, L. Jiang, D. Zhu, D. Yu and Y. Chi, *J. Am. Chem. Soc.*, 2005, **127**, 1120.
- 212 M. Tian, N. Kumar, S. Xu, J. Wang, J. S. Kurtz and M. H. W. Chan, *Phys. Rev. Lett.*, 2005, **95**, 076802.
- 213 K. Peng, Y. Xu, Y. Wu, Y. Yan, S.-T. Lee and J. Zhu, *Small*, 2005, **1**, 1062.
- 214 M. Law, L. E. Green, J. c. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, **4**, 455.
- 215 J. B. Baxter and E. S. Aydil, *Appl. Phys. Lett.*, 2005, **86**, 053114.
- 216 M. Y. Song, Y. R. Ahn, S. M. Jo, D. Y. Kim and J.-P. Ahn, *Appl. Phys. Lett.*, 2005, **87**, 113113.
- 217 S. F. Bidoz, A. C. Arsenault, I. Manners and G. A. Ozin, *Chem. Commun.*, 2005, 441.
- 218 L. Qian, S. Park, L. Huang and C. A. Mirkin, *Science*, 2005, **309**, 113.
- 219 G. S. D. Beach, C. Nistor, C. Knutson, M. Tsoi and J. L. Erskine, *Nat. Mater.*, 2005, **4**, 741.
- 220 C. Li, B. Lei, Z. Luo, S. han, Z. Liu, D. Zhang and C. Zhou, *Adv. Mater.*, 2005, **17**, 1548.
- 221 D. S. Han, S. Y. Bae, H. W. Seo, Y. J. Kang, J. Park, G. Lee, J.-P. Ahn, S. Kim and J. Chang, *J. Phys. Chem. B*, 2005, **109**, 9311.
- 222 A. R. Armstrong, G. Armstrong, J. Canales, R. Garcia and P. G. Bruce, *Adv. Mater.*, 2005, **17**, 862.
- 223 M. A. L. Devlin, C. L. Asher, B. J. Taft, R. Gasparac, M. A. Roberts and S. O. Kelly, *Nano Lett.*, 2005, **5**, 1051.
- 224 T. R. Kline, W. F. Paxton, T. E. Mallouk and A. Sen, *Angew. Chem., Int. Ed.*, 2005, **44**, 744.
- 225 B. S. Kang, F. Ren, Y. W. Heo, L. C. Tien, D. P. Norton and S. J. Pearton, *Appl. Phys. Lett.*, 2005, **86**, 112105.
- 226 C. S. Rout, S. H. Krishna, S. R. C. Vivekchand, A. Govindaraj and C. N. R. Rao, *Chem. Phys. Lett.*, 2006, **418**, 586.
- 227 Z. Fan and J. G. Lu, *Appl. Phys. Lett.*, 2005, **86**, 123510.
- 228 X. Qi and F. E. Osterloh, *J. Am. Chem. Soc.*, 2005, **127**, 7666.
- 229 C. Li, M. Curreli, H. Lin, B. Lei, F. N. Ishikawa, R. Datar, R. J. Cote, M. E. Thompson and C. Zhou, *J. Am. Chem. Soc.*, 2005, **127**, 12484.
- 230 C. Yu, Q. Hao, S. Saha, L. Shi, X. Kong and Z. L. Wang, *Appl. Phys. Lett.*, 2005, **86**, 063101.
- 231 G. Zheng, F. Patolsky, Y. Cui, W. U. Wang and C. M. Lieber, *Nat. Biotechnol.*, 2005, **23**, 1294.
- 232 B. Wu, A. Heidelberg and B. J. Boland, *Nat. Mater.*, 2005, **4**, 525.
- 233 J. Song, X. Wang, E. Riedo and Z. L. Wang, *Nano Lett.*, 2005, **5**, 1954.

- 234 X. Li, X. Wang, Q. Xiong and P. C. Eklund, *Nano Lett.*, 2005, **5**, 1982.
- 235 S. R. C. Vivekchand, U. Ramamurthy and C. N. R. Rao, *Nanotechnology*, 2006, **17**, S344.
- 236 C. N. R. Rao and M. Nath, *Dalton Trans.*, 2003, 1.
- 237 H. Yu, Z. Zhang, M. Han, X. Hao and F. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 2378.
- 238 (a) J. M. Macak, H. Tsuchiya and P. Schumuki, *Angew. Chem., Int. Ed.*, 2005, **44**, 2100; (b) C. Ruan, M. Paulose, O. K. Varghese, G. K. Mor and C. A. Grimes, *J. Phys. Chem. B*, 2005, **109**, 15754.
- 239 G. Armstrong, A. R. Armstrong, J. Canales and P. G. Bruce, *Chem. Commun.*, 2005, 2454.
- 240 R. Ma, T. Sasaki and Y. Bando, *Chem. Commun.*, 2005, 948.
- 241 Q. Ji and T. Shimizu, *Chem. Commun.*, 2005, 4411.
- 242 J. H. Jung, T. Shimizu and S. Shinkai, *J. Mater. Chem.*, 2005, **15**, 3979.
- 243 C.-J. Jia, L.-D. Sun, Z.-G. Yan, L.-P. You, F. Luo, X.-D. Han, Y.-C. Pang, Z. Zhang and C. H. Yan, *Angew. Chem., Int. Ed.*, 2005, **44**, 4328.
- 244 Z. Liu, D. Zhang, S. Han, C. Li, B. Lei, W. Lu, J. Fang and C. Zhou, *J. Am. Chem. Soc.*, 2005, **127**, 6.
- 245 C. Tang, Y. Bando, B. Liu and D. Goldberg, *Adv. Mater.*, 2005, **17**, 3005.
- 246 J. wang, V. K. Kayastha, Y. K. Yap, Z. Fan, J. G. Lu, Z. Pan, I. N. Ivanov, A. A. Puzetky and D. B. Geohegan, *Nano Lett.*, 2005, **5**, 2528.
- 247 U. K. Gautam, S. R. C. Vivekchand, A. Govindaraj, G. U. Kulkarni, N. R. Selvi and C. N. R. Rao, *J. Am. Chem. Soc.*, 2005, **127**, 3658.
- 248 Q. Wu, Z. Hu, C. Liu, X. Wang, Y. Chen and Y. Lu, *J. Phys. Chem. B*, 2005, **109**, 19719.
- 249 M. S. Sander and H. Gao, *J. Am. Chem. Soc.*, 2005, **127**, 12158.
- 250 Y. Aoki, J. Huang and T. Kunitake, *J. Mater. Chem.*, 2006, **16**, 292.
- 251 C. Zhi, Y. Bando, C. Tang, R. Xie, T. Sekiguchi and D. Goldberg, *J. Am. Chem. Soc.*, 2005, **127**, 15996.
- 252 S.-Y. Xie, W. Wang, K. A. S. Fernando, X. Wang, Y. Lin and Y.-P. Sun, *Chem. Commun.*, 2005, 3670.
- 253 C. Zhi, Y. Bando, C. Tang, S. Honda, K. Sato, H. Kuwahara and D. Goldberg, *Angew. Chem., Int. Ed.*, 2005, **44**, 7932.
- 254 C. Tang, Y. Bando, Y. Huang, S. Yue, C. Gu, F. Xu and D. Goldberg, *J. Am. Chem. Soc.*, 2005, **127**, 6552.
- 255 R. Fan, R. Karnik, M. Yue, D. Li, A. Mujumdar and P. Yang, *Nano Lett.*, 2005, **5**, 1633.
- 256 Q. Ji, S. Kamiya, J.-H. Jung and T. Shimizu, *J. Mater. Chem.*, 2005, **15**, 743.
- 257 X. Chen, X. P. Gao, H. Zhang, Z. Zhou, W. K. Hu, G. L. Pan, H. Y. Zhu, T. Y. Yan and D. Y. Song, *J. Phys. Chem. B*, 2005, **109**, 11525.
- 258 C.-C. Chen, Y.-C. Liu, C.-H. Wu, C.-C. Yeh, M.-T. Su and Y.-C. Wu, *Adv. Mater.*, 2005, **17**, 404.
- 259 Z. Siwy, L. Trofin, P. Kohli, L. A. Baker, C. Trautmann and C. R. Martin, *J. Am. Chem. Soc.*, 2005, **127**, 5000.
- 260 B. A. H. Sancez, K.-S. Chang, M. T. Scancella, J. L. Burriss, S. Kohli, E. R. Fischer and P. K. Dorhout, *Chem. Mater.*, 2005, **17**, 5909.
- 261 X. Y. Zhang, C. W. Lai, X. Zhao, D. Y. Wang and Y. Y. Dai, *Appl. Phys. Lett.*, 2005, **87**, 143102.
- 262 Z. Sun, H. Yaun, Z. Liu, B. Han and X. Zhang, *Adv. Mater.*, 2005, **17**, 2993.
- 263 J. Chen, L. Xu, W. Li and X. Gou, *Adv. Mater.*, 2005, **17**, 582.
- 264 X. Li, F. Cheng, B. Guo and J. Chen, *J. Phys. Chem. B*, 2005, **109**, 14017.
- 265 R. Fan, M. Yue, R. Karnik, A. Mujumdar and P. Yang, *Phys. Rev. Lett.*, 2005, **95**, 086607.
- 266 D. G. Shchukin, G. B. Sukhurov, R. R. Price and Y. M. Lvov, *Small*, 2005, **1**, 510.