CrystEngComm

Dynamic Article Links

Cite this: *CrystEngComm*, 2012, **14**, 7531–7534

www.rsc.org/crystengcomm

EDITORIAL

Nanocrystals

Shu-Hong Yu,*[a] Leonard R. MacGillivray*[b] and Christoph Janiak*[c]

DOI: 10.1039/c2ce90082c

Introduction

Nanocrystals are of significant interest for technological applications in science and industry. The controlled and reproducible synthesis of defined and stable nanoparticles with a narrow size distribution is important for a wide range of applications. Engineering crystals with at least one dimension on the order of 100 nm is attracting attention for optical, electronic, mechanical and chemical properties and potential applications (*e.g.*, optoelectronics, field emission, energy conversion, catalysis, sensing). Thus, it is fitting that a journal which carries *Crystal Engineering* in its name devotes a special issue to the science of nanocrystals.

As guest editors, we are pleased with the variety of topics within the nanocrystals theme, as well as the combination of synthesis and application aspects in the manuscripts. This first *CrystEngComm* themed issue on nanocrystals brings together papers concerning recent developments in synthesis, crystal shape-, morphology- and phase-control of nanocrystals, hybrid-nanocrystals, nanoalloys, core-shell nanocrystals, nanorods – nanocables – nanowires, nanotubes and ordered superstructure arrays. The reader will find examples of uses of nanocrystals as semiconductors, in luminescence, in catalysis—including photocatalysis, for near-infrared absorption, for thermoelectric devices, in magnetism and as superparamagnets for magnet resonance imaging.

It is evident that the chemistry and physics of nanoparticles with their high surface-to-volume ratio is dominated by its surface energy. In a Highlight contribution, Lee *et al.* (DOI: 10.1039/c2ce25815c) report and analyze examples of nanoparticle chemical conversion and dynamic nanoparticle composition/morphology changes, which take full advantage of the highly reactive nature of the nanoparticle surface and interface.

Metal and alloy nanocrystals

Gold nanowires with diameters of ~55 nm and large aspect ratios were prepared by Wang *et al.* (DOI: 10.1039/c2ce25726b) in the presence of H_2PtCl_6 and polyvinylpyrrolidone (PVP) in a seed-free aqueous solution route using *in-situ* prepared 5-hydroxy-2-pyrrolidone from 2-pyrrolidinone as the reductant.

Various Au architectures can be tailored with branched shapes, including flower-, cauliflower-, raspberry-, urchin- and confeito-like architectures, in aqueous solution at room temperature without the need for any template, seed, or additive according to Yamauchi *et al.* (DOI: 10.1039/c2ce26004b). The particle shapes and sizes of the Au architectures are controllable by simply changing the Au species from $HAuCl_4$ to $KAuBr_4$ and concentrations and by using a different reducing agent ($NaBH_4$, catechol or ascorbic acid) in the presence of gum Arabic.

Using the nonionic biosurfactant ethoxylated sterol (BPS-30), Zheng *et al.* (DOI: 10.1039/c2ce25840d) obtained relatively monodisperse gold nanoparticles between 55 to 24 nm that are stable for months under ambient conditions. The catalytic efficiency of the nanoparticles capped by BPS-30 was evaluated by using the reduction of 4-nitroaniline by potassium borohydride in aqueous solution.

Small 1.0–2.3 nm Pt nanocrystals exhibit long-term stability even in weakly-coordinating media like ionic liquids (ILs) and diphenylmethane without the typical capping ligands for metal nanoparticles, as Janiak *et al.* (DOI: 10.1039/c2ce25904d) show. Pt nanocrystals are important catalysts and the Pt/IL dispersion is highly active for biphasic hydrosilylation of phenylacetylene with triethylsilane to yield triethyl(2- and 1-phenylvinyl) silane.

A method for the fabrication of cubic nickel frames by an etchant-assisted solution method is presented by Ma, Yao *et al.* (DOI: 10.1039/c2ce25816a). These Ni nano-to-micro frames exhibit enhanced coercivity over similar-sized Ni spheres and show an excellent ability to adsorb and thereby remove heavy metal ions in water treatment.

Stable Ag and Ag:AgCl hybrid nanocolloids were selectively synthesized by Li, Aisa *et al.* (DOI: 10.1039/c2ce25364j) through phytoreduction with the extract of *Vernonia anthelmintica* wild seed acting both as reducing and stabilizing agent.

Monodispersed and ferromagnetic $FeNi_2$ alloy nanostructures by Wei *et al.* (DOI: 10.1039/c2ce25457c) revealed a size-dependent saturation magnetization value (up to 116.5 emu g^{-1}). Furthermore, the $FeNi_2$ alloys act as reusable heterogeneous catalysts for the reduction of *p*-nitrophenol to *p*-aminophenol by $NaBH_4$ with size-dependent catalytic rate constants.

In a theoretical approach, Hennes, Mayr *et al.* (DOI: 10.1039/c2ce25817j)

[a]*Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at Microscale (HFNL), Department of Chemistry, University of Science and Technology of China, Jinzhai Road 96, Hefei, 230026, P. R. China. E-mail: shyu@ustc.edu.cn*
[b]*Department of Chemistry, University of Iowa, Iowa City, IA 52245, USA. E-mail: len-macgillivray@uiowa.edu*
[c]*Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany. E-mail: janiak@hhu.de*

employ a combined Molecular-Dynamics/Metropolis-Monte-Carlo (MD/MMC) simulation approach to analyze equilibrium segregation profiles in less known Cu/Ni clusters. They suggest that the clusters adopt an ordered state with Janus-like core structures and that surface segregation of Cu is a key mechanism in the evolution of the clusters towards equilibrium.

Hou, Gao *et al.* (DOI: 10.1039/c2ce25802a) demonstrate the shape-controlled synthesis of FePt concave nanocubes which due to their concave structure exhibit higher electrocatalytic activity than normal FePt nanocubes or commercial Pt catalysts in methanol oxidation.

Octahedral and decahedral Au@Ag core-shell and hybrid nanocrystals have been prepared by Tsuji *et al.* (DOI: 10.1039/c2ce25569c) in high yields using a two-step reduction method from first $HAuCl_4{\cdot}4H_2O$ in di- or tetraethylene glycol in the presence of polyvinylpyrrolidone, followed by $AgNO_3$/*N*,*N*-dimethylformamide. Non-uniform Ag attachments to Au–NPs were formed under fast microwave heating.

The semi-metal silicon (Si) was prepared as nanocrystals (Si–NCs) from size-controlled Stöber silica (SiO_2) particles by reduction with Mg powder at 500 °C in a contribution by Veinot *et al.* (DOI: 10.1039/c2ce25950h). The necessary nanoparticle stabilization was achieved by reacting the hydride terminated Si–NCs with trioctylphosphine oxide (TOPO) to yield hydroxyl terminated and TOPO-encapsulated Si–NCs. The Si–NCs exhibit red luminescence.

Metal oxide and element oxide nanocrystals

Anatase titanium dioxide (TiO_2) draws high attention due to its wide applications in photocatalysis, solar cells, photochromic devices, and gas sensors. Hence, the control of the shape and size of TiO_2 nanocrystals is important.

Jing, Wang *et al.* (DOI: 10.1039/c2ce25812a) illustrate the discontinuous growth of anatase TiO_2 nanoparticles in the presence of oleic acid, oleylamine and sulfuric acid where the nano-seeds grow into mesocrystals and finally porous hollow nanoparticles. This work may provide inside into the crystal growth mechanism by both oriented attachment and Ostwald ripening.

Zhou, Zou *et al.* (DOI: 10.1039/c2ce25162k) fabricate TiO_2 nanotube arrays, which are promising photoanodes for energy conversion, water splitting and optoelectronics, with a template- and fluorine-free electrochemical spark discharge process. Hu, Zhang *et al.* (DOI: 10.1039/c2ce25323b) use a dissolution–recrystallization procedure of anodic TiO_2 nanotubes (TNTs) to assemble hierarchical TiO_2 nanotube arrays with higher specific surface area and better crystallinity than the original TNTs through *in situ* chemical etching with hydrofluoric acid.

A one-pot solvothermal method has been developed by Liu *et al.* (DOI: 10.1039/c2ce25563d) for the preparation of nitrogen-doped TiO_2 nanorods with anatase/brookite structures, using hydrazine hydrate and TiO_2 colloids as the starting materials. Synergistic effects from N-doping and rod-structure were seen as the basis for enhanced photocatalytic activity for decomposing methyl orange and 4-chlorophenol compared with TiO_2 nanoparticle counterparts under UV and/or visible light illumination.

N-doped TiO_2 nanorods have also been synthesized by Li *et al.* (DOI: 10.1039/c2ce25827g) directly from a TiN precursor by a hydrothermal method in the presence of HCl solution. The nanorods are highly crystalline with a rutile phase and exhibit both straight and V-shaped morphologies. These N-doped TiO_2 nanorods exhibit an enhanced visible light absorption and red-shift in band gap in comparison with pure rutile TiO_2 nanopowders.

The crystal grain size and crystallinity in nanoscale TiO_2 is important to the photocatalytic activity of this material. Hence, Yin *et al.* (DOI: 10.1039/c2ce25799h) demonstrate the synthesis of anatase titania microspheres with controllable grain sizes through impregnating porous networks of amorphous titania microspheres with silicate oligomers from the addition and hydrolysis of the precursor tetraethyl orthosilicate and calcining the composite. Furthermore, the study determined an optimum balance between grain size and surface area from the photocatalytic degradation of rhodamine B under UV irradiation.

ZnO is an important semiconductor with a direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature. It has attracted much attention mainly because of unique optical and electrical properties, as well as potential applications in optical waveguides, surface acoustic wave transducers, blue light-emitting diodes, solar cells, chemical sensors and photocatalysts. Interesting shape dependent optoelectronic and gas sensing properties of ZnO make researchers explore facile methods to prepare ZnO particles with controlled nanostructures.

A systematic shape-controlled synthesis of wurtzite-type tetrapod-like ZnO micro-nanocrystals using a tin-assisted vapor-phase transport (VPT) method is reported by Li *et al.* (DOI: 10.1039/c2ce25963j).

In related work, one-dimensional coaxial nanostructures composed of ZnO nanorod cores, intermediate amorphous carbonaceous layers, and CdS nanoparticle sheaths (*i.e.* ZnO/C/CdS nanocables) have been assembled *via* a multi-step process from ZnO nanorods, glucose in water and CdS nanoparticles by Hu *et al.* (DOI: 10.1039/c2ce25540e) The fabricated nanohybrids demonstrated an enhanced photocatalytic activity over that of pure ZnO nanorods, pure CdS, ZnO/CdS binary composites for the degradation of rhodamine-B (RhB) and methylene blue (MB) under visible-light irradiation due to stronger adsorption, and the synergistic effect of the ternary ZnO/C/CdS interface.

Hematite (α-Fe_2O_3), an environmentally friendly n-type semiconductor has been prepared by Jiang *et al.* (DOI: 10.1039/c2ce25575h) as flowerlike hierarchical nanocrystalline architectures *via* a one-step biphasic interfacial route from $Fe(acac)_3$ at the benzene–water interface. The flowerlike α-Fe_2O_3 showed high photocatalytic activity for the degradation of RhB and potential applications in water treatment to adsorb and, thereby, remove the heavy metal ion Cr(VI).

Tantalate, $(Me_4N)_4Ta_6O_{17}{\cdot}nH_2O$ with interests as catalysts, photocatalysts, and photoluminescent materials, was formulated as highly water-dispersable layered nanocrystals of $\sim$50 nm lateral size consisting of 6 to 12 tantalate layers by Ban *et al.* (DOI: 10.1039/c2ce25531f).

Ultrathin nanosheets of layered protonated titanate (LPT) hierarchical microspheres were obtained by Kuang, Xie *et al.* (DOI: 10.1039/c2ce25797a) through a one step solvothermal reaction from $Ti(OBu)_4$

in the presence of hexamethylenetetramine. These LPT hierarchical microspheres possess large surface areas, of up to 450 $m^2\ g^{-1}$, and they display specific adsorption selectivity towards methylene blue over other organic dyes.

CeO_2 nano-cubes with enhanced catalytic properties in CO catalytic oxidation and CeO_2 truncated nano-octahedra have been synthesized by Jiang, Xie *et al.* (DOI: 10.1039/c2ce25333j) with different capping agents in alkaline environment.

Sun *et al.* (DOI: 10.1039/c2ce25713k) use coordination polymers for the shape-controlled synthesis phase-pure Co_3O_4 nanocrystals by annealing under oxygen above 400 °C. The porous Co_3O_4 samples exhibited good catalytic properties for the thermal decomposition of ammonium perchlorate.

A disordered thin film of rubidium tungsten bronze (Rb_xWO_3) nanoparticles showed promising potential as an effective solar filter, because it has high transparency for visible light and excellent absorption of heat rays, that is near-infrared light, as presented by Guo *et al.* (DOI: 10.1039/c2ce25460c).

Superparamagnetic Fe_3O_4–Ag hybrid nanocrystals in the 10–20 nm diameter range and with a magnetization saturation of over 40 emu g^1 were tested by Gao, Cui *et al.* (DOI: 10.1039/c2ce25395j) for *in vivo* magnetic resonance imaging in mice.

Royer, Alamdari *et al.* (DOI: 10.1039/c2ce25737h) highlight the potential of high surface area nanocrystalline hexaaluminate materials in heterogeneous catalysis (*e.g.* in CO and CH_4 oxidation tests with BaMn-, $BaMn_2$- or $BaMnPd_{0.07}$-hexaaluminate supported formulations).

Annealing of $SiC@SiO_2$ nanocables under nitrogen at 1400 °C led to the dewetting of the SiO_2 shell, and the nanocables were transformed into SiC/SiO_2 necklace-like nanostructures with promising applications as robust nanocomposites, sensors, drug release and optical components. The dewetting mechanism of the silica shell has been attributed mainly to the Rayleigh instability by Bechelany *et al.* (DOI: 10.1039/c2ce25636c).

Metal sulfide and telluride nanocrystals

ZnS as nanostructured sphalerite, the cubic or zinc blende phase, is used in diverse fields including bio-technology, optoelectronics, catalysis, photovoltaics, gas chemical, and bio-sensors, field effect transistors and field emitters. Barnard, Russo *et al.* (DOI: 10.1039/c2ce25814e) employed a generalised shape-dependent thermodynamic model to predict the equilibrium morphology of cubic ZnS nanoparticles as a function of size, and temperature and partial pressure of sulphur to guide the modification of experimental conditions.

Wu, Qu *et al.* (DOI: 10.1039/c2ce25144b) describe superhydrophobic ZnS nanowire bundles and nanorod arrays with yellow photoluminescence.

The important metal chalcogenide Bi_2S_3 with its direct band gap of 1.3 eV is a focus for low dimensional nanostructure and ordered superstructure arrays. Hu and Cao (DOI: 10.1039/c2ce25454a) employed a hydrothermal process for rectangular grid-shaped bismuth sulfide planar networks, which consist of crossed bismuth sulfide single-crystalline nanorods.

Song *et al.* (DOI: 10.1039/c2ce25809a) demonstrated a precise size control of Cu_2S nanocrystals from 3 nm to 8 nm by varying the concentration of alkyl-thiol in a two-phase microwave-assisted synthesis from $CuSO_4$.

Hybrid nanocrystals permanently combine two or more different nanostructures with chemical and physical synergetic properties different from their disparate component. As such Liu, Wang *et al.* (DOI: 10.1039/c2ce25253h) show how to tune the size of metal–semiconductor Au–PbS hybrid nanocrystals.

A selective growth of metal sulfide tips onto elongated Cd chalcogenide nanostructures should be interesting for semiconductor nanocrystal research. From the thermal decomposition of metal thiocarbamate precursors Ag_2S, $Cu_{2-x}S$ and PbS nanostructures with controllable size were grown primarily on CdS but also CdSe nanostructures (rods, tetrapods and cubes) by Mokari *et al.* (DOI: 10.1039/c2ce25795e).

PbTe-based quaternary alloys are considered ideal thermoelectric (TE) materials at elevated temperature due to enhanced TE performance. In this realm the synthesis, growth mechanism and shape-dependent electrical transportation properties of $AgPb_{10}LaTe_{12}$ materials are studied by Chen, Wang *et al.* (DOI: 10.1039/c2ce25512j). Rod-like particles of the quaternary phase had the highest power factor of about 900 $\mu W\ K^{-2}\ m^{-1}$.

Metal halide nanocrystals

Wang *et al.* (DOI: 10.1039/c2ce25165e) report a synthetic protocol for the assembly of highly-efficient fluorescent materials EuF_3:Ln^{3+} and EuF_3:Ln^{3+}/NH_4^+ (Ln = Y, Gd, Tb, Dy, Ho, Er, and Tm) as nanocrystallites with a controlled architecture of hexagon-shaped sub-microcages and hollow sub-microspheres.

AgBr nanocubes prepared by Guo *et al.* (DOI: 10.1039/c2ce25750e) in a precipitation reaction with the aid of pyridine were shown to exhibit excellent photocatalytic activity for the photodegradation of methyl orange dye under visible-light irradiation.

Organic nanocrystals

In the less developed area of organic nanocrystals, Li, Chen *et al.* (DOI: 10.1039/c2ce25187f) use a surfactant-assisted reaction to derive porous and luminescent porphyrinato zinc particles with prismatic, octahedral, and rod shape. Such nano-scale coordination polymers are attractive for gas storage, optics, catalysis and as sensors.

The cyclic transformation in shape and crystal structure of C_{60} microcrystals in dispersion from as-grown rod-shape to hexagonal disc-shape, then to belt-shape, and again back to rod-shape are demonstrated by Masuhara *et al.* (DOI: 10.1039/c2ce25798j). The transformation is viewed as a way to prepare well-defined hybridized nanocrystals between C_{60} and many other compounds in the near future.

Microribbons composed of crystalline 4-chlorocinnamic acid show a photoinduced twisting. Bardeen *et al.* (DOI: 10.1039/c2ce25811k) illustrate that the solid-state photomechanical response depends on crystal shape and size, is dominated by the irreversible [2 + 2] photodimerization reaction, and that a new crystal phase is formed.

In related work, MacGillivray *et al.* (DOI: 10.1039/c2ce26000j) describe the generation of nanocrystals of the well-known organic molecule [2.2]paracyclophane. A cyclophane obtained from a templated [2 + 2] photodimerization in

the solid state is also demonstrated to form nanocrystals that exhibit enhanced fluorescence emission.

Charge-transfer Cu^{+}-$TCNQ^{-}$ nanocrystals were prepared by Onodera *et al.* (DOI: 10.1039/c2ce25926e) using a reprecipitation method. With the resulting composition ratio of Cu : TCNQ = 1.3 : 1 and the same crystal structure as bulk crystalline (Cu : TCNQ = 1 : 1) the nanocrystals contained both the TCNQ anion and dianion. The nanocrystals exhibited a strong absorption peak in NIR region, with the peak position dependent on the content of the TCNQ dianion.

The guest editors would like to thank all of the above authors who contributed articles to this themed issue. We feel that these contributions provide a cross section to the current development of nanocrystals, and indicate future research directions. We hope that this collection of articles will inspire researchers, stimulate new ideas and advance the field. The future of nanoscience to which nanocrystals are an integral part has, indeed, just begun.