A Review for Synthesis of Nanoflowers

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Abstract: The data on nanoflower-like nanostructures are generalized for several groups of inorganic compounds (carbon, elemental metals, their alloys and compounds with the elements of V and VI Groups of the Periodic Table), as well as for a few coordination and organic compounds. Their synthetic techniques include oxidation of elemental metals, reduction of metal salts, thermal decomposition of relatively unstable compounds, or electrochemical route. Some current and possible applications of nanoflowers are noted.

Keywords: Nanoflowers, deposition, oxidation, reduction, hydrothermal reaction, condensation, growth.

This bouquet of nano***FLOWERS*** is dedicated to the anniversary of my wife Dr. Oxana Vasilievna Kharissova (born February 25, 1969).

INTRODUCTION

Starting from the last decade of XX century, the nanotechnology boom has resulted in discovery of a host of forms of nanoparticles/nanoaggregates. Some of them are *nanopowders*, *nanotubes*, *nanowires*, *nanorices*, *nanolines*, *nanodumbbells*, *nanoclusters*, *nanosheets*, *nanorods*, *nanodots*, *nanoalloys*, *nanobelts*, *nanoribbons*, *nanoplates*, *nanoneedles*, *nanocones*, and *nanofilms*, which have a lot of applications, in particular as catalysts, magnetic materials, nanocomposites, nanodevices, chemical sensors, degradation of toxic chemicals, or even as possible carriers of isotopes for medical applications. Formed nanostructures are sometimes attributed with difficulty to a definite group above; the possibility of formation of various nanoforms frequently depends on the synthesis conditions; additionally, some forms seem similar to each other, so the determination of the final correct form depends much on the imagination of authors. Thus, such "non-standard", but already common terms as *nanotowers*, *nanoshuttles*, *nanobowlings*, *nanowheels*, *nanofans*, *nanopencils*, *nanotrees*, *nanoarrows*, *nanonails*, *nanobottles*, or *nanovolcanoes* are known. Fig. (**1**) shows [1] some of these ZnO nanostructures.

Nanoflowers (flower-like nanoparticles) are not currently reported so frequently, as, for example, nanowires [2] or one of the hottest nanotechnology area - well-known carbon nanotubes. However, last decade the number of related literature is being increased. Last years, a series of various nanoflower and nanoflower-like structures have been obtained, frequently together or in equilibrium with other nanoforms, depending on reaction conditions. Current and possible applications of nanoflowers as optoelectronics devices or sensors, in catalysis, and solar cells caused a definite interest to them. This microreview covers state-of-the-art synthesis of nanoflowers for various groups of compounds, obtained up to date.

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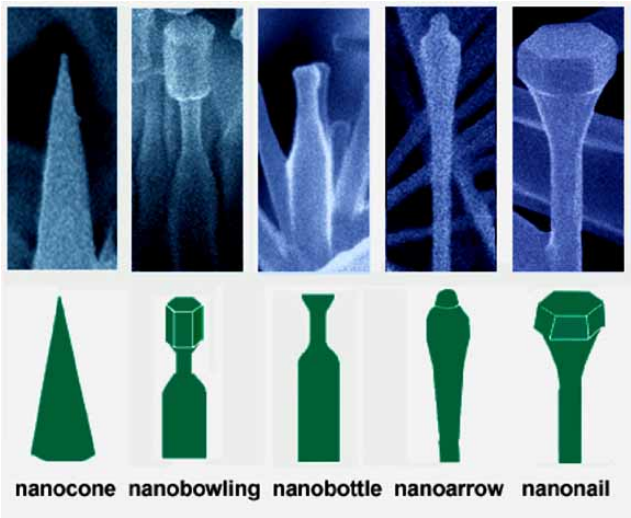

Fig. (1). Varios ZnO nanoforms [1].

ELEMENTAL NANOFLOWERS (METALS AND CARBON)

There are several elemental metals (mainly Au), for which the forms of nanoflower and flowerlike nanoparticles have been obtained by reduction of metal salts or other compounds. In case of gold, $HAuCl_4$ was always used as a precursor. Thus, the sheet-like gold nanoparticles, prepared in colloidal form under UV light irradiation of the mixture of $HAuCl_4$ aqueous solution and poly(vinylpyrrolidone) (PVP) ethanol solution in the presence of silver ions, were found to self-assemble into nanoflowers by a centrifuging process [3]. Ag ions and PVP served as structure-directing agents to produce the sheet-like particles with only suitable size, which could assemble into the flower-like structures due to the combination of Van der Waals force and the anisotropic hydrophobic attraction between the nanoparticles. Gold nanoflowers were also obtained by a one-pot synthesis using N-2-hydroxyethylpiperazine-N-2-ethanesulphonic acid as a reducing/stabilizing agent and $HAuCl_4$ as a gold source [4]. The obtained Au nanoflowers showed excellent electro-

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catalytic activity toward the oxidation of methanol and the reduction of oxygen to H_2O_2, better than that of the spherically shaped citrate-stabilized Au nanoparticles. Citrate anion is one of common reductants for nanostructure obtaining. Thus, $HAuCl_4$ and trisodium citrate were used as precursors to obtain various gold nanoforms (flowerlike nanoparticles arrays, nanoflowers Fig. (**2**), nanowire networks, and nanosheets of gold on the solid substrates) [5]. The first two nanostructures were formed at ratios trisodium citrate/$HAuCl_4$ 1:1 and 2.6:1, respectively. Au nanoflowers (300-400 nm diameter) and Fe_3O_4/Au composite nanomaterials were also prepared in similar conditions in the presence of citrate, poly(ethylene glycol), and sodium acetate [6].

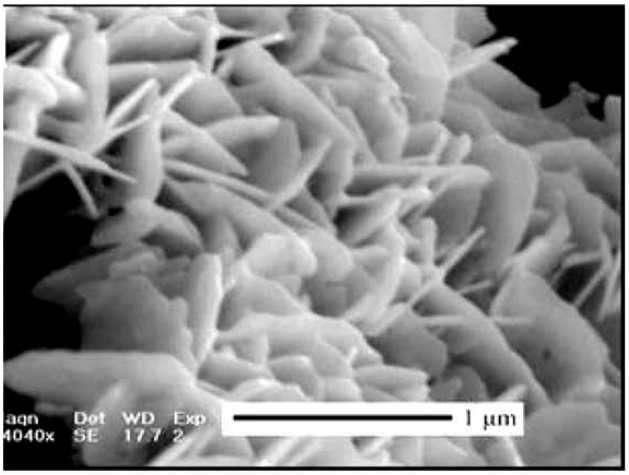

Fig. (2). SEM images of gold nanoflowers (30 min. reaction time) [5].

Additionally to monometallic gold nanoflowers [7], novel Au-Pt bimetallic flower nanostructures, including two parts (the "light" and the "pale" part) and consisting of many small bimetallic nanoparticles, were fabricated on a polyamidoamine dendrimers-modified surface by electrodeposition using H_2PtCl_6 and $HAuCl_4$ as sources of metal atoms [8]. Stable polyamidoamine dendrimers assisted the formation of nanoflowers during the electrodeposition process; the morphologies of bimetallic nanoflowers depended on the electrodeposition time and potential and the layer number of assembled dendrimers. The content of Au element in the nanoflowers was higher than that of Pt element.

Uniform nickel nanoflowers, consisting of hundreds of smaller primary nanoparticles with an average dimension of about 6.3 nm, were prepared by reduction of nickel chloride with hydrazine hydrate in the presence of PVP in ethylene glycol in the presence of an appropriate amount of Na_2CO_3 under microwave irradiation [9]. The authors noted that small amount of NaOH and a higher concentration of hydrazine were beneficial to the formation of Ni nanoflowers with a smaller diameter and a narrower distribution. Among nanoflowers of other elemental metals, Pt nanoflowers are known [10]; those prepared Fig. (**3**) [11] by reduction of $H_2PtCl_6.7H_2O$ with $NaBH_4$, showed good performance (both

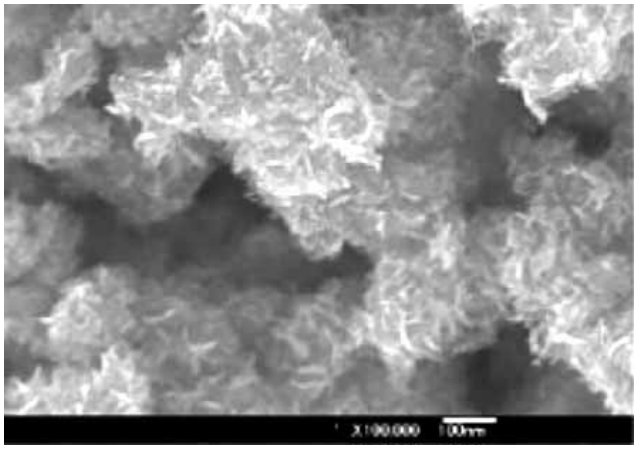

Fig. (3). Platinum nanoflowers [11].

high sensitivity and high molecular weight) for surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS) of various biomolecules, including peptides and phospholipids. Additionally, zinc electrode material, containing nanoflowers each provided with a 40-300 nm core and 3-20 radial branches with diameter of 10-50 nm and length of 0.3-1.0 μm [12], and tin nanoflowers [13] were also recently reported. Various controlled shapes and sizes of colloidal ferromagnetic cobalt nanoparticles were fabricated by the polyol process using $Co(acac)_3$, 1,2-hexadecanediol, oleylamine, and oleic acid within octylether [14]. Additionally, the composites of flowery hexagonal close-packed cobalt crystallites covered with multi-wall carbon nanotubes (MWCNTs) were fabricated in high yield via a catalytic pyrolysis method [15].

In respect of carbon itself, additionally to thousands of patents, books, experimental and review articles, dedicated to intensively studied carbon nanotubes and fullerenes, this element was obtained also in the nanoflower form. Thus, carbon nanoflowers with graphitic feature were prepared at 650°C with high yields using a reduction-pyrolysis-catalysis route using glycerin as carbon source, and magnesium and ferrocene as reductants and catalysts [16]. The obtained nanoflowers with a hollow core had diameters ranging from 200 to 600 nm. In another report [17], iron was used as a catalyst for CNTs flowers formation from a gas mixture of Ar and C_2H_2 at a temperature range of 700-900 K for 300 s (5 min). Iron wire was sparked for 1, 2, 10 and 100 times to form iron dots/islands on the glass slides, where CNTs, composed of carbon with hexagonal structure, were further grown. Also, carbon nanoflowers, among other nanostructures (fullerene, carbon nanopowders, nanofibers, and nanotubes), were produced by carrying out a gas membrane microarc discharge on a cathode in an aqueous solution (basic electrolyte, 0.01-2 mol/L solutions of mineral acids, bases, or chlorides) [18].

METAL OXIDE NANOFLOWERS

In a difference with elemental metals, their oxides, together with sulfides, have been obtained in the nanoflower form much more frequently. Their synthesis is based mainly on zero-valent metal oxidation or decomposition of hydro-

xides or other compounds. Among reported metal oxides, ZnO Fig. (**4**) has been mostly characterized and its several applications, for example for solar cells [19]. were proposed. Its morphologies usually include nanowires, nanorods, nanobelts, nanorings, nanosheets, nanodisks, nanoflowers, nanoneedles, nanonails, nanopencils, and nanoflakes [20-22]. As another important application of ZnO nanoflowers, a new amperometric biosensor for hydrogen peroxide was developed based on adsorption of horseradish peroxidase at the glassy carbon electrode modified with zinc oxide nanoflowers, produced by electrodeposition onto multi-walled carbon nanotubes film [23]. Rapid response, expanded linear response range, and excellent stability were found for this biosensor.

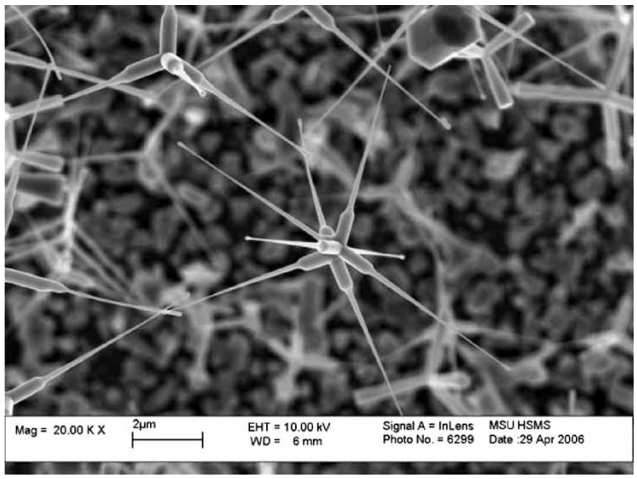

Fig. (4). ZnO tetrapods (snowflakes) [19].

ZnO nanoflowers having two typical morphologies - plate-like and bush-like and composed of pyramidal nanorods, growing from a central point, were synthesized on AlN films by solution method [24]. ZnO nanostructures, including single-crystal nanowires, nanoneedles, nanoflowers, and tubular whiskers, depending their morphology on the temperature zone and the pressure of oxygen, were fabricated Fig. (**5**) at 550°C via the oxidation of metallic Zn powder without a metal catalyst according to simple Scheme **1** [25]. Nanoflowers were composed of hundreds of "nanopetals" which have a tadpole-like structure, and tubular whisker has a hexagonal hollow cone structure. The growth process of ZnO nanostructures was attributed by authors to the vapor-solid process, rather than the more common catalyst-assisted vapor-liquid-solid process.

$$Zn\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow ZnO \qquad (1)$$

ZnO nanoflowers, among many other nanostructures (nanotowers, nanovolcanoes, nanorods, nanotubes, nanocorns, nanoshuttles, nanoworms, and nanowires), formed depending on the reaction conditions Fig. (**6**), were prepared using the hydrothermal technique [26, 27] starting from zinc nitrate, cetyltrimethylammoniumbromide (CTAB) and hexamethylenetetramine (HMT) at 80-90°C for 0.5-6 h (Scheme 2). Other related information on ZnO nanoflowers is reported in [28-33] and shown also in Table **1**.

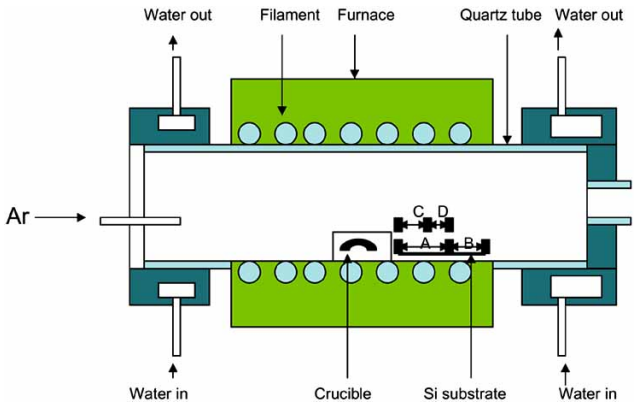

Fig. (5). A schematic diagram of the experimental apparatus for growth of ZnO nanostructures by the solid-vapor phase process [26].

$$Zn^{2+} + CH_3(CH_2)_{15}N(Br)(CH_3)_3/C_6H_{12}N_4 \rightarrow Zn^{2+}\text{-amino complex} \rightarrow Zn(OH)_2 \rightarrow ZnO \qquad (2)$$

Adjusting experimental parameters in MgO nanostructures production by chemical vapor transport and condensation [34], its distinct nanoforms could be obtained. Thus, single crystalline MgO nanoflowers, consisting of MgO nanofibers (20-80 nm), were synthesized via conventional evaporation method using the high-purity magnesium powders and distilled water as starting materials [35]. The obtained MgO nanoflowers have a much higher relative dielectric constant as compared with MgO micropowders and may be useful in providing insight into the formation of microbiological systems and reinforcing composite materials. Formation mechanism of MgO nanoflowers was discussed in [36] and includes Mg particles formation on the Si substrate, formation of MgO clusters as nucleation centers on the magnesium melt surface and the nucleation of short MgO nanofibers, then growth of the MgO nanofibers occurred, and finally MgO nanoflowers formation. The authors noted that nucleation and growth process of the nanoflowers seems to be a vapor-solid mechanism, similarly as it was shown for obtaining ZnO nanoflowers from zinc and oxygen [25], and that the total heating time during the reaction process is a critical factor for the development of MgO nanoflowers. This is not an unique example of nanofiber-containing nanoflowers: thus, weakly ferromagnetic at ~34 K Co_3O_4 nanoflowers, consisting of numerous Co_3O_4 nanofibers (diameters of 20-40 nm and lengths 100-500 nm), were prepared through a sequential process of a hydrothermal reaction and heat treatment [37].

CuO nanoflowers {containing a very large number of nanometer-scaled flakes (petals) and each petal further branched into tips at its end} were synthesized directly on Cu plates in KOH solution at room temperature [38] as a result of a series of steps, including oxidation, complex formation, condensation, *Ostwald* ripening and dissolution. Hierarchical porous NiO nanoflowers with porous petals were fabricated by calcining the isomorphological *β*-$Ni(OH)_2$ precursor, preliminary prepared from nickel dimethylglyoximate and NaOH [39]. In comparison with that of the standard nanoparticles, the higher electrochemical

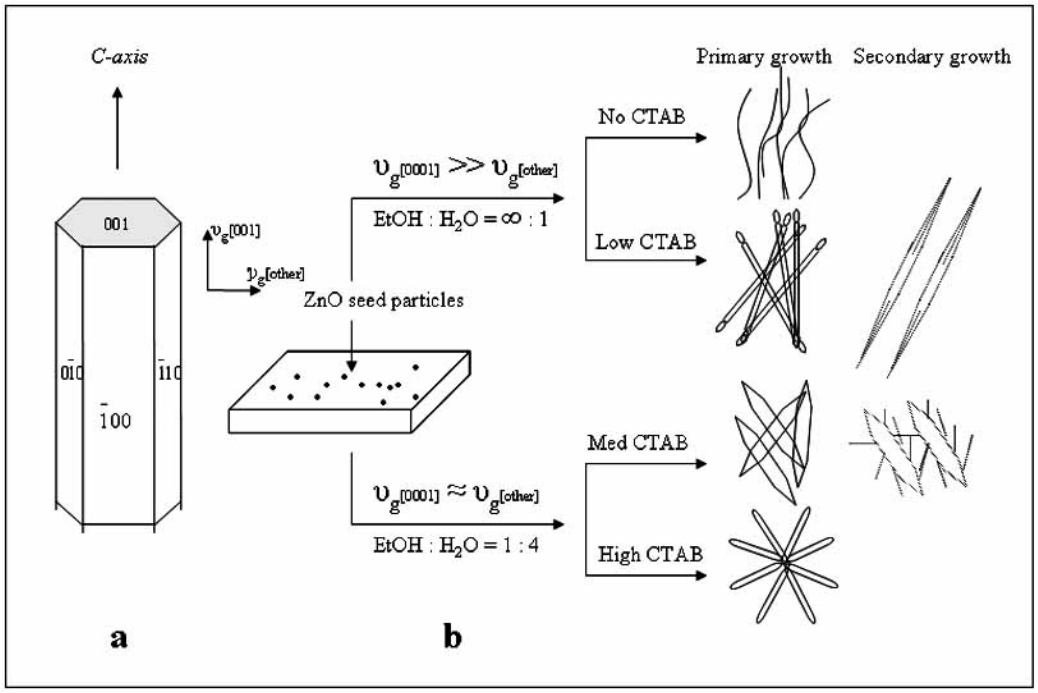

Fig. (6). (a) Illustration of a zincite crystal with various planes marked; (b) growth schematic diagram of ZnO nanostructures in different experimental conditions [28].

lithium intercalation could be ascribed to their special nanoporous structure.

The α-MnO_2 nanocrystal nanoflowers, together with nanowires and nanoplates, have been successfully synthesized by a common hydrothermal treatment of different solutions containing $KMnO_4$ and NH_4X (X = Cl^-, Ac^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) at 140°C for 24 h [40]. The patterned SnO_2 nanoflowers arrays, with a unit diameter of ~50 μm and composed of nanorods, were synthesized *via* vapor phase transport method using a patterned Au catalyst film, prepared on the silicon wafer by radio frequency magnetron sputtering and photolithographic patterning processes [41]. Evolution processes for MoO_3 nanoflowers and its other morphologies (nanosheets and nanobelts), obtained from metallic molybdenum and H_2O_2 with further exposition in autoclave to decompose the formed $H_2Mo_2O_3(O_2)_4$ (Scheme 3), were studied in [42]. It was proposed that the environmentally friendly synthesis process may be extended for obtaining nanostructures of other metal (W, Ti, and Cr) oxides.

$$2Mo + 10H_2O_2 \rightarrow [Mo_2O_3(O_2)_4]^{2-} + 2H^+ + 9H_2O \quad (3)$$

Single crystalline and nearly monodisperse In_2O_3 nanocrystals with both dot and flower shapes were prepared using indium carboxylates as the precursors with or without alcohol as the activating reagents in a hydrocarbon solvent under elevated temperatures [43]. The 3D nature of these nanoflowers was confirmed by rotation experiments (Fig. **7**). When the specimen was rotated either way (left and right image), the twodimensional projection of each nanoflower roughly remained the same, but the structural detail of each flower changed substantially. This indicated that the nanoflowers are true three-dimensional structures, instead of plates with their thickness different from their diameter.

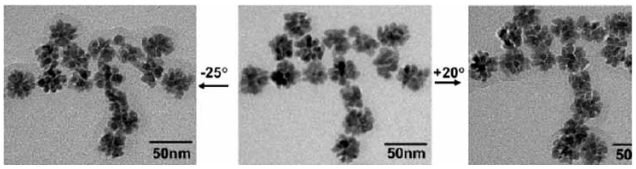

Fig. (7). Rotation of a group of In_2O_3 nanoflowers [43].

Application of a new approach, so-called "*limited ligand protection*" (LLP) resulted 3D nanoflowers for In_2O_3, ZnO, CoO, and MnO, meanwhile when the system had sufficient ligand protection for the nanocrystals, nanodots were found to be the stable products [44, 45]. Its function is that LLP destabilizes the primary nanoparticles and promotes their three-dimensionally oriented attachment into complex nanostructures. Other reported oxide-based nanoflowers include those of amorphous silica flowerlike nanowire [46, 47] or porous silica microflowers (obtained by adding supercritical CO_2 - reactant and modifier to the morphology and porosity of silica - into the sodium silicate aqueous solutions) [48].

NANOFLOWERS OF HYDROXIDES AND OXO-SALTS

Only a few reported examples of nanoflowers are known up to date for metal hydroxides and oxo-salts. Thus, uniform $Mg(OH)_2$ nanoflowers were prepared by a simple hydrothermal reaction of $MgCl_2$ and $CO(NH_2)_2$, without any organic additive or catalyst [49]. The influence of temperature on the formation of $Mg(OH)_2$ nanoflowers was studied. Similar $Mg(OH)_2$ nanoroses were reported in [19] Fig. (**8**). Nickel hydroxide nanoflowers (together with

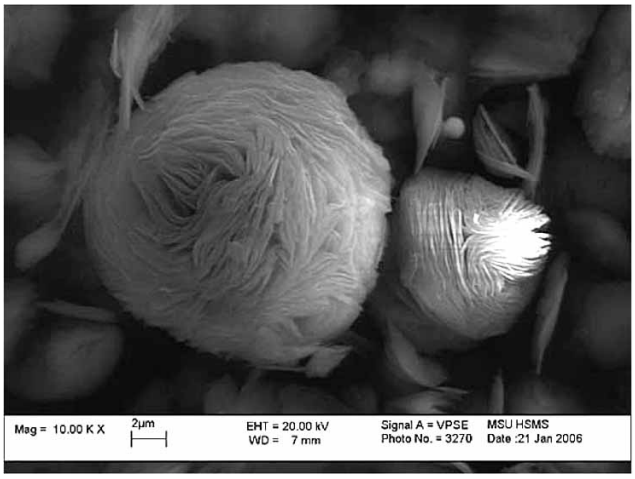

Fig. (8). $Mg(OH)_2$ nanoroses [19].

nanosheets) have been hydrothermally synthesized using $Ni(CH_3COO)_2 \cdot 4H_2O$ in mixed solvents of ethylene glycol or ethanol and deionized water at 200°C [50]. The biomineral botallackite $Cu_2(OH)_3Cl$ nanoflowers (Fig. **9**) were obtained with the aid of Au_3Cu hollow nanostructures at room temperature, prepared by the reaction (Schemes 4-6) of Cu nanoparticles (synthesized by laser ablation of CuO powder in propanol) with $HAuCl_4$ [51]. Both hollow nanospheres and nanoflowers presented antimicrobial activity toward *Streptococcus aureus*.

$$3Cu(s) + 2AuCl_4^- \rightarrow 2Au(s) + 3Cu^{2+} + 8Cl^- \quad (4)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (5)$$

$$2Cu^{2+} + Cl^- + 3OH^- \rightarrow Cu_2(OH)_3Cl \quad (6)$$

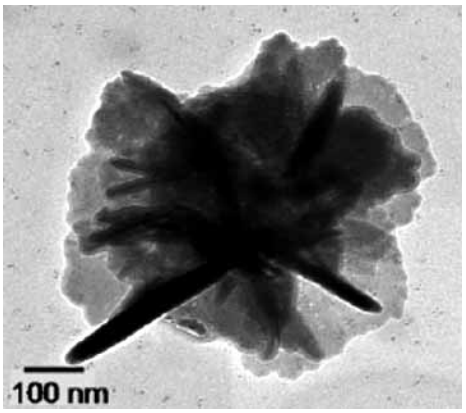

Fig. (9). TEM image of a single $Cu_2(OH)_3Cl$ nanoflower [51].

3D nanostructured $Cd_4Cl_3(OH)_5$ nanoflower arrays were controllably synthesized through a low temperature hydrothermal process [52]. Source of cadmium ions, concentration in solution, temperature and reaction time are the factors influencing the possibility of formation of flower-like structure. The $Cd_4Cl_3(OH)_5$ nanoflowers as template compounds were further transformed into $Cd(OH)_2$ and CdS nanoflowers by an anion-exchange reaction. Some other metal salts in the form of nanoflowers are shown in Table **1**.

SULPHIDE, SELENIDE AND TELLURIDE NANOFLOWERS

The first two groups of title nanoflower structures are widely represented and possess a series of useful applications. Thus, highly ordered hierarchical structures wurtzite urchin-like CdS nanoflowers, made of CdS nanorods, were produced via solvothermal approach from $Cd(Ac)_2 \cdot 2H_2O$, $CS(NH_2)_2$ as precursors in a mixed solution made of diethylenetriamine (DETA) and deionized water (DIW) [53]. The possibility to obtain different morphologies of CdS(Se) nanocrystals can be easily controlled via tuning the volume ratio of DETA and DIW; solvothermal reaction in a mixed amine/water can access a variety of complex morphologies of semiconductor materials. Various CdS nanostructures possess a photocatalytic activity, demonstrated in the photodegradation of acid fuchsine at ambient temperature and related due to unique structural feature of CdS. A microwave-induced semi-solvothermal reaction (i.e., involving simultaneous usage of nonaqueous and aqueous solvents) between the same reagents was also used to produce CdS nanoflowers, among other obtained nanostructures [54]. Simultaneous application of microwave and ultrasound treatment allowed obtaining CdS nanoflowers too. Thus, well-defined flower-like CdS nanostructures, consisting of hexagonal nanopyramids and/or nanoplates depending on different sulfur sources, were synthesized by applying ultrasound and microwave at the same time [55]. It is shown that the synergistic effect of microwave and sonochemistry is the main mechanism for the formation of the nanoflowers. Due to the induced shift in optical properties, this nanostructure may have potential applications in optoelectronics devices, catalysis, and solar cells.

Visually striking nanoflowers composed of $ZnS:Mn^{2+}$ nanoparticles of 2-5 nm in size were prepared and characterized [56]. The observed blue-green emissions were attributed to structural defects and are the dominant luminescence from the nanoflowers. ZnSe nanoflowers with a zinc blende structure were synthesized by using a nontoxic, simple, cheap, and reproducible strategy, which meets the standard of green chemistry, from ZnO, Se, and olive oil at 330°C [57]. The mechanism of ZnSe nanoflowers formation was offered, based on the formation of mononuclear complexes due to the reaction of ZnO and olive oil, their further conversion to multinuclear compounds and reaction of Zn ions with injected Se forming closely connected ZnSe particles, thus looking like nanoflowers. ZnTe nanocrystals in different forms, including nanoflowers, were obtained by using a series of amines as activation agents for the zinc precursor (zinc stearate), octylamine (OA), dodecylamine (DDA), octadecylamine (ODA), and trioctylamine (TOA) [58]. The steric effect of alkyl chains plays an important role in the formation of nanoflowers: they are only produced when no amine or TOA was used. Non-stoichiometric copper sulfides (Cu_7S_4), having uniform hexapetalous snowflake-like morphology, were synthesized in high yields by one-step solvothermal method at 150°C [59]. CoS nanowires, assembled with nanoflowers, were isolated by a biomolecule-assisted hydrothermal process, in which l-cysteine is used as the sulfide source and directing molecule [60].

Bi_2S_3 nanoflowers were prepared from different precursors: $Bi(NO_3)_3$ (on a alumina template by a photochemical method in the presence of thioacetamide and nitrilotriacetic acid at room temperature) [61], Bi-thiol complexes $Bi(SCl_2)_3$ (nanorods, evolution further to nanoflowers over time, were formed reaction with thioacetamide in a coordinating solvent, dodecanethiol, at 95°C) [62], and the single-source precursor $Bi(SCOPh)_3$ or multiple-source precursors (nanoflowers and other morphologies (nanorods, dandelion-like nanostructures, nanoleaves, and nanocabbages) were formed by using a colloidal solution or hydrothermal methods) [63].

Preparation of GaS and GaSe nanowalls/nanoflowers by thermal exfoliation around 900°C and their transformation to Ga_2O_3 and GaN nanowalls was reported in [64]. Elegant three-dimensional MoS_2 nanoflowers Fig. (**10**), consisting of tens to hundreds of hexagonal petals (100-300 nm wide and several nms thick) and exhibiting excellent field emitter properties, were uniformly formed via heating a MoO_2 thin film formed on a Mo foil in a vapor sulfur atmosphere at 950-1000°C [65]. Hydrothermal synthesis leaded to different MoS_2 morphologies, in particular nanoflowers at much longer aging period [66]. SnS nanoflowers (product composed of well-crystallized orthorhombic SnS nanoflowers) were synthesized via thioglycollic acid (TGA)-assisted hydrothermal process at 250°C [67]. Critical factors (e.g., TGA, $SnCl_2/Na_2S$ mol ratio of the reactants, hydro-thermal temperature, and sulfur source) for hydrothermal formation of the SnS nanoflowers were discussed. PbS downy-velvet-flower-like nanostructures, together with other morphologies (rod-like, belt-like, and dendrite-like), were fabricated in aqueous solution by the assistance of a classic surfactant cetyltrimethylammoniumbromide (CTAB) [68], already mentioned above for ZnO nanoflowers preparation [27]. In this method, basic acetate of lead, formed at initial reaction step, was a precursor to control the crystal nucleation rate. PbSe and PbTe flower-like structures were described in [69].

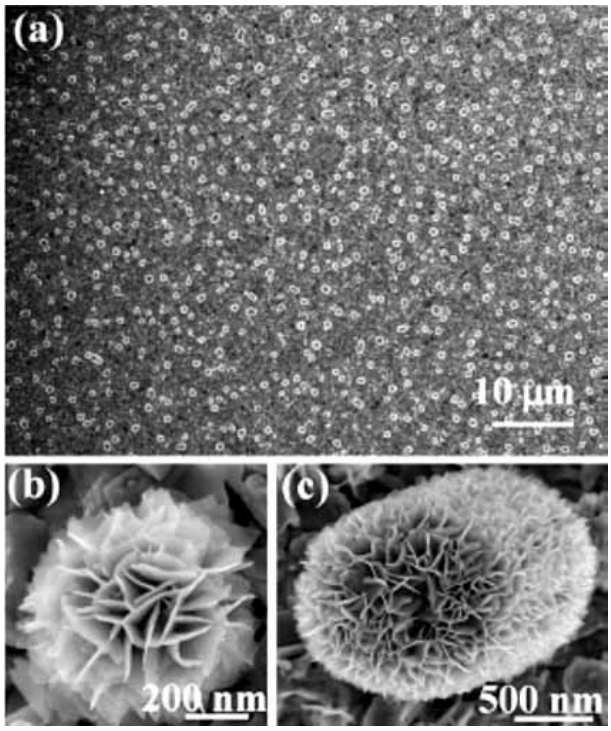

Fig. (10). SEM images of MoS_2 flower-like nanostructures: a) low magnification view; b) and c) high magnification view [65].

A few double sulfides-nanoflowers were reported; for example, $CuInS_2$ flower vaselike nanostructure arrays were successfully prepared on Cu-tape substrates by a so-called "copper indium sulfide on Cu-tape" (CISCuT) method without using any template or catalyst [70]. $CoMoS_4$ nanoflowers was synthesized by precipitation method from Na_2MoO_4, $CoCl_2 \cdot 6H_2O$ and CH_3CSNH_2 as starting materials [71].

NITRIDE AND PHOSPHIDE NANOFLOWERS

A considerably lesser number of nanoflowers, based on title compounds, is known in comparison with metal compounds with VI Group elements. Thus, flowerlike Si-doped AlN nanoneedle array (several microns in length, base and tip diameters of 50-150 and tip diameters of 5-30 nm) was grown from cobalt particles seeded on Si substrate by evaporating $AlCl_3$ and $SiCl_4$ in NH_3 medium [72]. This method may facilitate the development of efficient AlN nanostructure field emission devices. Among other structures, AlN nanoflowers were studied by Auger electron spectroscopy [73]. Hexangular InN nanoflower pattern (Fig. **11**) [74,75] was grown on c-plane (0001) sapphire by metal organic chemical vapor deposition (MOCVD) using trimethylindium and ammonia as precursors with intentional introduction of hydrogen gas. A stable existence of metallic indium is achieved with the aid of hydrogen. This will induce the growth of InN nanoflowers via self-catalysis vapor-liquid-solid process. The impact of metallic indium clusters on the optical properties of InN was analyzed [76].

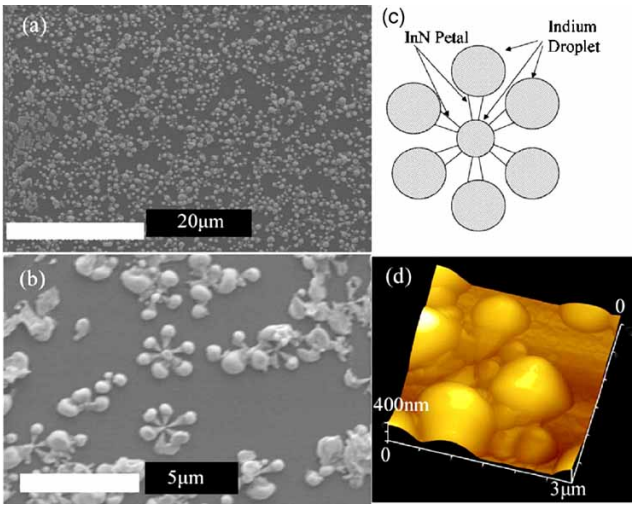

Fig. (11). InN nanoflowers: a) large-area SEM, b) high-magnification SEM top view, c) schematic illustration, and d) AFM stereo view [74].

Crystalline GaP nanoflowers Fig. (**12**) with cubic structure composed of numerous GaP nanowires were synthesized through heating InP and Ga_2O_3 powders [77]. Cathodoluminescence measurements showed that GaP nanoflowers emit at ~600 nm and additional low-intensity

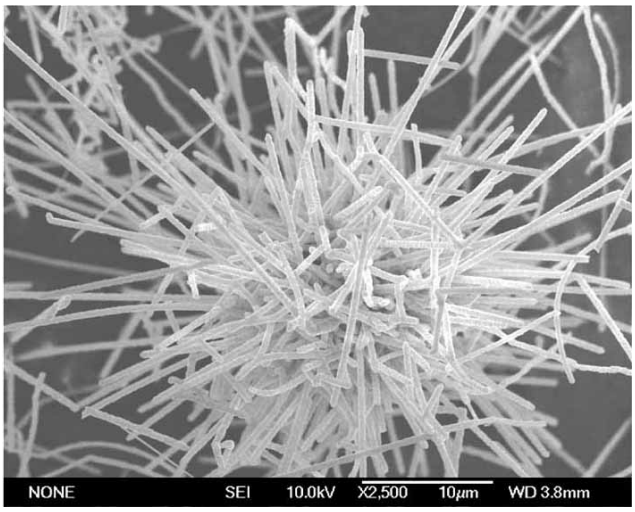

Fig. (12). GaP nanoflowers [77].

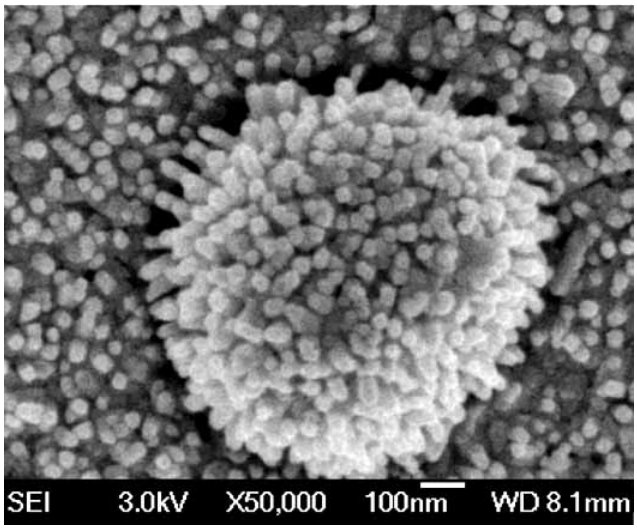

Fig. (13). Copper phthalocyanine nanoflower [82].

emission peaks were observed at ~450 nm. The authors proposed that GaP nanoflowers may be valuable for future nanodevice design. Similar nanoflower-like GaP nanostructures, constituted also by numerous nanowires (diameters of 80-300 nm; lengths varying from several to tens of mcms), were fabricated by another route: through the close-spaced vapor transport technique (CSVT) by growing on crystalline GaAs, using a GaP powder source in the absence of any catalyst [78]. Co_2P flower-like nanocrystals, together with nanorods, were synthesized by a polymer-assisted hydrothermal method at 190-220°C using $CoCl_2 \cdot 6H_2O$ as Co-source, yellow phosphorous as P-source, and polyacrylamide as surfactant [79].

NANOFLOWERS FORMED BY ORGANIC AND COORDINATION COMPOUNDS

According to the available bibliography, nanoflowers of organic and related compounds are currently a practically non-developed area; a few compounds are only reported. Thus, nanorods and nanoflowers (bundles of nanorods) of bis(8-hydroxyquinolinato)cadmium (CdQ_2) complex were fabricated in an oleic acid-Na oleate-EtOH-hexane-H_2O system at 55-100°C [80]. It was revealed that a longer time and a higher temperature would result in nanoflowers, while hihger concentrations of the reactants and the surfactant with a lower temperature and a shorter reaction time would be appropriate for the formation of nanorods. The obtained CdQ_2 nanorods could be introduced as the building blocks for novel optoelectronic devices. Field emission scanning electron microscopy (FESEM) images showed nanoflower like structure (among other structures observed: nanoparticles, nanocabbages, and nanoribbons) for the gold-coated quartz substrates of copper phthalocyanine (CuPc) thin films deposited at room temperature (30°C) on quartz and annealed at 750°C Fig. (**13**) [81, 82]. More extensive study for this and other MPc (M = Cu, Ni, Sn, Mg, and Zn) was reported in [83]. Nanoflowers, nanosheets and nanoribbons of the alkali earth phenylphosphonates were prepared via solvothermal approach by reaction of alkali earth metal salt with phenylphosphonate in ethylene glycol [84]. Uniform self-doped poly(o-aminobenzenesulfonic-acid-co-aniline) nanoflowers, exhibiting a remarkable electroactivity at an extended pH range from 3 to 13.5, were prepared by an electrochemical preparation without any other supporting electrolytes [85]. Nanoflowers of 1,1,2,3, 4,5-hexaphenylsilole (HPS), together with nanoglobules and microglobules, were obtained on reprecipitation with THF as solvent and water as non-solvent [86].

Selected representative examples of obtained nanoflowers are shown in Table **1** [87-110].

CURRENT & FUTURE DEVELOPMENTS

Nanoflower-type nanostructures are currently known for several main groups of mostly inorganic compounds (carbon, elemental metals, their alloys and compounds with the elements of V and VI Groups of the Periodic Table) and a few coordination and organic compounds. Their main methods of fabrication include oxidation of elemental metals, reduction of metal salts, thermal decomposition of relatively unstable compounds, hydrothermally or electrochemically. Frequently, formation of nanoflowers is competitive or in equilibrium with other nanoforms, depending on reagents ratio, temperature and other conditions; this nanoform can be changed over time. Nanoflower structure may consist of such more simple nanostructures, as nanorods, nanowalls, or nanowires.

Nowadays, in the period of nanotechnology boom, a lot of above mentioned nanoforms for inorganic and organic compounds and materials are monthly reported. Nanoflowers obviously are at the initial stage of their research in comparison with, for instance, nanowires or nanotubes. It is expected further intensive development of this area, and we hope that the organic nanoflowers, practically unknown at present, will be represented by a considerably higher number of intriguing examples.

Table 1. Representative Examples on Nanoflowers Fabrication

Compound	Synthesis method	Variety of formed nanostructures, including nanoflowers	Reference
Ni	Non-aqueous sol-gel route involving the reaction of nickel acetylacetonate with benzyl alcohol (solvent and reductant) at 200°C in the presence of varying magnetic fields.	Nanospheres, nanowires, and nanoflowers.	[87]
Ag	Reduction of silver nitrate in solution of sodium acetate, *L*-ascorbic acid, sodium citrate and poly(ethylene glycol).	Rose-, spike-, and snowflake-shaped silver nanostructures.	[88]
ZnO	CVD	Nanosleeve-fishes, radial nanowire arrays, nanocombs and nanoflowers (adjusting the source temperature and the gas flow rate). Sisal-like nanoflowers.	[89,90]
	Thermal treatment of $Zn(NH_3)_4^{2+}$ precursor in aqueous solvent, using ammonia as the structure directing agent.	Flower-like ZnO nano/microstructures.	[91]
	Solution deposition method	Nanorods and nanoflowers (nanoflowers were synthesized on the nanorods).	[92]
	Ultrasonic pyrolysis of $Zn(CH_3COO)_2 \cdot 2H_2O$ at 380-500 °C.	Nanoblades and nanoflowers.	[93]
	Solvothermal method.	Nanoflowers, assembled by many thin and uniform hexagonal-structured ZnO nanosheets, with a thickness of around 6 nm.	[94]
	At 90°C for 5 h without surfactant assistance, varying concentrations of NaOH and different amounts of $N_2H_4 \cdot H_2O$).	Rod-like and chrysanthemum-like ZnO nanostructures contained many radial nanorods.	[95]
SnO_2	Controlled shape-preserving thermal oxidation process (precursor - 3D Sn nanoflowers).	Super-hydrophobic 3D flowers with nanoporous petals.	[96]
CoO	Decomposition of Co(II) oleate complex at 280-320°C in noncoordinating solvent octadecene containing dodecanol/oleic acid.	Cubic nanocrystals with various morphologies and sizes.	[97]
Bi_2O_3	Oxidative metal vapor phase deposition technique with controlled flow of oxygen and constant working pressures.	The large-area arrays of one-dimensional (1D) nanowires and nanoflowers.	[98]
α-Fe_2O_3 (hematite)	Stirring $Fe(NO_3)_3$, urea and ethylene glycol as precursors at 170°C and further calcination at 450°C.	Flowerlike micrometer-sized hematite particles.	[99]
	Solvo-thermal reactions at 140°C using ethanol solution of $FeCl_3 \cdot 6H_2O$ as a precursor and sequential calcinations.	The flower-like nanostructures, composed of nanosheets with a thickness of ~ 20 nm.	[100]
$Y_2O_3:Eu^{3+}$	Hydrothermal reaction and sequential calcinations.	Flower-like nanoarchitectures.	[101]
CeO_2	Rapid thermolysis of $(NH_4)_2Ce(NO_3)_6$ in oleic acid /oleylamine.	Nanoflowers with controlled shape (cubic, four-petaled, and starlike) and tunable size (10-40 nm).	[102]
WS_2	Atmospheric pressure chemical vapor deposition (APCVD) process.	MoS_2 and WS_2 inorganic fullerene-like nanostructures (onion-like nanoparticles, nanotubes) and elegant three-dimensional nanoflowers.	[103]
Bi_2S_3	Synthesis via different surfactants such as Triton X-100+OP-10, TX-10, Triton X-100 by refluxing with bismuth nitrate and thiourea as reactants (at 85-110°C, 3 h).	Well-crystallized nanoflowers with different morphologies.	[104]

(Table 1) Contd….

Compound	Synthesis method	Variety of formed nanostructures, including nanoflowers	Reference
AlN	Direct nitridation of aluminum precursor.	AlN conic nanoflowers, nanowires, quasi-aligned nanocones and polycrystalline thin film.	[105]
EuF_3	Ultrasonic irradiation; reaction in solution of $Eu(NO_3)_3$ and KBF_4 under ambient conditions without any template or surfactant.	Single-crystalline nanoflower with a novel three-dimensional (3D) nanostructure.	[106]
$CoWO_4$	Alcohol–thermal process at 180°C without any surfactants and structure-directing agents.	Flowerlike hollow nanostructures, which consist of $CoWO_4$ nanorods.	[107]
$MgCO_3$	Interaction in solution of $MgCl_2{\cdot}6H_2O$, urea, dispersant at 80-99°C in water bath, 3-8 h, aging for 1-3 h, filtering precipitate, water-washing, and drying at 100°C for 3 h.	3D nanoflower structure.	[108]
$Pb(Zr_{0.52}Ti_{0.48})O_3$	Pulsed-laser deposition.	Flower-like nanostructures on the $CoFe_2O_4$ seeds.	[109]
$CaTiO_3$	Environmentally friendly solvothermal technique.	$CaTiO_3$ nanoflowers (or also $SrTiO_3$ nanocubes, and $BaTiO_3$ nanospheres). Red fluorescence originating from intra 4f 1D2-3H4 transition of Pr^{3+} is observed by doping Pr^{3+} ions in $CaTiO_3$ nanoflowers.	[110]

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