Dynamic self-assembly of nanoparticles using thermotropic liquid crystals

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ABSTRACT

3D nanoparticle-based materials with reconfigurable structure have gained vast attention due to the unique possibility of tailoring nanoparticle-related quantum confinement effects. These properties make active nanoparticle assemblies promising candidates for future optoelectronic and metamaterial technologies; however, integration of these materials into real-world applications is still challenging. In this context, the use of stimuli responsive liquid-crystals (LCs) offers a fascinating and industrially feasible strategy for active directing of NPs. Here, we briefly review LCs/NPs hybrid systems in which dynamic behaviour is achieved by affecting either LC matrix or LC ligands. We also experimentally evaluate a complementary strategy based on directly affecting metallic core of LC-covered NPs in an Ostwald ripening process.

1. Introduction

During the last two decades we have witnessed a rapid progress in the field of 3D nanoparticle-based materials, propelled by their exciting plasmonic, luminescent and up-converting properties. [1,2] Beyond purely scientific interest these materials provide unique opportunities to solve a variety of technological problems such as overcoming speed and bandwidth limitations of modern electronic devices, surpassing current limits of solar energy harvesting devices [3], retrieving waste (heat) energy from thermal engines [4], preparing cloaking materials [5] or flat lenses construction. [6] However, practical realisation of these applications has been hampered by limited possibilities for post-synthetic control of nanoparticle assemblies. [7] This relates especially to fully capitalising on anisotropic electrooptical properties of non-spherical NPs [8] and exploring distant-dependent collective interactions. [9] Thus, methods for controlling long-range orientational and translational order of NPs in their assemblies are being intensively developed. [10–12]

The post-synthetic tuning methods presented up-to-date usually rely on affecting surroundings of nanocrystals: matrix material in which they are embedded (Figure 1(a)), their surface ligands (Figure 1(b)). [12] This approach allows modifying anisotropic and/or distant-dependent properties of NPs by dynamic control over their orientational and/or translational order. Successful examples of this approach encompass a variety of materials and techniques. Reversible tuning of NPs orientation was achieved for example by T. Hanrhah et al. [13] for CdSe/CdS nanorods (NRs). These authors used vapour annealing technique for this purpose and observed switchable absorption of the material. Reversible changes of particle spatial distribution were observed for example by Fan et al. [14] for 5.5 nm diameter spherical silver NPs. These authors used vapour annealing technique for this purpose and observed switchable absorption of the material. Reversible changes of particle spatial distribution were observed for example by Fan et al. [14] for 5.5 nm diameter spherical silver NPs. These authors covered these NPs with poly(N-isopropylacrylamide) coating and observed thermo-responsive behaviour of the localised surface plasmon resonance (LSPR) peak. Alternative strategies for achieving structural and functional tunability in nanoparticle solids were also proposed, which are based on affecting NPs size and shape directly [15] (Figure 1(c)). In this regard few examples exploiting, e.g. Ostwald ripening process [16–18] were already presented.
The described modes of nanoparticle solid’s tunability (Figure 1) can also be achieved using liquid crystals (LCs).\textsuperscript{21} Intrinsic long-range order, switchability and established technological applications make LCs ideal candidates for this purpose. Here, we review and present new research related to thermotropic LCs/NPs composite materials, which rely on using external fields for inducing structural reorganisation of NPs (changing their spatial or orientational order). Thus, it can be generalised that all the described systems fall into the category of dynamically self-assembling nanoparticles, which depends on dissipating of the external energy input. In fact, the part of the composite materials that is directly affected by the external fields is the basis for structuring this article. We first pay attention to LCs with nano-inclusions (Section 4), which rely on affecting LC matrix material. Then we discuss dynamic systems in which energy is dissipated by LCs serving as NPs surface ligands (Section 5). Finally, we present original research in which metallic cores of LCs/NPs composite are affected by Ostwald-ripening process (Section 6). A general description of physical phenomena crucial for each of these approaches is given in Section 3. From the physical point of view it is also worth noticing that structural reconfigurability of nanoparticles assemblies allows to achieve switchable optoelectronic characteristics. We briefly discuss how orientational and translational order translates to the physical characteristics of nanoparticle-based materials in Section 2. Specific examples of optoelectronic switchability for LCs/NPs hybrid materials will be discussed throughout the text.

Finally it is worth mentioning the restrictions of the scope of the article. The marriage between nanoscience and liquid crystals is a fascinating research area that goes far beyond the topics covered here, as reviewed recently.\textsuperscript{21–32} Some of the related fields that we do not discuss are: using NPs to influence physical properties of LCs \textsuperscript{33}, composites of NPs with lyotropic liquid crystals \textsuperscript{34}, active plasmonic materials based on birefringence switching \textsuperscript{35–37}, LCs with micro-inclusions \textsuperscript{38}, using NPs as probes for LC phase transitions \textsuperscript{39} as well as NPs synthesis in LCs.\textsuperscript{33}

2. Basics of plasmonic, up-converting and semiconductor nanocrystals

Plasmonic nanoparticles are nanostructures in which light can excite collective surface oscillations of free charge carriers (localised surface plasmon resonances, LSPRs). LSPR gives unique opportunity to confine and propagate light energy (information) at the nanometre scale resulting in tremendous electromagnetic field enhancements in the vicinity of nanoparticles surface.\textsuperscript{40} These properties of solid state materials made of

Figure 1. (Colour online) Schematic representation of applying external stimuli (red arrows) to induce nanoparticles rearrangement (blue arrows). Stimulus is applied to (a) LC matrix material (grey), (b) LC surface ligands of NPs or (c) nanocrystals (gold). Exemplary scheme of (d) orientational and (e) positional rearrangements in nanoparticle assemblies; surface ligands are omitted for clarity. (a) and (b) were adapted from \textsuperscript{19} with permission of The Royal Society of Chemistry. (e) was adapted from \textsuperscript{20} with permission of The Royal Society of Chemistry.
plasmonic NPs allow solving a variety of interdisciplinary problems by delivering structures with properties not known in nature (so-called metamaterials).[41]

Semiconductor nanocrystals (referred to as quantum dots, QDs) are structures with diameters comparable to the size of Bohr radius of the exciton (electron/hole pair). Due to high quantum efficiency of luminescence and the possibility to tune the bandgap energy, quantum dot solids (solid state materials made of QDs) have been under the spotlight of scientific and industrial research for more than a decade as – among others – versatile sources of light. They are already used commercially for displays and further investigated for use in other light-emitting and solar energy harvesting technologies.[42,43]

Up-conversion nanoparticles (UC NPs) are nanostructures that have the capability of converting long-wavelength near-infrared excitation into short-wavelength visible emission due to the long-lived, metastable excited states of the lanthanide dopants. This feature is a base for a number of intriguing applications of UC NPs such as photovoltaics, solid state lighting and display technologies.[44]

Two important facts should be discussed briefly. First, shape anisotropy of the NPs translates to exhibiting anisotropic properties.[45] In this regard longitudinal and transverse LSPR modes can be identified that correspond to charges of oscillations along long and short axes of the nanocrystals, respectively. Shape anisotropy may also enable polarised emission form nanoparticles if they exhibit long-range orientational order and luminescent properties.[46] Second, collective interactions of NPs, which depend on interparticle spacing, allow deviating from properties of individual nanocrystals. For example, redshift of the plasmonic band maxima is observed when spherical metal nanoparticles are at close distance[47] in comparison to isolated particles. Similarly, changes in luminescent properties of semiconductor nanocrystals[48] or enhancement rate in hybrid plasmonic–up-converting nanomaterials[49] are strongly dependent on the interparticle distance.

In summary, by changing orientation and spacing of NPs, it is possible to dynamically tune plasmonic, luminescent or up-converting properties of materials.

3. Basics of LC–NPs interactions in composites

Three different roles of LCs in structurally switchable LCs/NPs composites are considered throughout this article: LCs as a bulk matrix that is doped (Sections 3.3 and 4), LCs as NP surface ligands in liquid-crystalline nanoparticles (Sections 3.2 and 5) and LCs as NP surface ligands mediating Ostwald ripening process (Sections 3.3 and 6). To fully understand the dynamic behaviour of these systems, we briefly introduce below the basic physical description of interactions between NPs and LCs for each case. It should be noted that only a general description is given here with the purpose of facilitating understanding of design principles of LCs/NPs dynamic materials, while more detailed information on physical aspects of LCs interactions with nano-/microparticles can be found, for example, in reviews by Lacaze et al. [28] and Hegman et al.[26]

3.1. Thermotropic LC matrix material doped with nanoparticles

The most important parameters that decide on nanoparticle behaviour in LC matrix are LC anchoring at nanoparticle surface, nanoparticle size, interparticle interactions and entropic effects.[26,28] The interplay between these parameters decides whether assemblies can be formed in bulk LC, at interfaces or within LC distorted areas or topological defects.

In practice, by tuning the above enumerated parameters one can achieve control over nanoparticle assemblies. One strategy that has proved fruitful for achieving ordered NPs assemblies in LC matrix is mitigating elastic distortions around the particle by proper choice of surface coating layer (e.g. polymers). For nanorods this approach can result in materials exhibiting long-range orientational order with nanoparticle long axis parallel or perpendicular to the nematic director. Switchability is then achieved by changing orientation of LC host molecules, followed by reorientation of nanorods.

Another family of dynamic self-assembly strategies is based on the fact that usually small NPs are well soluble in LC host at high temperatures, that is in the isotropic phase of LC matrix. After lowering the temperature of such composite materials and transition from isotropic to liquid crystalline phase, nanoparticles undergo assembly strongly influencing interparticle distances. In the absence of LC defects nanoparticles form random aggregates driven by minimisation of disorder in the system and by interparticle interactions. However, if distorted LC areas are present (e.g. disclinations in smectics or blue phases) nanoparticles tend to assemble there driven by energy gain of the system due to minimisation of elastic deformations.

More detailed description of successful examples for which dynamic rearrangement has been achieved in NPs-doped LCs is given in Section 4.
3.2. LC ligands in thermotropic LC–nanoparticles

It is known that liquid crystalline assemblies are formed by anisotropic building blocks. This applies not only to molecular entities but has also been shown for nanoparticles, e.g. gold nanobipiramids. However, building LC phases with nanoparticles does not necessarily require using anisotropic nanoparticles. It has been shown that for sufficiently small isotropic nanoparticles, when grafted with LC ligands (or with a mixture of LC and \( n \)-alkylthiol ligands), formation of LC phases is possible.

How to achieve dynamic self-assembly of LC-covered NPs? It is now commonly argued that switchability of LC-covered NPs is driven by changes in spatial distribution of ligands covering inorganic nanoparticle.[27] At low temperatures, LC ligands bundle allowing formation of structurally and chemically anisotropic organic shell that translates to the formation of long-range ordered assemblies of nanocrystals. Heating of such materials causes rebundling and eventually melting of the ligands. These events influence the shape of organic coating, thus they affect spatial distribution of nanoparticles. The observed effects have also been identified for NPs covered with alkylthiols.[50,51]

As in the case of nanoparticles in LC host (Section 3.1) also here the size of nanoparticle plays a crucial role for successful preparation of anisotropic and dynamic systems. Until now this strategy proved fruitful for isotropic NPs with diameter less than 13 nm. Importantly, other design parameters were already identified which give insight into physical principles governing the self-assembly process in LC NPs. For example, nanocrystals’ shape, LC molecules’ design and alkane coligand length [21] can, respectively, affect organic coating layer shape, flexibility and deformability, which all strongly influence the ability of LC NPs to exhibit dynamic self-assembly. It is also worth noting that we collectively call “LC ligands” both mesogenic and promesogenic molecules that result in the formation of LC phases when grafted onto nanoparticle.

A more detailed description of examples of successful achievement of dynamic rearrangement in LC NPs is given in Section 5.

3.3. LC ligands in Ostwald ripening process

Many examples of nanocrystals fragmentation, enlargement or reshaping can be found in the literature.[15] Obviously, changes in NPs size and morphology must influence their self-assembly properties. The most widely recognised thermal processes that induce nanocrystals transformations are digestive ripening (DR) and Ostwald ripening (OR). In the digestive process an excess of stabilising molecules (digestive agents) have the ability to reduce the size of NPs. Thus, DR has been proposed as a feasible tool for narrowing the size distribution of NPs; this phenomenon often results in the formation of ordered nanoparticle supracrystals.[52] Ostwald ripening is a phenomenon opposite to digestive ripening and can be qualitatively understood as a combination of two processes: nanoparticle fragmentation and growth of larger nanoparticles at the expense of smaller ones. In the long term the net effect is enlarging of the mean NP size. Ostwald ripening is usually studied for solutions and only few examples of OR in long-range ordered NPs solids were reported.[17–21] Due to limited literature on OR in NPs solids, it is not yet possible to give a detailed physical description of parameters that influence the process. An important aspect of the LC ligands’ role is the higher molecular mass/lower volatility of the ligands in comparison to \( n \)-alkylthiols studied to date. This, as it will be shown in Section 6, translates to higher nanoparticle stability and slows down nanoparticle growth, which in turn allows for better control of the OR process. However, further investigation in the field of OR in NPs solids is necessary to fully understand details of the process or direct the growth towards anisotropic structures. Here, we present the first reported successful example of OR process for LC-coated NPs, which leads to the formation of long-range ordered structures.

4. Affecting LC-matrix

Hybrid materials comprising NPs and thermotropic LCs have gained vast attention from liquid crystal research community due to the possibility of using nanoinclusions to manipulate application-relevant LC materials’ characteristics.[24] A few recent examples encompass lowering electro-optical response times [53] and operating voltage [54], improving optical contrast [54], decreasing the Fredericksz threshold [55], enabling NIR-switchable reflections form LC–photonic superstructures [33] or manipulating LC phase temperature range.[56] The reverse phenomenon that is using LCs as a tool to manipulate physical characteristics of NPs is also feasible. This can be achieved by changing electrooptical properties of the matrix without affecting positions of NPs (e.g. [30,57]) or by exerting control over orientational and translational order of NPs, as will be reviewed here. It is worth noting that in these systems reconfiguration phenomena depend on many variables such as entropic effects, decreased local order around the NPs [56] as well as long-range elastic [28] and electrostatic forces.[58]
4.1. Controlling orientational order of nanoparticles

Major achievements in the area of generating thermotropic LC-based devices with switchable long-range orientational order of anisotropic NPs come from I. Smalyukh group. Preceded by substantial work in switchable lyotropic LC–NPs systems [59] and static, ordered LC–NPs thermotropic materials, [60] authors recently reported on a successful attempt to build a switchable device of interest (Figure 2(a)). [61] For this purpose they prepared three types of anisotropic gold NPs: gold nanorods of two different sizes (20 × 50 and 14 × 88 nm) and gold nanotriangles (NTs, 50 nm edge length and 13 nm thickness), all covered with 5 kDa thiol-terminated methoxy-poly (ethylene glycol) (PEG-SH). Stable dispersions of these NPs in 5CB matrix were obtained using a clever protocol. First, NPs were mixed with the LC at 40°C while sonicating to obtain a clear dispersion in the isotropic phase of 5CB. Then, vigorous stirring was maintained while cooling down to the nematic phase and this mixture was introduced into LC cell with photoalignment layer. Polarised blue light illumination was used to align the composite macroscopically with the nematic director (N) along the direction perpendicular to the incident light polarisation. This procedure also enabled achieving long-range orientational order of nanorods (NRs) and nanotriangles (NTs) with their long axes parallel to N. This type of assembly was achieved since PEG-SH coating allows for weak tangential boundary conditions for orientation of anisotropic host LC molecules at the nanoparticle surface. Thus, elastic distortions imposed by surface boundary conditions on these nanoparticles are mitigated, so that no additional elasticity-mediated interactions emerge, that could result in uncontrolled nanoparticle aggregation. Under applied voltage the long axes of nanoparticles aligned vertically to the plane of the cell, following the changes of direction of nematic director. The electrical switching of NRs and NTs orientation was evidenced by spectroscopic investigation with polarised light. For the samples with short NRs, in the initial OFF state with polariser being parallel to the long axes of NRs, mainly longitudinal localised surface plasmon resonance was observed. However, for the same orientation of polariser with voltage ON only transverse plasmon mode was observed attesting the reorganisation of NRs. Control experiments with polariser perpendicular to the rubbing direction further confirmed the assumed reorganisation scheme. Importantly, the observed spectral changes were accompanied by a clear colour change of the sample.

Similar switching behaviour was obtained for composites with gold NTs. In this case in the OFF state, with light polarised along rubbing direction, maxima of the absorption is at ca. 680 nm, corresponding to the in-plane LSPR of NTs. After switching to the ON state a blueshift of the LSPR is observed due to excitation of mainly out-of-plane LSPR mode.

Several important developments were proposed by the authors to the methodology described above. In the same article [61] they evidenced that not only thermal, but also optical stimuli can be used to achieve dynamic reconfiguration of NPs orientation translating to colour-switchable systems. It has been achieved by light-induced change of boundary conditions at LC plates.
leading to twisted and non-twisted areas exhibiting different colours under illumination with polarised white light. Thus, authors demonstrated a feasible and effective way to achieve dynamic NPs/LC system with potential applications as tunable nanoantennae, plasmonic polarisers, plasmonic diffraction components, smart windows etc.

Later [62] authors have shown that they can expand applicability of the method to other types of NPs. Specifically they evidenced dynamic control over orientation of β-NaYF₄ up-converting NRs. In this work authors were able to observe polarised emission from the up-converting NPs. Combined with orientationally ordered arrays of this kind of nanoparticles, the modification of polarisation of luminescent light of UCNPs in various LC hosts, may be used to construct novel sources of light, potentially including distributed-feedback mirror-free cholesteric lasers.

Importantly, Smalyukh et al. [63] were also able to achieve control over NPs alignment in LC matrix by tuning interactions with the LC matrix. In this report NPs were covered with N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) instead of PEG derivative. For surfaces DMOAP usually produces perpendicular surface boundary conditions for the LC director; however, when covering relatively small nanoparticles the surface anchoring tendency and bulk elastic deformation costs compete. Thus, weaker distortions and deviation from the easy-axis orientation are expected, resulting in long axes of NRs and NTs being orthogonal to the director of bulk nematic. As in the previous example electrical switching of the composite was evaluated using spectroscopic techniques. Importantly, it was shown that NRs require 50% more time to reorient than the nematic director.

Methodology based on using DMOAP as the organic coating of NPs have been shown to be applicable not only to NRs and NTs but also NPs with more complicated geometry, namely Au-Ag alloy nanoframes (NFs). Smalyukh and Yuan [64] prepared long-range ordered assemblies of NPs using previously developed protocol. However, these NPs exhibit different alignment than NTs and NRs – normal to their surface forms a double cone around director of the nematic phase in a planar cell. This orientation derivates from minimisation of the surface anchoring energy at LC–NFs interfaces. Authors argued that an optimal orientation, here ~45° angle between bulk nematic director and normal to the plane of the nanoframe, can be deduced from simple geometrical considerations for NFs with square cross-sections. Importantly, orientation of this double cone can be changed by applying voltage. This directly influences spectral characteristics of the material; however, in contrast to the above-described cases probing polarisation parallel and perpendicular to the rubbing direction give similar results. In this case, significant variations of the LSPR can be observed for 45° angle between rubbing and probing directions.

In all the above-given examples fine control over LC-anchoring orientation and strength at NPs surface was necessary. However, it is also possible to deviate from this requirement by using crystal defects – linear smectic disclinations (called oily streaks) to trap NRs, as recently shown by Lacaze et al. [65] In this strategy LCs act as a large-scale ordered template for NPs assembly. In particular, NPs can be trapped and assembled in the smectic disclinations, reducing the molecular disorder and the free energy of the LC phase introduced with NPs. This way single particle chains can be achieved in oily streaks, although it should be remembered that also other types of defects can trap NPs (grain boundaries and curvature walls). In this work, semiconductor CdSe/CdS dot-in-rods, which behave as single-photon emitters are confined in the linear defects, forming single or thick chains depending on nanoparticle concentration. The achieved orientation of dot-in-rods along a unique direction for a given substrate.

Recently, dynamic reorientation of NPs in confined LC spaces was also shown. He et al. [66] prepared NRs dispersions in 5CB as described earlier [61], then introduced the mixture to silicone oil, and droplets of the composite material were formed. Within the droplet the NRs aligned radially; however, upon applying electric field the long axes of Au NRs become preferentially oriented parallel to the electric field.

It is also worth mentioning that it is possible not only to control orientation of individual NPs but also clusters of NPs embedded within LC host. This strategy was used to achieve electric field switching of hexadecanethiol functionalised gold nanorods (50 nm length, aspect ratio 2.5) in E7 and 5CB LCs.[67] These nanorods form disc-like assemblies, which orient so that Au NRs’ long axes follow the nematic director. Recently, this strategy was also shown to be applicable to DMOAP-coated silica particles (spherical, 50 and 100 nm diameter).[68] In this case, when no external field is applied, particles assemble into chains that have no preferential ordering; however, locally they are roughly perpendicular to the director. When the electric field is applied the director domains align, which translates to orientation of the aggregate structures in direction perpendicular to the applied field.

Prospective applications of nanoparticle-based materials with switchable orientation of nanoinclusions
have been proposed in, e.g. in tunable nanoantennae, plasmonic diffraction components, smart windows, switchable plasmonic polarisers [61], novel sources of light, potentially including distributed-feedback mirror-free cholesteric lasers [62], colour filters [63], LC-droplet-based optical vortex generators as well as microresonator cavities. [66] Recently, it was theoretically shown that these materials can also be used as total absorbers and epsilon-zero medium. [69]

4.2. Controlling translational order of nanoparticles

Probably the most straightforward route to change interparticle spacing is by using assembly/disassembly approach. This strategy allows to achieve wide tunability of materials properties by evoking collective interactions when going from isolated NPs to NPs assemblies. [70] Many examples exploiting this approach can be found in the literature, including the use of LCs. [71] Often the LC-driven (dis)assembly strategy relies on the lowering miscibility of NPs when transition from isotropic melt to mesophase occurs, causing NPs assembly in LC defect sites and at interfaces [28] due to lowering disorder of the system introduced by nanoparticles.

A strategy based on using LC defects to organise NPs (small enough not to induce elastic distortion) has been introduced few years ago. [72] Recently, this methodology was developed towards achieving fine tuning of interparticle spacing. [73] In this work Lacaze et al. prepared a mixture of 8CB and Au NPs (two batches of spherical Au NPs with 3.9 and 4.2 nm diameters were used) in toluene. Composite films were achieved by evaporating solvent from the mixture. A 40 nm shift of LSPR peak was measured when polarised light parallel or perpendicular to defect lines of 8CB was used, evidencing anisotropic distribution of NPs. Spacing of NPs within the defects (NPs form chain-like structure) was carefully investigated allowing tuning interparticle spacing by controlling toluene evaporation rate from the initial LC/NPs mixture. The achieved interparticle distances can be explained by kinetics of the solvent evaporation. For a controlled solvent evaporation NPs’ surface ligands can disentangle during formation of the linear NP assembly and the LC-induced repulsion between NPs appears to control the interparticle spacing. Conversely, for an abrupt solvent evaporation this interaction is not able to compete with the strong van der Waals attraction between NP ligands, thus spacing in this case is mainly dependent on surface ligands’ length.

Feasibility of such systems to exert dynamic control of interparticle spacing was evidenced by Reven et al. [74] Authors prepared 4.7 nm diameter Au NPs covered with a mixed organic coating layer comprising 4’-(n-mercaptododecyl)oxy)-biphenyl-4-carbonitrile and hexanethiol. The NPs are well dispersed in the isotropic phase of 8CB; in the nematic phase they form circular assemblies, while further cooling to smectic phase enables formation of well-ordered, linear arrays of NPs. The change can be reversed by heating. The authors confirmed that the observed arrays result from nanoparticle decoration of periodic edge disclinations by careful analysis of the patterns formed in cavity and wedge cells.

Fine control of anisotropic NPs positions may be achieved using a modification of the above-mentioned strategies. Yang et al. [75] showed that gold nanorods (31 \times 11.3 \text{ nm}) covered with thiol-functionalised polystyrene were embedded within defects of 8CB smectic matrix, with the LC material homeotropically anchored to epoxy pillar arrays. At 40°C this composite material exhibits an isotropic phase in which nanorods, compressed side-to-side, give the absorption peak at 636 nm. The phase transition to the nematic phase is accompanied by a redshift of the LSPR-absorption maxima to 683 nm. Authors have argued that the unprecedentedly large shift is due to the change of side-to-side to end-to-end assembly of nanorods, driven by size compatibility between defect core and NP diameter. Further cooling of this hybrid system is accompanied by loosening of nanoparticle network as evidenced by further shift of the LSPR maxima. Interestingly, disassembly is observed when going from isotropic to nematic phase, which stands in opposition to the most commonly observed behaviour.

In all the works discussed above, interparticle distance within the assemblies is mainly defined by NPs organic coating. Surprisingly, it was recently shown (Figure 2(b)) [58] that lattice periodicity can also be much larger, in line with theoretical predictions. [76] Smalyukh et al. [58] prepared \( \beta\text{-Na}_{0.5}\text{Gd}_{0.5}\text{Yb}_{0.05}\text{Er}_{0.02}\text{F}_4 \) semiconducing, up-converting, rod-like shaped NPs, stabilised with methoxy-poly(ethylene glycol)silane. When dispersed in 5CB host, these NPs assembled into a long-range ordered colloidal crystals with triclinic symmetry and orientational ordering of NRs. Interestingly, dark-field video microscopy evidenced that nanorods can be electrically concentrated and ordered even in very diluted dispersions, forming a triclinic lattice with 0.5–1.6 \text{ \mu m} periodicity. Large unit cell size of NPs assembly was also obtained by Raven et al. [56] for 4.7 nm diameter spherical Au NPs covered with 4’-(12-mercaptoalkoxy) biphenyl-4-carbonitrile. These NPs were added to 6OCB/CB15 mixtures, which exhibited LC blue phases. In the isotropic melt no ordering of NPs is present;
however, after lowering the temperature well-ordered cubic arrangements of NPs were formed – simple cubic in BPII and body centred cubic in BPI phase. Periodicity of these NPs structures are similar to lattice constants of BP I and BP II phases, ca. 400 nm, meaning that nanoparticles selectively migrate to periodic strong trapping sites in the BP disclination lines.

It is also possible to control interparticle spacing by combined effects of particle confinement in topological singularities and particle manipulation using optical tweezers.[77] The former was used to entrap 5 × 20 nm CdSe/CdS nanorods, while latter enables controlling position of nanoburst gold (∼500 nm diameter discs with irregular sharp edges). This method allowed detailed investigation of plasmon–exciton interactions devoid of substrate effects. By using this approach a topological singularities can serve an environment for understanding of plasmon–exciton interaction as well as fluorescence blinking of semiconducting nanocrystals.

Prospective applications of nanoparticle-based materials with switchable interparticle distance encompass, e.g. optical transport of information[72], solar-to-electricity or solar-to-fuel photoconversion applications[77], metamaterials and catalysis.[75]

5. Affecting LC ligands

Achieving densely packed, reconfigurable assemblies of NPs have gained vast attention, since such materials are promising candidates for various applications in optoelectronic technologies. Among other methods of generating switchable assemblies, grafting LC ligands to the surface of NPs is especially interesting since it allows to realise shape-changing building blocks.[78]

A considerable research effort was undertaken to develop materials built with nanoparticles covered with LC ligands (hereafter referred to as LC NPs).[79–99] It enabled identification of crucial design parameters as discussed in Section 3.2. Also, synthetic strategies were developed based on ligand exchange reaction, reactions with functional groups of nanocrystals’ ligands or direct synthesis of NPs in the presence of LC molecules. The amassed knowledge was utilised to achieve a number of functional materials showing, e.g. plasmonic anisotropic or epsilon-near-zero properties. Very recently it enabled achieving chiral superstructures[100], optimisation of structure of NPs used as dopants to LC phases[99], preparing binary superlattice structures of unprecedented single inorganic components.[101] Below, we review only those systems for which dynamic control over NPs superstructure was achieved.

5.1. Controlling translational order of nanoparticles

Already at the beginning of LC–NPs research, thermally switchable materials were identified. In the work by Kim et al.[80] 2.7 nm diameter Au nanoparticles were covered with 4’-(12-mercaptododecyloxy) biphenyl-4-carbonitrile (compound 1, Table 1).

Based on small angle X-ray diffraction, authors identified a mesophase in the temperature range between 110°C and 130°C, most probably smectic phase, with interparticle distance within the layer of 2.9 nm and interlayer spacing of 6.3 nm. At 130°C clearing was observed, but unfortunately structural information for the isotropic phase were not given. As explained in Section 3.2, the observed switchability was ascribed to reorientation of LC ligands at NPs surface – bundled at low temperatures and isotropic after melting.

For practical reasons it is important to achieve control over the structure and stability of phases formed by LC-covered NPs. To this end, some of us have shown that phase transition temperature for LC–NPs may be tuned according to the needs[97] In this work 2.2 nm diameter spherical Au nanoparticles were grafted with a mixture of promesogenic (compound 2, Table 1) and alkanethiol ligands, using three different LC ligands and three alkanethiol co-ligands of different length. Self-assembly of these hybrid NPs into lamellar or 3D long-range ordered structures was evidenced depending on the alkyl-spacer length of the LC ligands, thus pointing to the crucial role of flexibility of the LC ligands – the longer the alkyl-spacer length the higher order was observed in the materials. Additionally, systematic investigation allowed us to identify clearing temperature relation on the length of the alkanethiols and LC molecules, thus to correlate it with the separation of gold nanocrystals. Noticeably, clearing temperature could be tuned over the range of 100°C.

Recently, Górecka et al.[98] have shown that it is possible to tune the LC NPs organisation by light. Authors prepared 2.5 ± 0.4 nm diameter Au NPs covered with one of the photosensitive azo compounds (compounds 3–6, Table 1) and n-hexanethiol. Depending on ligand the NPs exhibited either lamellar or columnar phase. When illuminated with UV light trans-to-cis isomerisation of azo units occurred, which caused a phase transition to the isotropic melt as evidenced in situ with small angle X-ray scattering, while turning off the UV light reversed the process. As in the case of thermal switching this behaviour was ascribed to the change of the geometry of the organic coating layer. In the trans state they were able to segregate and form bundles, while cis configuration weakened ligand–ligand interactions due to steric effects and produced isotropic organic shell.
More precise tuning of nanoparticle packing in LC assemblies can be observed for materials exhibiting phase transition between different long-range ordered structures – polymorphism of phases. Material with such properties was first presented by Ungar et al. [85] In this work authors prepared 1.7 ± 0.4 nm diameter Au NPs covered with a mixture of hexanethiol and a mesogenic ligand (compound 7, Table 1). At low temperatures the NPs are arranged into a 2D rectangular lattice of c2 mm symmetry, while heating to ca. 80°C caused reassembly into 2D hexagonal structure with p6 mm symmetry. This temperature induced reconfiguration was accompanied with a very small change of interparticle spacing.

Switching between more than two long-range ordered structures is also as shown by Wojcik et al. [90] These authors prepared 2–3 nm diameter gold nanoparticles covered with n-butane thiol and promesogenic molecules (compound 8, Table 1). At room temperature the NPs assembled into a lamellar structure. When heated to 152°C transition to a rectangular columnar phase was evidenced, followed by formation

| (Pro)mesogenic ligands | NPs type | NPs size (nm) | Compound | Ref. |
|-----------------------|----------|---------------|----------|-----|
| | Spherical Au | 2.7 | 1 | [80] |
| | Spherical Au | 2.2 | 2 | [97] |
| | Spherical Au | 2.5 ± 0.4 | 3 | [98] |
| | Spherical Au | 2.5 ± 0.4 | 4 | [98] |
| | Spherical Au | 2.5 ± 0.4 | 5 | [98] |
| | Spherical Au | 2.5 ± 0.4 | 6 | [98] |
| | Spherical Au | 1.7 ± 0.4 | 7 | [85] |
| | Spherical Au | 2–3 | 8 | [90] |
| | Spherical Au | 2.4 ± 0.3 | 9 | [95] |
| | Spherical Ag | 4.7 ± 0.6 | 10 | [102] |
| | Au Nanorods | 28.6 ± 2.0 length 6.5 ± 1.5 width | 11 | [96] |

R = C₃H₁₂Si(OCH₃)₂OSi(OCH₃)₂C₆H₅SH

Table 1. Structures of ligands mentioned throughout Section 5.
of hexagonal columnar phase at 158°C and clearing event at 162°C, as evidenced by SAXRD measurements of a quasi-monodomain structure (Figure 3 (a–c)).

Importantly, changes in nanoparticle spacing may be observed even without evoking phase transition. For a few systems it was shown that unit cell dimensions may be altered keeping the symmetry of the system. Some of us reported on 2.4 ± 0.3 nm diameter gold nanoparticles covered with a mixture of octanethiol and LC ligand (compound 9, Table 1).[95] Temperature-dependent SAXRD measurements evidenced changes in parameters of a modulated smectic phase. At 90°C the interlayer distance was 11.6 nm, the modulation period along the layers 29.4 nm and the in-layer distance between NPs 4.3 nm. At 170°C those values were 11.2, 42.3 and 5.5 nm, respectively, but noticeably the period of modulation along layers corresponds to 7 – 8 in-plane nanoparticle distances for all temperatures.[95] This behaviour can be understood in the context of enlarging the energy that has to be dissipated by the ligands, which may cause melting of the alkylthiol ligands and introduce disorder to the LC bundles.

From the applicative point of view it is crucial that the LC-ligands-based self-assembly strategy can be applied for functional, plasmonic metal NPs. Two groups reported on the assembly of plasmonic Au NPs in 2012. Kanie et al. [92] prepared 6.8 ± 0.7 nm diameter Au particles grafted with LC dendrimers for which phases with different symmetries were evidenced. Unfortunately, phase sequence was not clear most probably due to their metastable character. Mehl et al. [94] prepared 10 ± 2.2 nm diameter Au NPs grafted selectively with LC ligand. For these NPs, melting to nematic phase and transition to isotropic phase were reported. Unfortunately, changes in plasmonic properties of the material were not evidenced. Recently, some of us have prepared LC-covered NPs for which structural switchability (Figure 3 (d)) was accompanied by dynamic changes of plasmonic properties.[102] 4.7 nm diameter Ag NPs covered with a mixed layer of LC ligands (compound 10, Table 1) and dodecanethiol were reported. At low temperatures NPs assembled into a lamellar phase with inter-layer spacing of 8.4 nm and in-layer distance of 6.1 nm. Heating above 90°C causing reorganisation to isotropic phase was observed; at 130°C the mean interparticle distance was 7.4 nm. This reversible change of nanoparticle spatial distribution caused a 20 nm shift of LSPR maxima, driven mainly by variation of the nearest neighbour distance (1.7 vs. 3 nm) as confirmed by theoretical modelling. Interestingly, beyond active plasmonic properties, this material was the first example of switchable epsilon-near-zero material made of NPs. More recently [20] 4.4 nm diameter Au NPs based switchable active plasmonic material was developed. After thermal annealing these NPs assemble into 3D structure with tetragonal symmetry, which is stable up to 95°C. Above this temperature reorganisation to body centred cubic phase was evidenced using SAXRD, revealing long-to-long range type reconfiguration. The rearrangement was accompanied by 8 nm shift of LSPR band maxima.

Figure 3. (Colour online) Thermally switchable assemblies of NPs with LC surface ligands. (a–c) 2D small angle X-ray patterns recorded for oriented sample of gold NPs covered with compound 8 in (a) smectic, (b) columnar rectangular and (c) columnar hexagonal phase. Orientation of the sample was induced by shearing.[90] (d) Rearrangement of silver NPs covered with dodecanethiol and compound 10 between smectic and isotropic phases.[102] (a–c) was reprinted from [90] with permission of The Royal Society of Chemistry.
5.2. Controlling orientational order of nanoparticles

Reorientation of LC nanoparticles has not been thoroughly investigated. Crucial example comes from Hegmann et al. [96] showing that it may occur under the influence of magnetic stimuli. Authors prepared gold nanorods with 28.6 ± 2 nm length and 6.5 ± 1.5 nm width covered with a mixture of LC ligands (compound 11, Table 1) and cetyltrimethylammonium bromide molecules. Pristine material exhibited only short-range order of NPs; however, when doped with a small amount of free LC ligands large-area self-assembled structures with either smectic-like or end-to-end type organisations were evidenced by TEM imaging. Importantly, dynamic rearrangement of the nanorods orientation was possible using a hand-held magnet, allowing to change orientation of nanorods long axes from perpendicular to parallel to the substrate.

Such systems have great significance as future metamaterials, SERS substrates, nanorod-based high-efficiency polarisers, and other prominent applications in biological and technological fields.

6. Affecting NPS

6.1. Ostwald ripening of nanoparticles

As shown in the previous sections, precise control over electrooptical characteristics of nanoparticle-based LC materials can be realised by affecting surroundings of nanoparticles. However, the observed tunability is limited by intrinsic properties of a given type of nanocrystal. Additional variability allowing to surpass this limit can be introduced by dynamic control over the structure of the nanocrystals core. This additional variability may be achieved by inducing nanoparticle growth using Ostwald ripening process on preformed, solid state assemblies of nanoparticles.

Substantial contribution in this field comes from the group of Krogel et al. [21] who, e.g. demonstrated that superlattice made of 1.8 nm diameter dodecanethiol coated Au NPs can undergo subsequent transformations from body centred cubic, through hexagonal close-packed, binary simple cubic AB\textsubscript{13} to finally achieve hexagonal AB\textsubscript{5} symmetry. Also, Pilení et al. [18] reported on the formation of binary structures with NaCl, AlB\textsubscript{2}, NaZn\textsubscript{13} and MgZn\textsubscript{2} symmetries was achieved when 2.2 nm diameter oleylamine-coated Ag NPs were heated. However, application of this method to producing ordered nanoparticle assemblies is still at its infancy and to date this approach has not been used for LC NPs.

Here we focus on inducing high-temperature Ostwald ripening process for NPs covered with promesogenic ligands. The main objective was to assess OR applicability to achieving long-to-long-range ordered superlattice transformation in thin films of LC NPs.

6.2. Results and discussion

For our purposes of investigating OR process in LC NPs assemblies we have decided to use silver nanoparticles. First, we have synthesised dodecanethiol-coated Ag NPs (AgC\textsubscript{12}) adapting procedure proposed by Chen and Wang [103] as previously described. [35] Then, these Ag NPs were subjected to ligand exchange to graft promesogenic ligand (L, for synthesis details see Supplementary material) onto their surface. Based on 1H NMR measurements (as described previously [34]), we established that in two separate ligand exchange reactions materials with ca. 40% (material AgL04) and 70% (AgL07) alkanethiol ligands exchanged were prepared (Figure 4). Diameter of these hybrid was 4.3 nm as determined with TEM.

First we determined whether the composition of the organic coating layer influences temperature stability of metallic nanoparticles in solutions. We probed the OR process by a series of small angle X-ray scattering studies for AgC\textsubscript{12}, AgL04 and AgL07 materials. To enable high-temperature measurements, nanoparticles solutions in octadecene (bp 314.4°C) were prepared, introduced to a glass capillary, sealed and subjected to temperature rise tests. Diffractograms were collected for samples heated consecutively to 30°C, 120°C, 150°C, 180°C, 210°C and 240°C. At each temperature, 100-s-long scan was collected. Only at 180°C samples were kept longer to perform five scans.

This protocol was elucidated based on initial results and previous research showing Ag LC NPs decomposition at temperatures slightly higher than 180°C. [95] Each SAXS pattern was fitted with theoretical curves calculated for spherical NPs using NanoFit software and plotted at Figure 5.

It is clear (Figure 5(a)) that AgC\textsubscript{12} nanoparticles’ size and size distribution were not affected by temperatures lower than 180°C. However, when kept at 180°C, the NPs diameter increased from ca. 4.3 to ca. 5.6 nm, evidencing Ostwald ripening process. Also, the size distribution of NPs increased, making it impossible to properly verify the size of individual nanocrystallites at 210°C. Clearly this effect relates to uncontrolled particle sintering event.

In the case of material AgL04 (Figure 5(b)), silver nanoparticles enlargement was not detectable even at 180°C (the measured diameter is approx. 4.4–4.6 nm). However, it is noticeable that size distribution of NPs was growing at 180°C, most probably evidencing that a slow OR process started. At 210°C the calculated relative standard deviation of diameter reaches 50% attesting a high level of uncontrolled sintering of metallic nanocrystals.
Figure 4. (Colour online) (a) Scheme of composite material synthesis (AgL, on the right) in a ligand exchange process using AC12 starting material (on the left). (b) Promesogenic ligand (L) structure: 1–4–((4-((11-mercaptoundecanoyl)oxy)phenoxy)carbonyl)phenyl 4–(2-undecyltetradecyloxy)benzoate.

Figure 5. Changes in the size and size distribution probed by SANS for solutions of (a) AgC12, (b) AgL04 and (c) AgL07 nanoparticles in octadecene.
For material AgL07 (Figure 5(c)) only minute change of NPs size was observed throughout the entire temperature range (30–240°C). In analogy to the previous samples the increase of the temperature resulted in broadening of NPs size distribution; however, here the calculated changes were relatively small (increase from 10% at 30°C to 18% at 240°C).

Therefore, based on the described SAXS studies it can be concluded that promesogenic ligands stabilise Ag NPs more efficiently than short alkanethiols, which is reasonable in view of previously performed TGA measurements.[102] Thus, we also tested whether OR of LC-covered NPs in the solid-state may be used for preparing ordered assemblies of NPs. For this purpose we drop-casted Ag NPs onto kapton foil and kept samples at 150°C or 180°C for 3.5 h. Throughout the heating period SAXRD patterns were collected every 5 min to probe structural changes occurring in the system, which were then plotted as time evolution map (Figure 6).
SAXRD pattern collected throughout the first 5 min of measurements of AgCl2 at 150°C evidenced relatively narrow signals centred at 6.1, 5.3 and 3.8 nm, which could be indexed as (111), (002) and (022) reflections from face centred cubic structure. Based on SAXS measurements for AgCl2 NPs solution, it can be assumed that this FCC structure (FCC1, Figure 6(a)) is formed with 4.4 nm diameter Ag NPs, thus interparticle spacing (surface-to-surface) between nearest-neighbour Ag spheres was estimated as 3.2 nm. This value corresponds to ca. doubled length of the dodecanethiol molecule in contrast to distances commonly measured at room temperature. This difference can be explained by enhanced thermal fluctuations of the ligands at elevated temperatures, which translate to increased stiffness of the organic coating layer and prevent interdigitation of ligands of neighbouring NPs. After heating the sample for additional 15 min, the SAXRD patterns revealed only two relatively broad reflections with positions ratio close to 1:3^{1/2} suggesting short-range 2D hexagonal structure of nanoparticles. The maxima of the signal moved towards smaller 2-theta values and stabilised after heating the sample for ca. 65 min. On the contrary, when the AgCl2 material was kept at 180°C after ca. 95 min, no signal was observed for which the position of the maxima could be determined, evidencing strong aggregation of NPs.

To establish influence of L ligand on solid state OR process, we then performed analogous measurements for AgL04 material. Diffractograms collected at 150°C (Figure 6(b)) revealed evolution of only one relatively narrow signal after 50 min of measurements. The signal position was stable for the probed time and most probably corresponds to isotropic distribution of Ag NPs. Similar results were obtained for heating AgL04 material at 180°C (Figure 6(e)), with the only difference that the signal position was not stable over the heating time and slowly shifted towards lower 2θ angle values. Thus in both cases OR process was evidenced; however, it did not allow us to generate long-range ordered assemblies of NPs. We assumed that the higher stability of Ag NPs against agglomeration could slow down Ostwald ripening process resolving the problem. Therefore, we performed SAXRD heat annealing measurements for Ag07 material.

Diffractograms collected for AgL07 material revealed three relatively sharp signals throughout the first 30 min of heat annealing at 150°C and for the first 5 min at 180°C (Figure 6(c)). In both cases signals were centred at 8.8, 7.6 and 5.4 nm and could be indexed as (111), (002) and (022) reflections from face centred cubic structure (structure FCC2, Figure 7(a,b)), the signals are broader for sample heated to 180°C). We can safely assume that Ag nanocrystals’ size did not significantly change in these conditions, thus unit cell parameters could be recalculated to 6.5 nm interparticle spacing. This value is substantially higher than in the case of AgCl2 material and corresponds to ca. doubled length of L. Further heating at 150°C revealed

Figure 7. (Colour online) Comparison of modelled (red line) and measured (circles) SAXRD profile for thermally annealed AgL07 material. (a) the first scan taken at 150°C (FCC2 structure), (b) the first scan taken at 180°C (FCC2; however, broader signals), (c) scan taken after 25 min of sample annealing at 180°C revealing FCC3 structure.
SAXRD patterns characteristic of short-range ordered hexagonal structure. In contrast, for the AgL07 sample annealed at 180°C for 25 min the SAXRD pattern characteristic of FCC structure with (111), (002) and (022) signals maxima centred at 12.0, 10.4 and 7.3 nm, respectively, was observed (FCC3, Figure 7(c)). Noticeably, the unit cell size of this structure is larger than that in the case of FCC2. The increase can be attributed to the growing size of nanocrystals, since ligands are fully extended at this temperature as evidenced for FCC2. These parameters attest substantial increase of NPs diameter from 4.4 to 8.3 nm, while still exhibiting long-range order. FCC3 structure is stable for 40 min after which transition to short-range ordered phase is observed.

The structure conversion FCC2→FCC3 evidenced by SAXRD demonstrates that OR process can be used to induce dynamic rearrangement between two long-range ordered nanoparticle assemblies (Figure 8). To further confirm the phenomena, we decided to visualise the evolution of AgL07 material at 180°C with TEM. For this purpose AgL07 solution was dropcasted onto TEM grids and kept at 180°C for 2 or 25 min. The heating times were chosen based on SAXRD measurements and correspond to formation of FCC2 and FCC3 structures, respectively. Also, AgCl2 material was dropcasted onto TEM grids at room temperature. The corresponding TEM micrographs are given in Figure 9. It can be clearly seen that all materials have the tendency to form 2D hexagonal assemblies. In the case of AgCl2 and AgL07 sample annealed for 2 min, no difference in NPs diameter was observed, confirming SAXRD measurements. In contrast, for AgL07 material annealed for 25 min, ca. 7.8 nm diameter Ag particles arranging into FCC-characteristic structures were observed, confirming results of SAXRD measurements.

7. Summary

In summary, we have shown that it is possible to modify NPs properties by dynamic self-assembly within thermotropic LCs. Two major strategies towards reconfigurability are based on applying external stimulus to LC matrix or LC ligands. These techniques were already shown to generate LC–NPs composites with properties interesting for a wide variety of optoelectronic and sensing applications; however, they are still at infancy. One of the major practical issues is self-assembly kinetics.

When employing electrical stimulus to LC matrix, switching times comparable to pure LCs have been evidenced; however, much longer times are required for thermally driven reconfiguration when affecting LC ligands. LC–NPs composites were also proven applicable to achieve tunability of particle spacing, which makes them suitable test bed for exploring interparticle coupling effects and also enables achieving practically interesting switchable metamaterials. From the metamaterial point of view, LC-based dynamic SA methods are especially interesting since they allow us to achieve both collective interactions of nanoparticles (usually observed for static assemblies) and dynamic self-assembly (usually achieved for low metal volume fraction solvated environments).

In addition to reviewed literature, we have also provided first experimental evidence for achieving dynamic rearrangement in LC nanoparticle solids using Ostwald ripening process. We have confirmed that by using OR process it is possible to enlarge nanoparticles while preserving internal long-range order. We have thus introduced a new strategy in which external stimulus affects not only nanoparticle surroundings (host materials or surface ligands) but directly nanoparticles. Importantly, we have also confirmed the ability to control the process by changing LC ligands population in the organic coating layer. We believe thus that further studies will prove this methodology to be practically useful by providing access to complex nanocrystal superlattice structures, by achieving precise control over OR by LC ligands design and finally to achieve multiresponsive systems.

The above-presented review and research attest that LC-based dynamic self-assembly of NPs are tailor able techniques with good prospects for future applications,
although further research is needed to explore design principles for thermotropic LC–NPs active composites. With the view of new research avenues such as pursuing multi-switchable systems, it can be foreseen that growing attention will be paid to this field.

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Figure 9. TEM micrographs of different Ag NPs assemblies revealing either hexagonal structure of a monolayer or 3D assembly with FCC structure. (a) AgC12 material dropcasted onto TEM grid without heating; (b, c) AgL07 material dropcasted onto TEM and annealed at 180°C for (b) 2 or (c) 25 min.
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