

A Study the small organic Molecule-based Low-Dimensional Nanomaterials with Optoelectronic Properties

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Abstract - Over the past few years, research & development activity in the vast as well as interdisciplinary field of nanostructure science & technology has exploded globally. Furthermore, their strategic place in the 21th century is already set. The field with the earliest beginning & most significant successes is the exploration of nanomaterials & nanostructures. The study of nanomaterials has received a lot of consideration in both academic & industrial research. Nanoscale materials composed of functional small organic molecules are the focus of this review. For organic nanostructures, we look at the various approaches that have been taken. Nanostructures ranging from 0D to 1D are studies.

Keywords - Nanomaterials, Nanoscale, Nanostructures, Organic Structure, Optical Properties, Morphology

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INTRODUCTION

There has been a surge in interest in studying nanomaterials over the last two decades; these are materials with at least one of their 3 dimensions between 1 nm & 100 nm made up of discrete objects. The surface effects, quantum size effect, macroscopic quantum tunnel effect etc. provides NMs their distinctive features. Nanomaterials' size-dependent optoelectronic capabilities have led to utilize the wide fields, such as bio-labeling & functionalization, novel luminous materials, nonlinear optics, chemical sensors, & high-density information storage. Inorganic NMs, organic macromolecular materials, depend on organic low-molecular-weight substances might be split into three categories if hybrids are omitted, and inorganic nanomaterials have received the most attention since the rise of nanoscience. Inorganic nanomaterials are the focus of the vast majority of nanoscience research. Scientists from all over the world have studied zero-dimensional (0D) inorganic NSs, such as NPs, clusters & quantum dots. So, for instance, many groups have reported on the preparation, shape control & size dependence of semiconductor quantum dots' optoelectronic properties. Light-emitting diodes & solar cells, chemical sensors and photodetectors are all examples of nanodevices that have been made using quantum dots. Metal & magnetic compound nanoparticles for bioapplications are an essential area of 0D inorganic NMs. 1D nanomaterials, such as carbon nanotubes, have attracted considerable research attention since their discovery in 1991.

Due to their new optoelectronic properties & applications, 1D nanostructures formed on semiconductor conjugated polymers like PF, PT & PPV are receiving a lot of attention in the scientific community. To make polymer 1D nanostructures, the most common techniques are electrochemical deposition, electrospinning, self-assembly, & template method. Supramolecular chemistry has also made it possible to create 1D nanostructures with macromolecules other than polymers, mainly through self-assembly. Nanoscale materials composed of functional small organic molecules are the focus of this review. For organic nanostructures, we look at the various approaches that have been taken. Nanostructures ranging from 0D to 1D are discussed in great detail. This paper concludes with an assessment of where we think research in this area is headed moving forward.

CONSTRUCTION OF ORGANIC NANOSTRUCTURES

According to Horn & Rieger[2001], indication of the preparation of 0D organic NPs, particularly those isolated in water, was comprehensive and detailed. It summarised several methods, including emulsification-diffusion, the supercritical fluids method & polyelectrolyte complexes method. Since organic nanoparticles have recently been developed, we will only briefly discuss this topic here before moving on to the construction of 1D organic NSs.

Methods for the Production of 0D Organic NPs

Organic NPs dispersed in water are the subject of the majority of current research. Reprecipitation is the simplest & most widely utilised preparation method, but other methods, such as laser ablation, microwaves, microemulsions, membrane reactors, and so on, have also been employed to aid in the formation of nanoparticles in an aqueous environment. It was also investigated how organic nanoparticles self-assemble, as well as how hybrid nanoparticles could be made, either by combining two types of small molecules or by combining small molecules & polymers.

- **Reprecipitation**

It was Nakanishi & coworkers who discovered the solvent displacement method known as reprecipitation. Dispersions of organic nanoparticles can be easily prepared using this method. In this method, the target compound is dissolved in an excellent solvent and an excess of a poor solvent is added to a small amount of concentrated stock solution. This method relies on a wide discrepancy in target compound solubility between good & bad solvents, as well as good compatibility between the two solvents. Stock solution and poor solvent are thought to have a detrimental effect on target compound molecules because of the rapid mixing of stock solution & poor solvent.

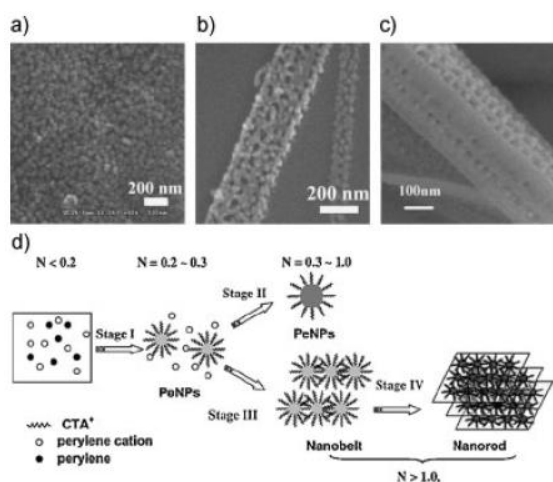


Figure 1. a) SEM image of quasi-spherical perylene nanoparticles with a size of ~25nm at $N=0.3$. b,c) The self-organization of the particles to nanobelts at $1.0 < N < 1.2$, and to square nanorods at $N > 2.0$. d) Schematic illustration representing formation of the perylene nanoparticles. Stage I, nucleation; stage II, growth; stages III and IV, 1D to 3D organization.

Chemical Reaction Method

Organic nanoparticles can be easily prepared by reprecipitation, but kinetically stable nanoparticle dispersions are difficult to obtain. In addition, the solubility of the target compound in the good solvent limits large-scale synthesis. Further complicating

things is that this method's heterogeneous environment makes it intricate to accurately control both initial nucleation and growth. Moreover, the heterogeneous environment of this method makes it difficult to precisely control the complicated nucleation process in the initial stages and the subsequent fast growth. Consequently, the broad distribution in both size and shape of the organic nanoparticles generated using this method prevents them from acting as building blocks for further self-organization.

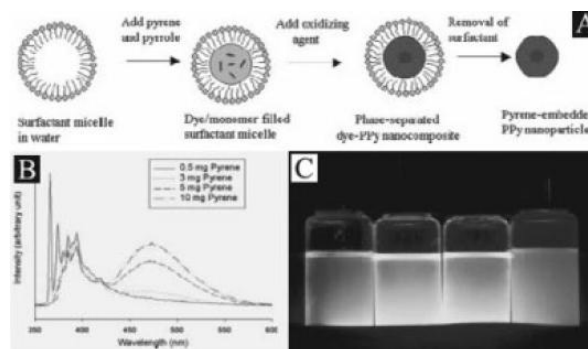


Figure 2. a) Schematic representation of the fabrication of polypyrrole nanoparticles with embedded pyrene. b) The photoluminescence spectra of pyrene-embedded polypyrrole nanoparticles for different pyrene loadings. c) Corresponding photograph (from left to right, the pyrene amounts are 0.5, 3, 5 and 10 mg).

Fabrication of Composite Organic Nanoparticles

It is possible to introduce new properties into composite materials, such as materials prepared of two or more basic materials with substantially unusual physical or chemical properties, through synergistic effects between constituents. Recent years have seen a rise in interest in organic nanoparticles with a variety of structures. The tunable emission properties of equally doped organic NPs are explained along with the introduction of nanoparticles with core/shell structures.

Methods for the construction of 1D organic Nanostructures

In comparison to their 0D counterparts, 1D NMs are better suited for the design of active nanodevices & interconnects, as mentioned in Section 1. Organic 1D nanostructure construction methods that are simple, mild, & widely applicable have recently been recognised as being of critical importance to science & technology. Organic nanomaterials have lower melting points & thermal instability than inorganic nanomaterials, making many current approaches to inorganic 1D nanomaterials inapplicable.

Self-Assembly in the Liquid Phase

Using the small organic functional molecules 2,4,5-triphenylimidazole (TPI) & inducing their self-assembly in water at various temperatures, Yao et al. [2007] demonstrated the fabrication of single-

crystalline nano- & sub-micrometer tubes. Figure 3 shows typical SEM & TEM images, as well as the SAED pattern of TPI tubes. The TPI tubes have opened structures with a high degree of monodispersity. The c-axis of the TPI crystal serves as the tube axis for each tube. Tuning the TPI tubes' length & diameter is possible through the use of sonication & temperature adjustments in the assembly.

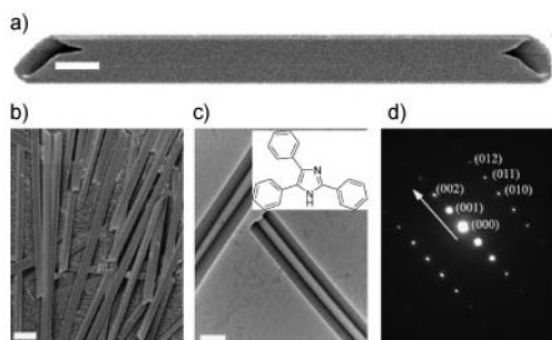


Figure 3. a) Typical SEM image of a single TPI nanotube; scale bar represents 200 nm. b) SEM image of the tubes; scale bar represents 500 nm. c) TEM image of the tubes; scale bar represents 200 nm. Inset: Chemical structure of a single TPI molecule. d) SAED pattern of the tubes along the zone axis with the main diffraction spots indexed.

Self-Assembly Through Organogelation

Each of the components in the mixture exists as its own continuous phase throughout the system, and this is what is meant by the term "Agel," which describes a diluted mixture of at least two components. There are two main types of gels, based on the interactions that hold the network structure together: chemical gels & physical gels.

Organogels can be used to create organic 1D NMs with a variety of structures & properties. Amphiphilic molecules, cyclohexane substitutions, & cholesterol-derived organogels are all included in this category. Despite the fact that long alkyl chains & steroidal groups are inactive and unacceptable for optoelectronic properties, they are utilized to achieve gelation in gelatormolecular structures. Park and coworkers reported a new class of LMOGs, 1-cyano-trans-1,2-bis(30,50-bistrifluoromethyl-biphenyl)ethylene (CN-TFMBE) with simple CF3 substituents. As displayed in Figure 4, thermoreversible gels were obtained by the gelation of dichloroethane by CN-TFMBE. The SEM images shown in Figure 4c suggest that CN-TFMBE created entangled 3D networks consisting of bundles of fibrous aggregates. Figure 4d indicates that the gelation induced strong fluorescence emission, although CN-TFMBE monomers are totally nonfluorescent in 1,2-dichloroethane solution. Analogue experiments proved that the unique gelation capability of CN-TFMBE was endowed by the simple CF3 groups through two structural features: 1) the rigid-rod-like aromatic segments exerted strong p-p stacking interactions, and

2) the CF3 components induced and stabilized molecular assembly with its strong secondary bonding forces.

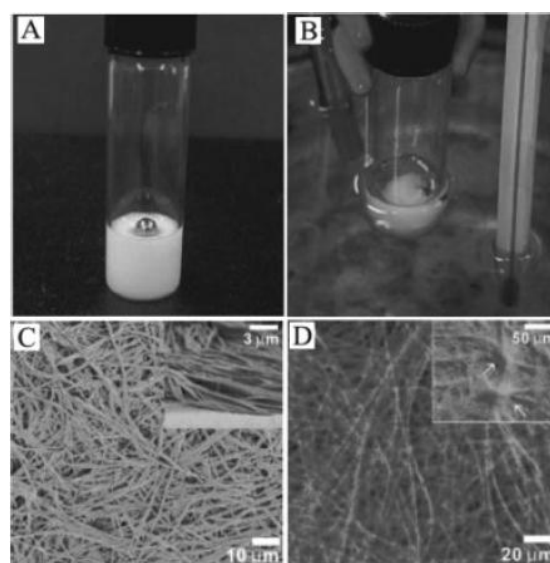


Figure 4. a) CN-TFMBE gel sample on which a metal ball is placed at room temperature. b) The same gel sample immersed in a temperature regulated bath at 51.8°C. c) SEM images of a dried CN-TFMBE gel. d) Fluorescence microscopy images of a CN-TFMBE organogel.

Self-Assembly with solvent Evaporation

When solvents evaporate, most organic materials solubilized in assured solvents would self-assemble & aggregate. Even so, it is intricate to control the assembled products' size, morphology, & uniformity, especially in the nanometer range, even though well-defined macroscopic single crystals can be achieved. TPI 1D nanomaterials with a wide range of properties were recently produced using sonication in the solvent evaporation process by Yao et al. (2006). We started with 5mL TPI solutions of various solvents and concentrations on the substrates (glass or quartz). After that, the solutions were sonicated for about 10 minutes in a commercial ultrasonic cleaning bath.

Vapor Deposition

Indirect & practical ways to make nanomaterials is through vapour deposition (VD), which has been used to make inorganic 1D NSs, polymeric thin films, & inorganic-polymer nanocomposite materials. When small organic molecules are chosen as deposition sources, it is difficult to control the monodispersity of the products. It is well-known that the saturation level in VD is the primary determinant of product morphology and dispersion, so processing most solids into 1D nanostructures should be feasible with low vapour saturation levels. In the VD preparation of organic 1D nanomaterials, local

supersaturation can be controlled using a variety of techniques.

Morphology control between 0D & 1D

Inorganic nanostructure morphologies have been effectively controlled by selecting the right materials & changing the synthesis methods. Controllable synthesis is a key task in nanoscale science. Moreover, the control of organic nanomaterials' morphology has been limited. Organic nanostructures are commonly modulated by making a series of derivatives with slightly altered molecular structures.

Self-assembly of dyes with different substituents

Solvent exchange induced target molecule self-assembly. SEM images of compounds 1 & 2 in nonsolvents are shown in Figures 5A & B, respectively. Changing the substituents clearly had a significant impact on the aggregate morphology. N-methylpyridinium (Nmpd) is an electron-withdrawing moiety, as illustrated in Figure 8C, while N-methylpyrrole (Nmpr) is an electron-releasing group, depicted in Figure 5. This time, the Nmpd moiety is Connected to 2 weaker electron-releasing groups, 4-hexadecyloxyphenyl. The aggregation & formation of 1D nanostructure is primarily driven by strong donor-acceptor interaction because one is planar molecule. In contrast, molecules 2 has weak donor-acceptor interactions & nonplanar. Since the ionized pyridine ring has two long, flexible alkyl side chains, molecules 2 is a typical amphiphilic one, with hydrophilic head & two long, flexible hydrophobic arms, leading to H-aggregates with monodisperse spherical morphologies as depicted in fig 8c.

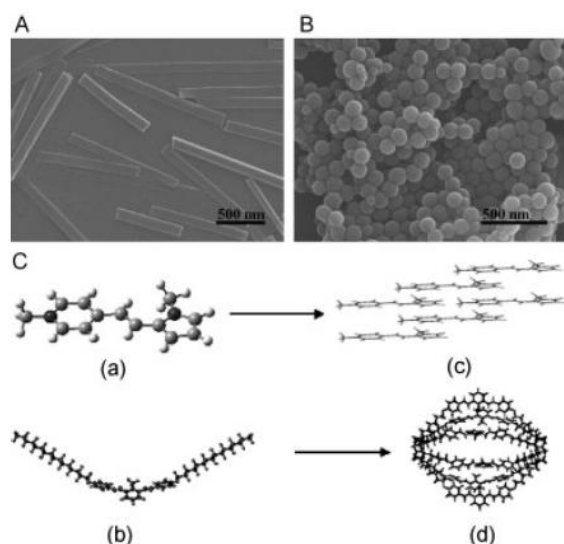


Figure 5. A) SEM image of the nanorods formed from 1. B) SEM image showing a large quantity of the nanospheres prepared with 2. C) Schematic illustration of the aggregation modes of target compounds, in which (a) and (b) are optimized structures of 1 and 2 single molecules, respectively; (c) and (d) are the simulated 1D and 0D aggregation of 1 and 2, respectively.

Beyond 0D & 1D Structure

Other organic NSs, such as hierarchical gatherings of simple nanoscale building blocks, were reported in addition to 0D & 1D nanomaterials. Due to its unique optoelectronic properties, organic building blocks have recently been the subject of extensive research into hierarchical self-assembly via the induction of noncovalent intermolecular interactions, such as hydrogen bonding, p-p stacking, van der Waals forces, & coordination interaction. The formation of the ordered mesostructures was attributed to multistage association, according to spectroscopy that COSY with 2D NOESY. By exploiting the coordination interaction between DPI & copper, the researchers further encouraged it to self-assemble into higher-order mesostructures at the copper-solution interface. In the formation of DPI mesostructures, DPI-copper complexes played a pivotal role.

OPTOELECTRONIC PROPERTIES

Organic nanomaterials aggregated in nanostructures via molecular aggregation have been studied for their unique optical or electronic properties in addition to the synthetic strategies. Intermolecular interactions between molecules in organic nanomaterials are generally weak, such as H-bonds, p-p stacking & van derWaals contacts. This means that the optical & electronic properties of organic nanomaterials are significantly similar from their inorganic counterparts. In this section, we give an overview of current studies on the optoelectronic performance of organic nanostructures. First, the size-dependent optical properties are discussed, then more attention will be paid to the unique photoluminescent properties, and finally the electric and electronic properties are also introduced briefly.

Size-Dependent Optical Properties

The size-dependent optical properties of organic nanoparticles, which are similar to but cannot be explained by the so-called quantum confinement effect observed in inorganic semiconductor quantum dots, were first observed in perylenenanocrystals and reported by Nakanishi and coworkers [1992]. In addition, Horn and coworkers investigated the effect of both supramolecular structure and particle size on the absorption spectra of b-carotene nanoparticles. Recently, Yao's group also systematically investigated the size-tunable optical properties of organic nanoparticles prepared from a series of aromatically substituted pyrazoline compounds. In the following four sections, we will outline the effect of size on the absorption and luminescence properties of these nanoparticles based on pyrazoline compounds.

Exciton Confinement Effect

To make nanoparticles, we used the method of reprecipitation to extract the nanoparticles from PDDP. As shown in Figure 6, the nanoparticles &

monomers of the PDDP are absorption spectra. The phenyl ring transition & pyrazoline ring n^* & π^* transitions result in three resolved absorption bands in solution, which are labelled P_{phenyl}, P _{$n^*\pi^*$} , and P _{$\pi^*\pi^*$} , respectively. When the solution concentration was changed from 1.0×10^{-5} to 1.0×10^{-3} mol L⁻¹, none of the three bands shifted. The P_{phenyl} & P _{$\pi^*\pi^*$} bands were experiential to shift to longer wavelengths as the nanoparticles grew in size from 10 to 100 of nanometers, new peak gradually emerged.

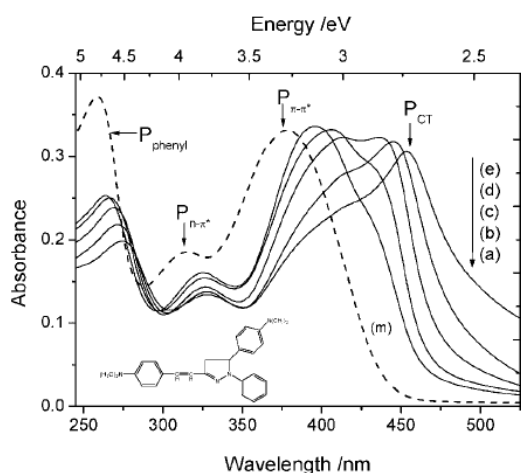


Figure 6. UV-vis absorption spectra of PDDP nanoparticle dispersions in water with different sizes: a) 20 nm, b) 50 nm, c) 105 nm, d) 190 nm, and e) 310 nm. Curve m: The spectrum of the PDDP/ethanol solution (1.0×10^{-5} mol/L).

Other Size-Dependent Properties

Furthermore, Yao and his colleagues analyzed the chirality of excitons in organic nanoparticles, in addition to the above-mentioned optical properties. Using (R)-(-)-1,10-bis(2-naphthol) dimethyl ether (BNDE), they created nanoparticles with particle sizes ranging from 25 to 100 nm. Circular dichroism (CD) spectra of the BNDE NPs showed positive exciton chirality in the 200–260 nm. The BNDE nanoparticles exhibited positive exciton chirality in the 200–260 nm region in CD spectra, which is completely opposite to CD spectra of the dilute solution. The exciton chirality peaks evolved to the low-energy side with an increase in particle size. Intermolecular exciton coupling between two neighboring BNDE molecules in the nanoparticles caused the chirality inversion, & increase in intermolecular interaction was responsible for the bathochromic shift of the peaks as the particle size rose. Nanoparticles were also produced using an azo transition metal chelate compound, & 3rd order nonlinear optical (NLO) properties were studied. It was verified that these nanoparticles exhibit increased and size-tunable off-resonant third-order NLO responses. Increased intramolecular CT process as a result of enhanced planarity of the ligands was shown to be the source of the NLO improvement of the nanoparticles compared to that of the monomer. The NLO responses of the nanoparticles vary in accordance with their size, and

this is attributed to the intermolecular CT taking over for the intramolecular CT as the particle size increases.

Other Optoelectronic Properties

Other optoelectronic properties of organic NMs have been details recently, among other luminescent ones. Many researchers have studied the conductance of organic nanowires & emission properties of nanowires, such as Jalili & Rafii-Tabar in 2005, respectively. A single-crystalline organic 1D nanomaterial was used by Kai Xiao [2007] to fabricate field-effect transistors (FETs), or optical waveguiding properties of organic nanowires were noted by the groups of F. Quochi [2005] & Takazawa [2007]. Another useful approach for organic 1D nanomaterials is the use of lasers.

CONCLUSION

An analysis of current study on NMs derived from small organic functional molecules has been presented, as well. We began by describing the methods used to build organic nanostructures. In the following section, we'll go over how to make 0D organic nanomaterials before moving on to 1D organic nanostructures. Also discussed was the control of organic NMs morphology by means of molecular design & syntheses. In the following section, we describe some of the organic nanomaterials that have been synthesised to date and their unique optical & electronic properties. Nanostructured patterns & thin films on solid substrates are necessary for the fabrication of realistic devices made from organic nanomaterials, including optical waveguides & optical/electrical pumped lasers, which are currently being studied.

REFERENCES

1. C. W. Evans, C. L. Raston, and K. S. Iyer, Nanosized luminescent superparamagnetic hybrids, *Green Chem.*, **12**, 1175–1179 (2010).
2. C. Xiangfeng, J. Dongli, A. B. Djuris'ic, and Y. H. Leung, Gas-sensing properties of thick film based on ZnO nano-tetrapods, *Chem. Phys. Lett.*, **401**, 426 (2005).
3. C. Zhai, N. Du, H. Zhang, J. Yu, and D. Yang, Multiwalled carbon nanotubes anchored with SnS₂ nanosheets as high-performance anode material of lithium-ion batteries, *ACS Appl. Mater. Interf.*, **3**, 4067, (2011).
4. C. Zuo, D.-W. Pang, D.-C. Wu, and Y.-B. Shi, Biofunctionalization of fluorescent-magnetic-bifunctional nanospheres and their applications, *Chem. Commun.*, 4276–4278 (2005).

5. Cao, C., Chu, Y., Zhou, Y., Zhang, C., & Qu, S. (2018). Recent advances in stretchable supercapacitors enabled by low-dimensional nanomaterials. *Small*, 14(52), 1803976.
6. Cao, M. S., Wang, X. X., Zhang, M., Shu, J. C., Cao, W. Q., Yang, H. J., ... & Yuan, J. (2019). Electromagnetic response and energy conversion for functions and devices in low-dimensional materials. *Advanced Functional Materials*, 29(25), 1807398.
7. Chen, P., Tong, Y., Wu, C., & Xie, Y. (2018). Surface/interfacial engineering of inorganic low-dimensional electrode materials for electrocatalysis. *Accounts of Chemical Research*, 51(11), 2857-2866.
8. D. Wang and H. Möhwald, Template-directed colloid self-assembly—The route to top-down nanochemical engineering, *J. Mater. Chem.*, 14, 459(2004).
9. D. B. Suyatin, J. Sun, A. Fuhrer, D. Wallin, L. E. Fröberg, L. S. Karlsson, I. Maximov, L. R. Wallenberg, L. Samuelson, and H.
10. D. G. Choi, H. K. Yu, S. G. Jang, and S. M. Yang, Colloidal lithographic nanopatterning via reactive ion etching, *J. Amer. Chem. Soc.*, **126**, 7019(2004).
11. D. Wang, M. P. Gil, G. Lu, and Y. Lu, Nanostructured systems from low-dimensional building blocks, in *Nanofabrication Towards Biomedical Applications: Techniques, Tools, Applications, and Impact*, in C. S. S. R. Kumar, J. Hormes, and C. Leuschner Eds., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG (2005).
12. D. Wang, T. Xie, Q. Peng, and Y. Li, Ag, Ag₂S, and Ag₂Se nanocrystals: Synthesis, assembly, and construction of meso-porous structures, *J. Amer. Chem. Soc.*, **130**, 4016(2008).
13. D. Xia, D. Li, Y. Luo, and S. R. J. Brueck, An approach to lithographically defined self-assembled nanoparticle films, *Adv. Mater.*, **18**, 930(2006).
14. D. Xu, Z. Liu, J. Liang, and Y. Qian, Solvothermal synthesis of CdS nanowires in a mixed solvent of ethylenediamine and dodecanethiol, *J. Phys. Chem. B*, **109**, 14344(2005).
15. D. Yuvaraj, R. Kaushik, and K. N. Rao. Optical, field-emission, and antimicrobial properties of ZnO nanostructured films deposited at room temperature by activated reactive evaporation, *ACS Appl. Mater. Interf.*, **2**, 1019(2010).

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