Synthesis and Applications of Functional Nanomaterials

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Abstract. The unique physical and chemical properties and variable application potential of nanomaterials are continuously devoted to stimulating scientists' studying enthusiasm. Extremely fine grains bring quantities excellent properties such as low density, low elastic modulus, high resistance and low thermal conductivity to nanomaterials, which has extensive use in the photoelectric field, environment, bioengineering and other fields. The research progress of graphene quantum dots, transparent reflective coatings and self-assembled nanotubes are mainly demonstrated. This paper shows the role of graphene quantum dots in solar cells, summarizes the synthesis methods of self-assembled nanotubes and their applications in bioengineering, and describes the development of transparent thermal reflective coatings for energy-saving glass attributed to providing relevant reference and basis for the development and research of nanomaterials.

1. Introduction
A newly developed material, nanomaterial has a microstructure modulated in nanoscale in at least one-dimensional [1]. The very small size and high surface area are devoted to its special properties, such as the quantum size effect, which enables scientists to utilize them in significant applications, including electronics, optics, biology, thermal and so on [2].

Since the advent of nanomaterials in the 1970s, with the invention of scanning the tunneling microscope and fullerene, nanomaterials have become the frontier hotspot of material science and condensed matter physics [3]. Entering the 21st century, with the help of sophisticated devices and comprehensive synthetic approaches, the joint utilization of nanomaterials in different directions has brought new light for the innovation of technology and applications. Among these nanomaterials, three particular nanomaterials have gained increasing attention due to their outstanding characteristics and high performance in corresponding applications.

As new carbon-based nanoparticles, graphene quantum dots are non-toxic with stable physical and chemical properties and have overcome the gapless limitation of traditional graphene materials. The transformation of particle size can greatly save the cost of preparing large-area graphene and reduce the difficulty of graphene production and increase the incident rate of light. These excellent performances make it widely used in the field of solar power generation.
By applying the responses of various nanomaterials to different wavelength radiations, heat reflection function coating materials could be constructed as another advanced application [4]. Since Airco company directly deposited metal heat reflection materials on the glass to form the one-layer film in the 1980s, the exploration of materials and synthesis methods of glass heat reflection nano-coating has never stopped [5]. Currently, many coating forming methods have been invented, and dozens of excellent materials have been found. The geometry of nanoparticles and layer number of the coating are also no longer single. Thanks to the efforts in materials and processes from scientists, the heat-reflection effect has been significantly improved. Some coatings can perform additional self-cleaning functions to make full use of the natural resource.

A type of self-assemble nanomaterials, self-assemble nanotube, has been largely focused on by scientists due to their unique long hollow cylinder structures and functional surfaces. The surface utilization with nanoparticles or functional groups, and nanocarrier properties with the scale of biomolecules, have enabled this amphiphilic functional nanomaterial in biomacromolecule encapsulation and drug delivery applications, which also brought the huge breakthroughs of host-guest science in bioengineering.

Focusing on the unique characteristics and function of the nanomaterials mentioned in the above three directions, this paper will discuss and summarize their core technologies and applications and guide researchers to optimize the synthesis methods or potentially develop more efficient products on this basis.

2. Graphene quantum dots

2.1. Synthesis of graphene quantum dots

In the current research on graphene quantum dots (GQDs), the most widely used preparation methods mainly include hydrothermal, solvothermal, phase transfer, electrostatic, electrochemical, and microwave-assisted preparation methods.

Kim et al. prepared a thin uniform film with CdSe QDs deposited on graphene by electrochemical deposition for the first time [6]. The results demonstrate that CdSe QDs are arranged in a hexagonal structure and evenly dispersed on the graphene surface without any damage to graphene sheets. This method enables the quantum dot layer to be directly combined with a graphene sheet without a bridge, which can effectively improve the electrical and mechanical properties of the material [7]. Yu et al. succeed in selectively depositing CdSe nanoparticles on reduced graphene oxide by the method of autocatalytic chemical vapor deposition (CVD), which provides an opportunity to make high-performance photovoltaic devices [8]. Yan et al. selectively grew CdS and CdSe QDs on the surface of the graphene sheet simultaneously, as shown in Fig. 1. Polymer chains are used as templates to induce the formation of nanoparticles, stabilize and prevent their further nucleation. The experimental results show that the absorption spectrum of the composite has been extended to the visible region, which has a promising future to be used as electrode material for photoelectrochemical solar cells.

![Fig. 1 The fabrication process of CdS/CdSe graphene [9]](image)
2.2. *Photoelectrochemical cell based on GQDs*

The unique electrical properties of graphene combined with the excellent luminescence properties of semiconductor quantum dots are all key parts to give the graphene semiconductor quantum dot composites great application potential in the field of optoelectronics. As an electronic channel, graphene can effectively improve the photoelectric conversion performance of semiconductors. One of the most typical applications is to apply GQDs to photoelectrochemical cells (PEC).

Graphene-CdS quantum dot composites synthesized by the in-situ method have significantly better battery cycle performance than graphene and natural graphite as cathode materials for lithium-ion batteries. For example, Chang et al. successively added Cd$^{2+}$ solution and S$^{2-}$ solution to PB-graphene functionalized by pyrene butyrate (PB) by in-situ growth method to obtain CdS QDs graphene complex [10]. Under illumination, electron-hole pairs are generated in CdS QDs and dissociated at the quantum dot/graphene interface. Then the electrons are transferred to the graphene support and transmitted to the indium tin oxide (ITO) electrode. The whole process is shown in Fig. 2. Compared with CdS/CNTs composites, quantum dot sensitive fossil graphene PEC shows better photocurrent generation ability and incident photo to electron conversion efficiency in the visible region. This improvement in efficiency is attributed to the unique lamellar morphology, electronic properties and the in-situ growth of quantum dots on graphene. This experiment has obtained a photoelectrochemical cell based on quantum dot sensitive fossil graphene for the first time, which provides a new platform for the application in the field of optoelectronic.

![Fig. 2 Whole process of in situ growth of CdS QDs on graphene and QDs sensitized graphene photoelectrodes [11]](image)

2.3. *Novel solar cells based on GQDs*

In recent years, a large number of studies have shown that GQDs composites can be made into photovoltaic equipment with excellent performance, which provides a new direction for the development of high-performance condensing devices and new solar cells.

However, there is little evidence that GNs (Graphene nanosheets)-semiconductor QD nanocomposites with high dispersion have been synthesized [12]. The main obstacle to the synthesis of semiconductor quantum dots on GNs surface is that introducing metal ions into GNs aqueous solution will lead to their immediate aggregation. Therefore, semiconductor quantum dots with good dispersion cannot be obtained by conventional methods. Wang et al. can directly synthesize graphene CDs and graphene ZnS quantum dot nanocomposites from graphene oxide by a simple one-step solvothermal method [13]. CDs and ZnS can be well dispersed on graphene nanosheets. Photoluminescence measurements showed that the combination of CDs and ZnS with graphene significantly reduced their photoluminescence. Transient photovoltage studies show that graphene CDs composites exhibit a very strong positive photovoltaic reaction, while pure graphene sheets and CdS quantum dots do not, indicating that the composites can be made into high-performance photovoltaic devices. The energy conversion phenomenon observed in the experiment may provide useful information for developing next-generation high-performance photovoltaic devices.
2.4. Dye sensitized battery based on GQDs
Quantum dot sensitized solar cells (QDSSCs) have attracted extensive interest as a method to manufacture high-efficiency and low-cost photovoltaic cells. In QDSSCs, quantum dots, such as graphene, CdS, CdSe and CdTe, are connected as photoanodes to broadband gap semiconductors, which are usually TiO$_2$ or ZnO. After light absorption, electrons are injected, and holes are transferred to the counter electrode through a suitable electrolyte. Due to the impact ionization effect, multiple electron-hole pairs can be generated in each photon by using the hot electrons in quantum dots. Therefore, the power conversion efficiency of QDSSCs is expected to exceed 31%. Despite these characteristics, the efficiency of QDSSCs based on these traditional photoanodes is still very low. Effective electron-hole pair dissociation and electron collection are still great challenges for QDSSCs. Chen et al. proposed an electrophoretic deposition method to assemble graphene CdSe (G-CdSe) nanocomposites (NPs) on flexible substrates, and the energy conversion efficiency (PCE) was 0.6%. The corresponding photoelectric conversion efficiency was as high as 17% [14]. Compared with graphene alone and pure quantum dots, the performance of QDSSCs was significantly improved, demonstrating the promising application future in the photovoltaic field.

3. Transparent heat reflective coatings materials

3.1. Basic principles
The 'unnecessary heat radiation' basically means near-infrared radiation (NIR). According to Brady's research, this radiation band that doesn't affect people's observation of the outside world brings in more than 50% of the heat [15]. The mission of almost all heat-reflecting coatings is to 'make enough visible light pass through' and 'block as much near-infrared radiation as possible'.

In this field, controlling the ability to reflect specific radiation is based on two main reaction mechanisms: reflectance and scattering [15]. The reflectance depends on the nanomaterial's optical properties-- which are closely related to the 'band gap'. And the scattering depends on the refractive index of the material---high refractive index could make the material have low emissivity.

In subsequent studies [16], the material's ability to reflect infrared light and its refractive index proved to be proportional. Based on these principles, scientists began to explore the manufacture and application of such nanomaterials. In 1992, the 'resin+ground micro-nano metal particles' coating structure had become a mature system [15]. And titanium dioxide, one of the typical transparent heat reflection materials, was also found and started to be applied.

3.2. New development in recent ten years
Scientists recently began to try to find the main greenhouse gas emissions and energy consumption fields and reduce them. As an important channel of heat exchange between the internal and external environment, Window is soon noticed by them. Heat reflective coating could indirectly reduce the energy use and greenhouse gas production of AC. At the same time, nanotechnology has become a new term that people are keen to use, which also inspires further innovation in this field.

Therefore, related transparent nano-coating research has developed rapidly, and there has been an evolution in material selection, synthesis technology, and configuration design.

3.3. More abundant reflective materials choices
After the early period, which used gold, silver, nickel, aluminium and other metals making single metal coating [17], many studies have proved the significance of TiO$_2$ in the field of nano-optics [18]. Its high visible light transmittance, high refractive index and wide gap are entirely born for the heat reflection of transparent coatings. It is also good at ultraviolet absorption and can also obtain self-cleaning function after super hydrophilic processing.

Like ZnO (or SnO$_2$), which is also a transparent conductive oxide (TCOs), having some similar properties with TiO$_2$, could be the matrix and dope a series of donors [19] to get excellent NIR reflection ability. In this kind of doped-type materials, the best effect can be achieved when the concentration of
donors is appropriate [20]. At the same time, these doped donors themselves can also be used as excellent NIR reflection materials [19].

Even only considering simple substance metal materials used in this field, some expensive (like Au, Ag) or inefficient materials (like Al) are being replaced. Contrarily, nanocopper has both low cost and good heat reflection ability and is accepted [18].

With the emergence of new elements --- lanthanides, a new important member has been added to the heat-reflecting coating family. After some lanthanide compounds undergoing the absorption/reflection spectrum and the transmittance examination and getting an excellent result, some scientists immediately applied them to the coating and obtained a stronger effect than previous reflective materials [21].

3.4. More abundant synthesis technology

Magnetron Sputtering: This method bombards the target material with given DC power high-energy particles and makes the target nanoparticles punched out and deposited on the glass surface to form a thin film layer [18, 22]. Those coatings that have a 'sandwich' structure with an elemental metal reflective core are always manufactured in this way.

MOCVD: The precursor gas that can react to form target nanoparticles is added, and then the coating is deposited under the protection of high-temperature inert gas [20]. Most coatings doped with extra carrier material are prepared in this way.

Above are the two most common deposition methods today [20], which are suitable for multilayer and doped coating production, respectively.

'Resin-ground nanoparticles': using resin to wrap reflective particles is still thought of as an unfailing approach that was inherited, but the choice of particles started to become new materials, like some compound of lanthanide metals discovered only a few years ago [21].

Sol-gel method [23]: The prepared sol with the properties of NIR interference filter are covered on the glass by the conventional impregnation method.

3.5. The trend of structural optimization

After reading dozens of journals of different periods, the author found that the morphology and structure of the content of nanomaterial heat reflection coating are complicated with the progress of technology. From the technology of heat reflective particles carried by resin became mature in 1992, almost all the research could not leave 'composites'. 'Doped' materials are a good example. Later, more auxiliary materials appeared, and more functions or effects were pursued. Hence, the composite coatings have evolved a meaningful structure---lamination structure.

The lamination structure allows the materials to be set in place according to their functions, rather than all the materials being jumbled together. Protective material layer (always SiO₂, has extremely stable physical and chemical properties [23]) could be set surround the vulnerable core reflective material in the middle for preventing harmful chemical reactions damaging the coating. Placing some dielectric material on the periphery can improve visible light transmittance [16], such as TiO₂.

Suppose the lamination structure upgrades the durability and transmittance of the heat-reflecting coating and gives it additional functionality. Is it possible that one of the structures itself contributes directly to heat reflection or insulation? The answer is yes. Microspheres have low thermal conductivity and light scattering ability. DHTSs used a coating of hollow nanospheres, and the original reflective material and the auxiliary material became applied to the microspheres (Fig. 3) [24, 25]. The typical TiO₂+SiO₂ structure is applied to those spheres, one layer of protection and one reflection layer. Combining the advantages of both lamination and microsphere structures in such products makes it become the latest technology of this year.
3.6. Comparison of old and new technologies

In this field, old and new technologies are relative. New technologies are not completely superior to old technologies, but each has its own characteristics.

The test results for almost every technique show high reflectivity in the near-infrared region. The highest claimed average near-infrared reflection rate is 85.6% (Fig. 4) from TiO$_2$/Cu/TiO$_2$ structure. However, most technologies reflect at least 50% near-infrared heat (for example, LaPO$_4$ reached about 70%), except for the sol-gel coatings ten years ago—the average reflectivity is only about 30%. But it claimed to be good for mass production, which means lower-cost and high popularizing rate. Therefore, coatings with lower reflectivity cannot be blindly excluded.

Those more efficient new coatings have their own problems, such as the coating containing LaPO$_4$ having its own colors, and nano-copper coating requiring precise scale control to appear neutral. Therefore, the transmittance is not as good as that of conventional TiO$_2$ coatings or other coatings.

Some technologies are setting TiO$_2$ at the outer layer. By processing hydrophilic TiO$_2$ with a low contact angle, they can absorb UV and obtain self-cleaning function [22, 23] through coagulating rainwater into a water film and blocking the dust or dirt away. At the same time, its photocatalytic ability can also promote the self-disintegration of stains. This special feature will increase energy efficiency, which is one of the advantages completely beyond early period technology. An outer layer that can also perform the self-cleaning function is nano ZnO [26].

3.7. Actual utility and prospects

Commonly, the transparent heat reflective coating naturally follows its development purpose and is applied on the glass to manufacture energy-saving windows, or what we call 'low-emissivity windows'.

Fig. 3 SEM image of nano-hollow microspheres and its chromatic structure diagram [24, 25]

Fig. 4 The transmittance/reflectance comparison of TiO$_2$/Cu/TiO$_2$ structure and traditional Ag core [18]
Such glass can be used in many situations, not only common house windows and vehicle windows but also windows of laboratories where the temperature is strictly controlled or windows of manned aircraft. However, in other cases, although it can also be used on other surfaces that need heat reflection processing, such as the surface of building materials [27], instrument surface, and the outer surface of various metal shells, its reflection ability is not as good as some colored coatings because the heat from visible light weaves could not be reflected by these coating—Unless keeping the color of the objects is important.

4. Self-assemble nanotubes
In this section, a type of functional nanomaterials with self-assembly properties, self-assemble nanotube, will be introduced. This novel nanomaterial with a unique tubular structure is developed by tube-forming amphiphilic molecules, which can self-assemble into one-dimensional (1D) hollow cylinder architectures with multi-layer membrane walls and an inner diameter of 10-100nm [28]. Unlike common carbon nanotubes formed by graphene sheets, the composition in self-assemble nanotube contains organic molecules and other macromolecules such as lipids, which is why self-assemble nanotube is also named "self-organic nanotubes" (S-ONTs). A scanning electron microscopy (SEM) image of S-ONTs derived from glycolipids and a fluorescent S-ONTs image are shown in Fig. 5. As self-assembly of nanoscale architecture in bottom-up technology becomes more popular in biological interactions such as host-guest systems, research on S-ONTs has been shifted toward a new era with exemplary applications like biomacromolecule encapsulation and drug delivery, which will be further discussed in this section, with its key properties and synthesis approaches [29].

Fig. 5 (a) SEM image of S-ONTs. (b) a fluorescent microscopic image of fluorescent S-ONTs [30]

4.1. Synthesis of S-ONTs
Synthesis methods of S-ONTs mainly depend on their inner and out surfaces. As a result of different reactants such as common tube-forming amphiphilic molecules or \(\alpha,\omega\)-Biopolar amphiphiles, and different formation processes, including helical formation and scrolling, S-ONTs can form identical or different inner and out surfaces, and consequently, have dissimilar synthetic approaches [30]. Moreover, the precise control of nanotube surfaces and their modifications are essential in the synthesis process, enabling S-ONTs to be functionally utilized in various applications.

Herein, we describe S-ONTs formation mechanism and surface properties, followed by examples of synthetic preparation with identical or different inner and outer surfaces.

4.1.1. Synthetic formation of S-ONTs
The synthetic formation of self-assemble nanotubes is based on the self-assembly process. Self-assembly is a spontaneous atomic or molecular arrangement where disordered molecule units become organized. It has provided a powerful way to design new materials and develop them into functional constructs for specific aims, especially in biological nanomaterials research, as the outcome of most biological nanostructure's formation, such as the formation of the helical structure of DNA, which is the
folding of polypeptide chains or the construction of cell membranes by the assembly of phospholipid [31, 32].

Naohiro et al. has reported a major self-assembly process among chiral and achiral amphiphiles [28]. As shown in Fig. 6, the new helical structure, like DNA, will combine tightly via hydrogen bonding to achieve low energy stability and form the nanotube. By contrast, achiral amphiphiles can self-assemble spontaneously through layer-by-layer (LbL) scrolling by the nature of energy minimization in solution. Both chiral and achiral head groups expose as polar hydrophilic groups in previous self-assembly nanoshells. They become surface components and make sure the inner and outer surfaces are identical and hydrophilic.

![Fig. 6 Chiral and non-chiral self-assemble formation mechanism [28]](image.png)

4.1.2. Synthesis examples of S-ONTs
A typical example of S-ONT synthesis uses glycolipids as monomers. Shimizu et al. has conducted research to synthesize glycolipids for self-assembly in an aqueous solution from glucose and cardanol taken out from cashew nutshell liquid (CNSL) [30,33]. However, this S-ONT has relatively low thermal stability due to a low transition temperature, about 40°C. To improve, scientists have replaced the phenoxy ring with an amide group to create more hydrogen bond matrix and enhance the crystallinity of glycolipid molecules. The result transition temperature has increased by 30°C. To develop mass production for industrial use, a low-cost and greener glycolipid by changing the position of carbon-carbon double bond has been produced and shows higher stability.

4.2. Applications of S-ONTs
4.2.1. Biomolecules encapsulation, stabilization and diffusion
Scientists have designed experiments to discover the ability of S-ONTs to encapsulate and transport biomolecules within the channel interiors via hydrogen bonding and electrostatic interaction [28]. An example of encapsulation via surface modification is binding biotin molecules such as zinc(II)-protoporphyrin IX (ZnPP) ligands. To achieve biotin capture, a type of protein-based nanotubes are synthesized from LbL scrolling and polyamino acid with opposite charges inside the membrane wall [32]. Functionalization with poly-L-arginine (PLA) and human serum albumin (HSA) generates nanotube with higher strength and large pores (great swelling) in water, which attracts ZnPP and other biotin particles to fulfill encapsulation.

As reported by Shimizu et al., a fluorescent resonance energy transfer test on DNA was successfully undergone inside an 80 nm-inner-diameter asymmetrical S-ONT with a cationic inner surface [33]. The interaction between donor particles at the outer surface and acceptor particles at inner surfaces shows the existence of DNA, which can be well detected.

The water confinement effect of S-ONTs can enhance the stability of biomolecules inside the nanotube. This unique effect facilitates a higher viscosity environment that reduces the nucleophilic attack (electron donation) of water molecules toward the molecules, thus protecting and restoring the biomolecules. Using S-ONTs to restore proteins has provided a new solution in long-term storage.
Experiments have shown that no thermal denaturation has been tested, and 90% native state of green fluorescent protein (GFT) has remained when encapsulated in S-ONTs with 10nm inner diameter [30].

The size of S-ONTs can affect the stabilizing efficiency. A narrow interior nanochannel (~10 nm) allows the restraint of mechanical movement and thermal loss from guest molecules. It will provide a protective environment for molecules to stay, fulfilling the stabilization aim. If the inner diameter increases, diffusion of guest particles may be obtained due to the relatively free geometry and decrease in viscosity. The diffusion effect will be more patent in small guest particles because of a lower electrostatic interaction with inner surfaces.

4.2.2. Drug delivery

An effective drug delivery system is essential to ensure sufficient drug bioavailability and well-controlled drug release. Therefore, the requirement of the drug delivery materials is always in the first concern: good drug release control, high binding efficiency, and amenable size and surface.

Amphiphilic inner surfaces of S-ONTs can provide a suitable space for drug delivery, whether the nanoscale guest molecules are hydrophilic or hydrophobic. The functional groups at asymmetrical nanotube surfaces harmlessly interact with drugs to achieve a controllable releasing process. The electrostatic interaction between drugs and inner surfaces can transform from drug storage to drug release via altering the pH condition. A type of S-ONT, β-sheet – nanotube, with distinctive surfaces, has been designed to be a good drug delivery system [34]. It contains charges on the inner surface which can be altered by regulating the solution pH. The drug is entrapped inside at neutral pH, and when pH changes, charges of the entrapped drugs are also led to change, and pH-responsive release of entrapped drugs occurs.

5. Conclusion and outlook

This review describes the synthesis and application of functional materials and makes a meaningful summary of the development of the field. GQDs, which could be synthesized in different methods and combined with some auxiliary materials, has been proved to dominate the design of photoelectrochemical cells, silicon-based solar cells and dye-sensitized cells in the future. Although the function of transparent heat reflection nanocoating is relatively simple in energy-saving and temperature control, its continuous improvement in materials, synthesis methods, and configuration gives it strong diversity and provides manufacturers with different choices based on their industry requirements. Because of the similar synthetic materials and methods as natural biomolecules, S-ONTs have high bio-amenities and a good host-guest system, which make it undertake the work of biomolecule encapsulation and drug delivery in the biomedical field.

Nanomaterials achieving breakthroughs mainly depend on the special properties of nanoscale particles or structures. With the progress of science and technology, scientists have gradually uncovered the microscopic secrets of many reactions, so the interference and optimization of these reactions must also be microscopic. Hence, in addition to these three fields, almost all material fields with physical and chemical reactions will develop functional materials in future to reach better reaction effects.

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