

Review Article

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Porphyrin Nanocomposites in Nanotechnology

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ABSTRACT

Nanocomposites are one form of nanomaterials. The porphyrin nucleus is an attractive skeleton to be functionalized with nanomaterials which can be further process to yield novel porphyrin nanocomposites. The latter is expected to possess novel properties. Porphyrin nanocomposites have found interesting applications in many realms such as antimicrobial agents, anti-tumor/anti-cancer agents, photodynamic therapy, drug discrimination, DNA detection, ascorbic acid sensing etc. The design, synthesis and application of porphyrin nanocomposites is increasing.

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Introduction

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material. This includes porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed¹. These include:

- <5 nm for catalytic activity
- <20 nm for making a hard magnetic material soft
- <50 nm for refractive index change
- <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement

Mechanically, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles such as minerals, sheets such as exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres) [2].

Porphyrins are a class of tetrapyrrolic macrocyclic compounds. The four pyrrole rings are joined by four methine bridges at the β -carbon of the pyrrole molecule. They are a class of heterocyclic molecules. They have a total of 26 π electrons of which 18 are in a planar, continuous conjugated macrocycle. Evidences for aromaticity are confirmed by measurements of their heats of combustion and the planarity of the nucleus. Both free base and metalloporphyrins are planar in nature. They can be functionalized to form extended superstructures, “picket fence” porphyrins. Free base porphyrins

are those without a metal in the centre. Fig. 1.0. shows the structure of a tetraphenyl porphyrin, a useful synthetic building block in supramolecular and nanotechnology. The four nitrogens in the centre can complex a range of transition metals to form a wide range of metalloporphyrins, each of which has its unique metalloporphyrin characteristics³. Fig. 1(b) also shows a zinc metalloporphyrin. Both “free base and metalloporphyrins” have rich photo fluorescence electronic properties. They have also found increasing application in catalysis and photocatalysis. Porphyrins because of their rich photosensing activities have been used in photodynamic therapy (PDT) to kill cancer cells. Porphyrins are usually synthesized via the traditional method involving the condensation reaction of pyrrole and benzaldehyde or the reaction of the condensation reaction of dipyrromethene with an aromatic aldehyde followed by oxidation with p-chloranil. In recent years, porphyrins have been finding increasing application in nanotechnology. Porphyrins continue to attract much theoretical interest, and have been called the “pigments of life”. Thus, this paper reviews the recent advances in porphyrins based nanocomposites

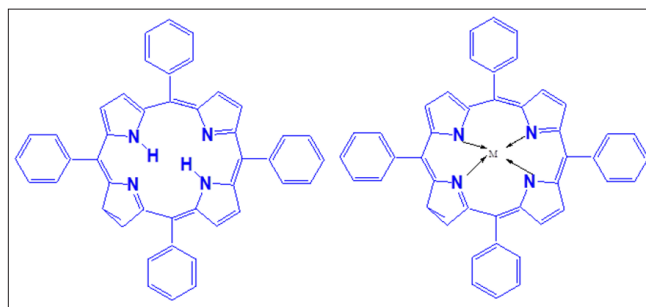


Figure 1: A Tetraphenyl Porphyrin (a) and the Corresponding Zinc Porphyrin

Porphyrin nanocomposites are a versatile class of materials that have been utilized in various fields of nanotechnology. They are known for their unique properties, such as enhanced optical properties, catalytic efficiency, applications in biomedicine and environmental remediation. Porphyrin nanocomposites have some salient properties. These include.

Enhanced Optical Properties: Porphyrin nanocomposite films have a reduced band gap and increased refractive index, making them suitable for applications in solar cells and other optical devices.

Catalytic Efficiency: They have been used to enhance photocatalytic efficiency for degrading organic pollutants in environmental remediation.

Biomedicine Applications: Some porphyrin composites have improved hydrophilicity, allowing for drug delivery, healing, and repairing of damaged organs.

Photodynamic and Sonodynamic Therapy: Porphyrins have been used in photodynamic and sonodynamic therapy, showcasing their versatility in clinical medicine.

These nanocomposites demonstrate the potential of porphyrins in advancing nanotechnology and improving various medical and environmental applications. Their unique properties and applications make them a significant area of research and development in the field of nanotechnology. This paper gives a review of the latest developments and advancements of porphyrin nanocomposites.

Mini Review on Porphyrin Nanocomposites

Porphyrin nanocomposites are a type of nanotechnology that combines porphyrins, a class of naturally occurring pigments, with other materials to create a new, hybrid material. These nanocomposites are being studied for their potential use in synergistic treatment and diagnostics.

Porphyrins have a wide role in photodynamic and sonodynamic therapy, magnetic resonance, fluorescence and photoacoustic imaging. There is a vast range of porphyrins that have been isolated or designed, but few of them have real clinical applications. Due to the hydrophobic properties of porphyrins, and their tendency to aggregate by stacking of the planar molecules they are difficult to work with in aqueous media. Therefore encapsulating them in nanoparticles (NPs) or attachment to various delivery vehicles have been used to improve delivery characteristics. Porphyrins can be used in a composite designed material with properties that allow specific targeting, immune tolerance, extended tissue lifetime and improved hydrophilicity. Drug delivery, healing and repairing of damaged organs, and cancer theranostics are some of the medical uses of porphyrin-based nanocomposites [4].

A one-step synthesis of novel porphyrin-based nanocomposites was achieved using a photochemical under visible light illumination strategy. The research strategy involves the synthesis of ZnTPP (zinc(II)tetrakis(4-phenyl)porphyrin) nanoparticles with Ag, Ag/AgCl/Cu, and Au/Ag/AgCl nanostructures as antibacterial agents. ZnTPP NPs were synthesized via the self-assembly of ZnTPP. The self-assembled ZnTPP nanoparticles were used to make ZnTPP/Ag NCs, ZnTPP/Ag/AgCl/Cu NCs, and ZnTPP/Au/Ag/AgCl NC. Antibacterial activity of porphyrin nanocomposites was investigated against *E. coli*, and *S. aureus*, using the plate count method, well diffusion tests, minimum inhibitory concentration (MIC), and minimum bactericidal concentration (MBC) values determination. The reactive oxygen species (ROS) were determined by the flow cytometry method. All the antibacterial tests and the flow cytometry ROS measurements were carried out under LED light and in dark. The (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay was applied to investigate the cytotoxicity of the ZnTPP/Ag/AgCl/Cu NCs, against Human foreskin fibroblast (HFF-1) normal cells. Due to the

specific properties such as admissible photosensitizing properties of porphyrin, mild reaction conditions, high antibacterial properties in the presence of LED light, crystal structure, and green synthesis, these nanocomposites were recognized as antibacterial materials that are activated in

visible light, got the potential for use in a broad range of medical applications, photodynamic therapy, and water treatment [5].

Core-shell nanocomposite particles which involves combining two or more compositions, possess enhanced or new functionalities that benefited from the synergistic coupling of the two components. New nanocomposite particles with self-assembled porphyrin arrays as the core surrounded by amorphous silica shell has been reported. The synthesis of such a nanocomposite nanoparticles was conducted through a combined surfactant micelle confined self-assembly and silicate sol-gel process using optically active porphyrin as a functional building block. Depending on kinetic conditions, these particles exhibit structure and function at multiple length scales and locations. At the molecular scale, the porphyrins as the building blocks provide well-defined macromolecular structures for noncovalent self-assembly and unique chemistry for high-yield generation of singlet oxygen for photodynamic therapy (PDT).

On the nanoscale, controlled noncovalent interactions of the porphyrin building block result in an extensive self-assembled porphyrin network that enables efficient energy transfer and impressive fluorescence for cell labeling, evidenced by absorption and photoluminescence spectra. The thin silicate shell on the nanoparticle surface allows for easy functionalization, and the resultant porphyrin-silica nanocomposites can selectively destroy tumor cells upon receiving light irradiation [6].

Porphyrin nanocomposites can release therapeutic drugs and photodynamic therapy agents in response to specific stimuli, leading to synergistic treatment. Photodynamic therapy uses light to activate porphyrins, causing them to generate reactive oxygen species that can kill cancer cells. Diagnostics: Porphyrin nanocomposites can be designed to serve as contrast agents for imaging, allowing for improved visualization of tissues and organs. Porphyrins can also be designed to bind specifically to disease-related biomarkers, making them useful for the early detection of diseases such as cancer. Overall, the ability of porphyrin nanocomposites to simultaneously provide both therapeutic and diagnostic functions represents a promising area of research with the potential to improve the efficiency and accuracy of disease treatment and diagnosis [7].

Porphyrins and their associated derivatives have been widely used as photosensitizers for photodynamic therapy (PDT) of tumors. To overcome the limitations of porphyrin photosensitizers in PDT, the combination of porphyrins and nanotechnology offers a new perspective to improve the efficacy and safety of porphyrin-based PDT. To date, various organic and inorganic nanoparticles have been developed for porphyrin delivery for high payload photosensitizers, protection from premature release of photosensitizers, and tumor-selective targeting. In this article, we summarize the strategies for porphyrin photosensitizer delivery, including encapsulation, covalent conjugation, self-assembly for PDT, and characterization methods of singlet oxygen (1O_2) generation. We focus on the summarized strategies of improving cancer PDT efficacy by nanotechnology. Finally, the challenges and outlook for porphyrin-based nanocomposites-mediated PDT are discussed.

Heparin (Hep), widely used in clinics as an anticoagulant drug, has high degrees of heterogeneity and shares a similar disaccharide repeating unit with its GAG analogues [8]. The development of reliable and convenient methods to discriminate Hep from its GAG analogues and detect trace GAG contaminants in Hep is meaningful for safe usage of Hep in clinics. Five porphyrin-GO nanocomposites denoted as PP1-GO, PP2a-GO, PP2b-GO, PP3-GO, and PP4-GO were synthesized by assembling corresponding positively charged porphyrins onto the surface of GO. Controlled by a different number and position of the 4-N-methyl-pyridyl groups substituted at the porphyrins, these nanocomposites were determined to be cross-reactive toward Hep and other three commonly used GAGs including Chs, HA, and DS. A NIR sensor array PP-GO was thus constructed using these nanocomposites for GAGs discrimination and Hep quality control through pattern-based recognition. HCA and LDA calculated results indicated that PP-GO was powerful for discrimination of Hep and its GAG analogues in both PBS and even 10% serum media. Moreover, the PP-GO sensor array was successfully applied for the reliable discrimination of trace GAG contaminants in Hep with 100% accuracy [9].

The precise design of nanocomposites with multiple functions has remained an ongoing challenge. Recently, a tumor microenvironment (TME)-responsive nanocomposite therapeutic platform with a core-shell structure using bismuth (Bi) as the core and iron-porphyrin-containing covalent-organic polymers (COPs) as the shell, has been synthesized and studied. Under the irradiation of an 808 nm laser, Bi efficiently inhibits tumor cell growth through photothermal therapy (PTT), and porphyrin-based COPs can produce reactive oxygen species (ROS) by photodynamic therapy (PDT) under the irradiation of a 660 nm laser combined with chemodynamic therapy (CDT). Bismuth, as a green metal with good biocompatibility also has the potential for use in X-ray computed tomography (CT) imaging and near-infrared (NIR) thermal imaging. Therefore, this nanocomposite integrated multifunctional treatment pathways (PTT, PDT, and CDT) and multimodal (CT and NIR) imaging to cope with the complexity and diversity of tumor cells, effectively improving therapeutic efficacy and becoming a potential candidate for tumor diagnosis and treatment [10].

A nanocomposite material consisting of CrGO (chemical reduced graphene oxide) and tetraphenylporphyrin derivatives, bearing one or four butyloxyphenyl groups, was prepared and fully characterized. The presence of these peripheral groups on the porphyrin skeleton improved both the dispersibility and the electron transfer ability. Furthermore, the non-covalent functionalization of CrGO, obtained through π - π interactions in the case of the mono-substituted porphyrin and additional hydrogen bonds for the tetrasubstituted macrocycle, led to nanocomposites suitable for bioconjugation, thus useful for the fabrication of biosensors devices. The authors reported the use of tetrabutyl-oxy-substituted porphyrin/CrGO hybrid for the detection

of DNA, with a LOD of 1 attomolar and evidenced the ability of the system to discriminate between DNA from RpoB gene of *M. Tuberculosis* strand and mutated in PCR sample [11].

A nanohybrid based on zinc porphyrin noncovalently functionalized graphene oxide has been obtained by Fan and co-authors by hydrogen bonding and π - π stacking interaction and applied as non-enzymatic electrochemical sensor. The scarce solubility of the employed porphyrin limited its application in electrochemistry, but

the authors enhanced the inner electroactivity of the macrocycle by addition of a cationic surfactant (TOAB) and the combination with electrochemically rGO: Such a strategy improved the electron transfer between porphyrin and the electrode (Figure 4). The fabricated system has been studied for ascorbic acid sensing also in real samples, showing high sensitivity (13.58 mA mM⁻¹), a wide linear concentration from 1.33 mM to 1.46 mM (R = 0.998), and a limit of detection as low as 0.28 mM [12].

Porphyrins can be used in a composite designed material with properties that allow specific targeting, immune tolerance, extended tissue lifetime and improved hydrophilicity. Drug delivery, healing and repairing of damaged organs, and cancer theranostics are some of the medical uses of porphyrin-based nanocomposites covered in this review [13].

Conclusion

Porphyrins can be combined with a wide range of materials to form nanocomposites. Some of these materials can be nanomaterials themselves. Nanocomposites have found application in many realm. These include antimicrobial agents, anticancer, photodynamic therapeutic agents, biosensors, electrochemical sensors etc.

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