



Porphyrins and their Hybrid Nanomaterials - Medical and Technical Applications

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The idea of this Editorial rose up from the question of D. H. Michael Bowen *Is Chemistry Useful?* published half a century ago in the Journal *Ind Eng Chem* [1]. In the editorial, Michael Bowen expressed the doubt concerning to the existence of chemistry itself “if chemists will be not concerned themselves with the utility of their profession”.

The position addressed to his colleagues by the American scientist George Simms Hammond, recognized as the father of organic photochemistry, was that the goals of research have to be oriented towards the benefit of society [2].

In this respect, the scientist declared that “The most fundamental and lasting objective of synthesis is not production of new compounds, but production of properties.”

Actual research is deeply concentrated at the border between obtaining of novel chemical structures and formulation of advanced multifunctional hybrid nanomaterials with tailored properties. In life processes porphyrins, metalloporphyrins and their derivatives are involved in catalysis, in photosynthesis and as transporters for small molecules [3].

Starting from this knowledge, the porphyrin supramolecular structures and their based hybrid nanomaterials [4-9] (silica-porphyrin, polymer-porphyrin, colloid-porphyrin, hybrids of cationic porphyrins (with fullerenes, carbon nanotubes and graphene) are designated for advanced optoelectronic devices, such as: optical, fluorescent and electrochemical sensors, photovoltaic cells based on dye and are intensively used as photosensitizers in PDT non-invasive treatments. Porphyrin-conjugated mesoporous silica nanoparticles loaded with anticancer drugs enhanced anticancer therapeutic ability and offer complementary imaging capacity. Porphyrin-hydrogels have range applications in tissue engineering, drug delivery, PDT, and photodynamic antimicrobial chemotherapy [7-9].

Metalloporphyrins-graphene oxide hybrid nanostructures are promising materials for quantitative detection of organic pollutants. This kind of approach is a suitable solution for heterogeneous catalysts based on porphyrins and for offering efficient and reusable catalysts [4]. Photocatalytic disinfection of water, a sustainable chemistry process, using porphyrin-TiO₂ or ZnO or Fe₂O₃ hybrids involves three components, each of them harmless to the environment, namely, the photosensitizer, light and molecular oxygen [10].

Near IR emitting devices are based on globular shape multi-porphyrin arrays that are obtained by integration of porphyrin moieties on dendrimers [11]. These types of dendritic porphyrins [12] were reported to be used for sensitization of oxygen, generating highly toxic singlet oxygen and offering the requirements for PDT.

The major purposes in porphyrins chemistry are focused in designing of new asymmetrically substituted A₃B, cis and trans A₂B₂, and ABCD porphyrin structures having the capacity to enhance both their fluorescence and hydrophilicity (required for PDT and antimycotic/antimicrobial applications) and also to develop new methods to immobilize these porphyrin structures into different inorganic or polymeric matrices preserving the dye optoelectronic properties [13-16]. Porphyrin-inorganic hybrid nanomaterials emphasizing self-lighting nanoparticles for PDT and colloidal and ceramic based nanoparticles as carriers for porphyrins were realized and successfully tested [17-22]. A plethora of strategies were designated to plasmonic hybrids represented by silver and gold nanoparticles functionalized with porphyrins and their applications in imaging, gas sensing and construction of photovoltaic cells [23-26].

Porphyrin/inorganic hybrid coatings prepared via the sol-gel process have garnered considerable research interest both due to the simple processing and relative low-cost and because of the creation of multi-functional surfaces

[27]. The sol-gel nanocoatings have enabled approaching in electronics, optics, solar energy harvesting, aerospace, automotive engineering and health care textiles. The applications envisage: anti-microbial surfaces; easy to clean surfaces; increasing of corrosion resistance; antistatic surfaces; UV protection equipment [28,29].

As a final conclusion and a pertinent answer to the question of Bowen, the researchers concerned with tetrapyrrolic macrocycles can respond: yes, the chemistry of porphyrins is useful.

REFERENCES

- [1] Michael Bowen DH. Is Chemistry Useful? *Ind Eng Chem*, **1969**, 61: 3.
- [2] George Hammond S, *Norris Award Lecture*, **1968**.
- [3] Zhang Y, Lovell JF. Porphyrins as theranostic agents from prehistoric to modern times. *Theranostics*, **2012**, 2: 905–915.
- [4] Mak CA, Pericas MA, Fagadar-Cosma E. Functionalization of A₃B-type porphyrin with Fe₃O₄ MNPs. Supramolecular assemblies, gas sensor and catalytic applications. *Catal Today*, **2017**.
- [5] Fagadar-Cosma E, Tarabukina E, Zakharova N, Birdeanu M, Taranu B, et al. Hybrids formed between polyvinylpyrrolidone and an A₃B porphyrin dye: Behavior in aqueous solutions and chemical response to CO₂ presence. *Polym Int*, **2016**, 65: 200–209.
- [6] Wang C, Yuan R, Chai Y, Chen S, Zhang Y, et al. Non-covalent iron(III)-porphyrin functionalized multi-walled carbon nanotubes for the simultaneous determination of ascorbic acid, dopamine, uric acid and nitrite, *Electrochimica Acta* **2012**, 62, 109–115.
- [7] Tu H-L, Lin YS, Lin HY, Hung Y, Lo LW, et al. In vitro studies of functionalized mesoporous silica nanoparticles for photodynamic therapy. *Adv Mater*, **2009**, 21: 172–177.
- [8] Jing L, Liang X, Li X, Lin L, Yang Y, et al. Mn-porphyrin conjugated Au nano-shells encapsulating doxorubicin for potential magnetic resonance imaging and light triggered synergistic therapy of cancer. *Theranostics*, **2014**, 4: 858–871.
- [9] Liu K, Liu Y, Yao Y, Yuan H, Wang S, Wang Z, et al. Supramolecular photosensitizers with enhanced antibacterial efficiency. *Angew Chem*, **2013**, 125: 8443–8447
- [10] Foster H A, Ditta I B, Varghese S, Steele A, Photocatalytic disinfection using titanium dioxide: Spectrum and mechanism of antimicrobial activity. *Appl Microbiol Biotechnol* **2011**, 90:1847-1868.
- [11] Koo Lee Y-E, Ulbrich EE, Kim G, Hah H, Strollo C, et al. Near infrared luminescent oxygen nano-sensors with nanoparticle matrix tailored sensitivity. *Anal Chem*, **2010**, 82: 8446–8455.
- [12] Lebedev AY, Cheprakov AV, Sakadzić S, Boas DA, Wilson DF, et al. Dendritic phosphorescent probes for oxygen imaging in biological systems. *ACS Appl Mater Interfaces*, 2009, 1: 1292–1304.
- [13] Vinogradov SA, Wilson DF. Metallo tetrabenzoporphyrins. New phosphorescent probes for oxygen measurements. *J ChemSoc Perkin Trans*, **1995**, 2: 103–111.
- [14] Sung T-W, Lo Y-L. Dual sensing of temperature and oxygen using PtTFPP-doped CdSe/SiO₂ core-shell nanoparticles. *Sens Actuators B*, **2012**, 173:406–413.
- [15] Luo D, Carter KA, Lovell JF. Nano-medical engineering: shaping future nano-medicines. *Wiley Interdiscip Rev Nanomed Nanobiotechnol*, **2014**, 7:169–188.
- [16] Svenson S, Tomalia DA. Dendrimers in biomedical applications—reflections on the field. *Adv Drug Deliv Rev* **2012**, 64: 102–115.
- [17] Hsu CY, Nieh MP, Lai PS. Facile self-assembly of porphyrin-embedded polymeric vesicles for theranostic applications. *Chem Commun*, **2012**, 48: 9343–9345.
- [18] Tam NCM, McVeigh PZ, MacDonald TD, Farhadi A, Wilson BC, et al. Porphyrin–lipid stabilized gold nanoparticles for surface enhanced Raman scattering based imaging. *Bioconjug Chem*, **2012**, 23: 1726–1730.
- [19] Fagadar-Cosma E, Cseh L, Badea V, Fagadar-Cosma G, Vlascici D. Combinatorial synthesis and characterization

- of new asymmetric porphyrins as potential photosensitizers in photodynamic therapy. *Comb Chem HT Screen*, **2007**, 10: 466-472.
- [20] He Q, Shi J. Mesoporous silica nanoparticle based nano drug delivery systems: Synthesis, controlled drug release and delivery, pharmacokinetics and biocompatibility. *J Mater Chem*, **2011**, 21: 5845–5855.
- [21] Liong M, Lu J, Kovichich M, Xia T, Ruehm SG, et al. Multifunctional inorganic nanoparticles for imaging, targeting and drug delivery. *ACS Nano*, **2008**, 2: 889–896.
- [22] Couleaud P, Morosini V, Frochot C, Richeter S, Raehm L, et al. Silica-based nanoparticles for photodynamic therapy applications. *Nanoscale*, **2010**, 2: 1083–1095.
- [23] Zhao T, Wu H, Yao SQ, Xu QH, Xu GQ. Nanocomposites containing gold nanorods and porphyrin-doped mesoporous silica with dual capability of two-photon imaging and photosensitization. *Langmuir*, **2010**, 26: 14937–14942.
- [24] Jang B, Park JY, Tung CH, Kim IH, Choi Y. Gold nanorod-photosensitizer complex for near-infrared fluorescence imaging and photodynamic/photothermal therapy in vivo. *ACS Nano*, **2011**, 5: 1086–1094.
- [25] Sebarchievici I, Tăranu BO, Birdeanu M, Rus SF, Făgădar-Cosma E. Electrocatalytic behavior and application of manganese porphyrin/gold nanoparticle- surface modified glassy carbon electrodes. *Appl Surf Sci*, **2016**, 390: 131–140
- [26] Fagadar-Cosma E, Sebarchievici I, Lascu A, Creanga I, Palade A, et al. Optical and electrochemical behavior of new nano-sized complexes based on gold-colloid and Co-porphyrin derivative in the presence of H₂O₂. *J Alloys Compds*, **2016**, 686: 896-904.
- [27] Fagadar-Cosma E, Enache C, Vlascici D, Fagadar-Cosma G, Vasile M, et al. Novel nanomaterials based on 5,10,15,20-tetrakis (3,4-dimethoxyphenyl)-21H,23H-porphyrin entrapped in silica matrices. *Mater Res Bull*, **2009**, 44: 2186–2193.
- [28] Popa I, Fagadar-Cosma E, Taranu BO, Birdeanu M, Fagadar-Cosma GR, et al. Corrosion protection efficiency of bilayer porphyrin-polyaniline film deposited on carbon steel. *Macromolecular Symposia*, **2015**, 352: 16-24.
- [29] Fagadar-Cosma G, Taranu BO, Birdeanu M, Popescu M, Fagadar-Cosma E. Influence of 5,10,15,20-tetrakis(4-pyridyl)-21h,23h-porphyrin on the corrosion of steel in aqueous sulfuric acid. *Dig J Nanomat Bios*, **2014**, 9: 551–557.