



The first solid state porphyrin-weak acid molecular complex: A novel metal free, nanosized and porous photocatalyst for large scale aerobic oxidations in water

Akram Heydari-turkmani, Saeed Zakavi*

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran



ARTICLE INFO

Article history:

Received 24 March 2018

Revised 8 June 2018

Accepted 10 June 2018

Keywords:

Photocatalysis
Porphyrin diacid
Sulfides
Sulfoxides
1,5-Dihydroxynaphthalene
Singlet oxygen
Oxidation in water

ABSTRACT

The first solid state porphyrin dication of a weak carboxylic acid was synthesized through the reaction of meso-tetrakis(N-methylpyridinium-4-yl)porphyrin (H_2TMPyP) supported on the sodium salt of Amberlyst 15 nanoparticles ($nanoAmbSO_3Na$) with formic acid. The polymer-porphyrin hybrid compound, $nanoAmbSO_3@H_2TMPyP(HCOOH)_2$, was characterized by FT-IR and diffuse reflectance (DR) UV-vis spectroscopy, EDX, BET, DLS, FESEM and TGA methods. Interestingly, the diacid was quite stable towards decomposition to the corresponding porphyrin and carboxylic acid in neat water as well as in acetonitrile. The protonation reaction was accompanied with the shift of the Soret band from 435 to 454 nm in DR UV-vis spectrum and a rapid color change from red brown to green. A particle size of 190 and <50 nm was estimated for the nanoparticles by DLS and FESEM, respectively. Also, the macroporous structure of the catalyst was revealed by BET experiments. $nanoAmbSO_3@H_2TMPyP(HCOOH)_2$ was used as photosensitizer for the highly chemoselective and large scale aerobic oxidation of sulfides to the corresponding sulfoxide in water within 3 h at room temperature. A conversion of ca. 95% was observed for the oxidation of sulfides to their corresponding sulfoxide in water with a selectivity of ca. 100%. The use of acetonitrile as solvent led to a significant decrease in the conversion values while retaining selectivity. The higher efficiency of the catalyst in water was in accord with greater singlet oxygen quantum yield (Φ_{Δ}) value of the photosensitizer in this solvent ($\Phi_{\Delta} = 0.41$) relative to that in acetonitrile ($\Phi_{\Delta} = 0.08$). Apparently, cooperative acid catalysis caused by the protic solvent and porphyrin diacid is involved in the preference of water over acetonitrile as the solvent for efficient oxidation of sulfides to sulfoxides. Furthermore, the photosensitizer was used for the efficient oxidation of 1,5-dihydroxynaphthalene (DHN) in water within 15 min. The photocatalyst was remarkably stable towards oxidative degradation so that it could be recovered and reused for at least 5 times without loss of activity. It is noteworthy that large scale photooxidation of sulfides (TON $\approx 5 \times 3000$) and DHN (TON $\approx 6 \times 1000$) were achieved in water, using $nanoAmbSO_3@H_2TMPyP(HCOOH)_2$ as the photosensitizer.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Porphyrins and derivatives have been extensively used as photosensitizer in different applications such as photodynamic therapy, water treatment, medicine and biological studies [1–5]. Recently, much attention has been given to the synthesis of novel porphyrinic photosensitizers with the aim of increasing their photocatalytic activity, product selectivity and oxidative stability [6–9]. Due to the potential toxicity of most transition metals, considerable attention was paid to the synthesis of metal free catalysts [10–12]. On the other hand, owing to the high quantum yields of

singlet oxygen production of metal free porphyrins as organic photosensitizers, a variety of photooxidation reactions were studied in the presence of porphyrin derivatives [13–15]. However, the recovery and reuse of catalyst has been the key challenge for using different compounds under homogeneous conditions [16]. Furthermore, the reduction of catalyst size to nanoscale is a common strategy to overcome the slow kinetics of the reaction catalyzed by heterogeneous catalysts [17–20]. On the other hand, the use of water as the most green solvent is a key component of green chemistry [21]. Porphyrin macrocycle may be substituted at the central nitrogen atoms as well as the peripheral positions [22,23]. In this regard, porphyrin core may be metallated [9], methylated [24] or protonated with different σ and π acceptors [25]. Porphyrin dications may be readily prepared by the treatment of porphyrins with

* Corresponding author.

E-mail address: zakavi@iasbs.ac.ir (S. Zakavi).

different acids in organic solvents and water. The red shifted absorption bands of porphyrins diprotonated species make them interesting alternatives to the corresponding free base porphyrins [26]. However, limited attention has been devoted to developing catalyst and photocatalyst based on porphyrins diprotonated species for organic transformations [27,28]. Recently, we have reported novel porphyrin photosensitizers formed by the molecular complexation of porphyrins with 2,3-dichloro-5,6-dicyano-1,4-benzoquinon (DDQ) and tetracyanoethylene (TCNE) [29]. The presence of DDQ and TCNE was shown to have significant effect on the photosensitizing ability of meso-tetra(aryl)porphyrins in aerobic photooxidation of olefins [25]. Also, very recently we have studied the photocatalytic activity of a series of meso-tetra(aryl)porphyrins immobilized on Amberlyst 15 nanoparticles (nanoAmb) in the form of diprotonated species [17]. In 2018, the dications of H₂TPP with different acids were used for chemoselective oxidation of sulfides to sulfoxides under homogeneous conditions [30]. In the present study, meso-tetrakis(N-methylpyridinium-4-yl)porphyrin (H₂TMPyP) was initially supported on the nano-sized anionic Amberlyst 15 formed by the alkaline treatment of this polymer. Then, the immobilized porphyrin was protonated with formic acid to prepare the core protonated porphyrin (Fig. 1). To our knowledge, it is the first report on the synthesis and characterization of a porphyrin dication with a weak carboxylic acid. Interestingly, the dication was completely stable in different solvents and water. Our previous studies [13] showed that the dications of soluble porphyrins with formic acid are readily decomposed to the corresponding free base porphyrins upon dilution in organic solvents or exposure to water. Also, the dications cannot be dried under vacuum or air flow. This observation gives evidence for remarkable impact of porphyrin immobilization on the stability of porphyrin diacid with weak acids. Furthermore, the solid compound is stable under light conditions and may be

stored for a long time. It is noteworthy that due to the low acid strength of formic acid ($pK_a = 3.75$) [31], the acid cannot reprotonate the neutralized Amberlyst 15 bed ($pK_a = -6.5$) [32]. Moreover, the major weakness of formic acid prevents its involvement in unexpected side reactions. The nano-sized catalyst was used for the aerobic photooxidation of sulfides in neat water as the solvent. The selective oxidation of sulfides to the corresponding sulfoxide is still a challenging synthetic problem that may be achieved through singlet oxygen mediated photooxidation of sulfides under mild conditions [33–35]. Herein, acid catalysis [36–38] induced by the porphyrin diacid and the protic solvent is also involved in the observed rate of the photooxidation reactions. It is noteworthy that sulfoxides are important intermediates in organic synthesis pharmaceutical industry [39,40]. Furthermore, the catalytic activity of the immobilized porphyrin diacid in the oxidation of 1,5-dihydroxynaphthalene (DHN) was investigated [41]. The product of oxidation or photooxidation of DHN, i.e. 5-hydroxy-1,4-naphthoquinone (Juglone) is a naturally occurring aromatic compound which plays an important role in the pharmaceutical and dye industries [42–44]. On the other hand, oxidative degradation of DHN is of importance for the removal of phenolic and naphtholic pollutants from wastewater [45]. The main objective of this study is to present the effects of weak carboxylic acids on the photocatalytic activity and oxidative stability of porphyrins in photooxidation of organic substrates in water under heterogeneous conditions.

2. Experimental

2.1. Instrumental

A Pharmacia Biotech Ultrospec 4000 UV–vis spectrophotometer and a Varian Cary 5000 UV–Vis–NIR absorption spectrometer were used for preparation of UV–vis and diffuse reflectance UV–vis spectra, respectively. ¹H NMR spectra were obtained on a Bruker Avance DPX-400 MHz spectrometer. The reaction mixtures were analyzed using a Varian-3800 gas chromatograph with a HP-5 capillary column and flame-ionization detector. FT-IR spectra were prepared using a Bruker Vector 22 instrument. A Belsorp max (Japan) instrument was employed for porosimetry analyses using the nitrogen adsorption/desorption method. The mean diameter and size distribution of the solid catalyst before and after loading of porphyrin were measured by Zetasizer Nano ZS (Malvern Instruments Ltd, United Kingdom) at 25 °C with a detection angle of 90°. For morphology characterization by FE-SEM, the crushed Amberlyst beads obtained after 24 h were placed on a clean glass slide and then vacuum-coated with gold. Digital images of the samples were taken with HitachiS4160 field emission scanning electron microscope operating at 20 kV.

2.2. Amberlyst 15 nanoparticles (nanoAmb)

Amberlyst 15 beads (dry, ion-exchange resin, ACROS) were stirred vigorously over a magnetic stirrer in ethyl acetate overnight at room temperature to obtain the pale yellow powder of nanoAmb. Details of nanoparticle characterization were described elsewhere [17].

2.3. Preparation of porphyrins

Meso-tetra(4-pyridyl)porphyrin (H₂TPyP) and 5,10,15,20-tetrakis(N-methylpyridinium-4-yl)porphyrin tetra(p-toluenesulfonate), H₂TMPyP, were prepared and purified according to the literature methods [46]. The UV–vis and ¹H NMR spectral data of the used porphyrin are as follows:

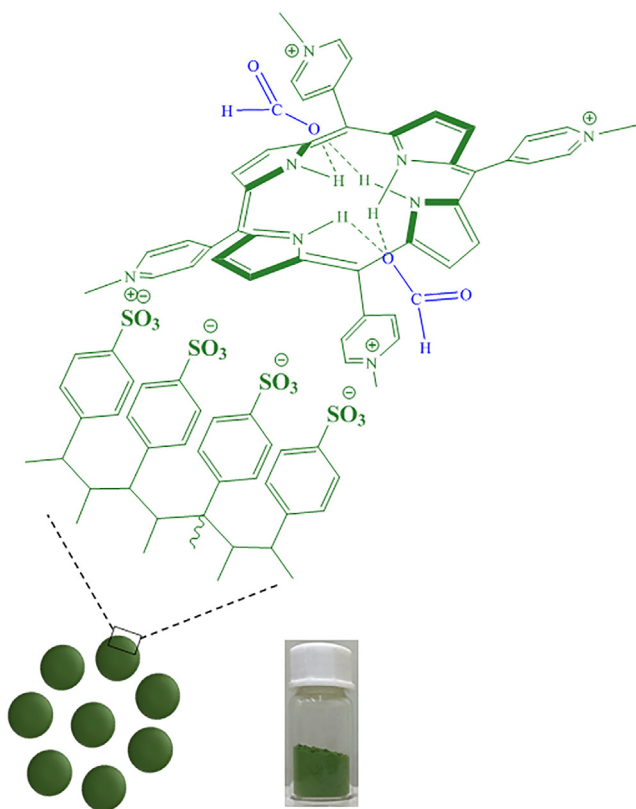


Fig. 1. Immobilization of H₂TMPyP on nanoAmbSO₃Na and its protonation with formic acid.

Download English Version:

<https://daneshyari.com/en/article/6526612>

Download Persian Version:

<https://daneshyari.com/article/6526612>

[Daneshyari.com](https://daneshyari.com)