



Research paper

Novel hybrids of graphitic carbon nitride sensitized with *free-base meso-tetrakis(carboxyphenyl) porphyrins* for efficient visible light photocatalytic hydrogen production

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ABSTRACT

Novel hybrid photocatalysts of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$, CN) sensitized with *free-base* porphyrins were prepared by impregnation through non-covalent interactions. Their photocatalytic activity was evaluated towards the generation of hydrogen (H_2) from water splitting. For this purpose, and in order to ascertain the influence of the carboxy substituents groups and their position on the porphyrin periphery on H_2 production, the porphyrins *meso*-tetraphenylporphyrin (TPP), *meso*-tetrakis(*meta*-carboxyphenyl)porphyrin (*m*TCPP) and *meso*-tetrakis(*para*-carboxyphenyl)porphyrin (*p*TCPP) were used. All the hybrids (TPP-CN, *m*TCPP-CN and *p*TCPP-CN) show higher performance for photocatalytic H_2 production than that of pure CN. Among all the hybrids, *m*TCPP-CN presents the highest amount of H_2 evolved, being of 326 and 48.4 μmol under 6 h of UV–vis and visible light ($\lambda > 400 \text{ nm}$) irradiation, respectively. This photocatalyst was fully characterized by UV–vis, FTIR, XRD, XPS, SEM, TEM, N_2 isotherms and steady-state and time-resolved fluorescence measurements. The fluorescence emission of the *m*TCPP porphyrin was remarkably quenched by CN semiconductor for the various hybrids *m*TCPP-CN containing different amounts of *m*TCPP, consistent with electron injection from the porphyrin excited state into the conduction band of the semiconductor. This work demonstrates that the sensitization of CN with dye porphyrins enhances the photocatalytic H_2 evolution under UV–vis and visible light irradiation, making it a potential material for solar conversion to produce hydrogen from water.

1. Introduction

The demand for energy is increasing with growing global population which is projecting toward 10.6 billion by 2050 [1]. In order to meet this challenge, and due to the gradual depletion of fossil fuel reserves and emission of greenhouse gases, the conventional hydrogen (H_2) production *via* steam reforming of fossil fuels has to be replaced by sustainable and environmentally friendly technologies. Among various potential solutions, solar H_2 production from water splitting using photocatalysts inspired in the natural process of photosynthesis [2–4] holds great promise as an environmentally clean energy for the future since it can be simultaneously considered as a method for both solar energy storage and chemical energy conversion [5,6]. In the last years

many catalysts have been designed and applied for hydrogen production. Yet, and despite all the advances that are being achieved, the quest for photocatalysts able to promote a high and efficient conversion of solar energy into chemical energy is still a challenge.

Over this infinity of compounds [7,8], the metal-free polymeric semiconductor graphitic carbon nitride, $g\text{-C}_3\text{N}_4$ [9], is regarded as the shining star due to its appealing features, which enable it to be employed both in energy conversion [9–11] and environmental remediation [12]. Among other features, $g\text{-C}_3\text{N}_4$ possesses valence (VB) and conduction (CB) band potentials suitable for both water reduction and oxidation (+1.4 V and –1.3 V vs. NHE at pH 7, respectively) [13,14], presents good chemical and physical stability and it is easy to synthesize from low-cost and environmentally friendly precursors, such as

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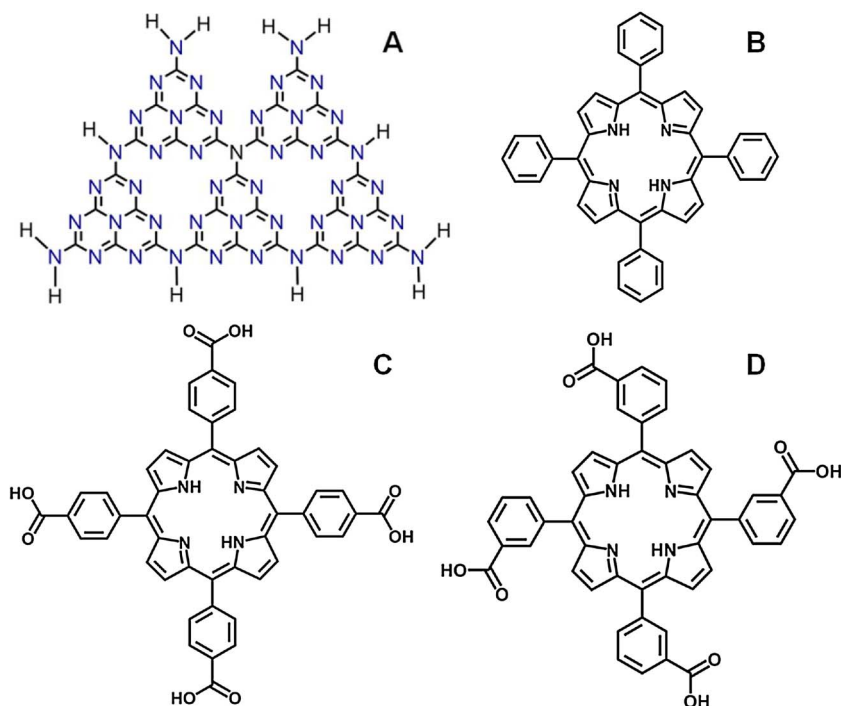


Fig. 1. Chemical structures of the semiconductor CN (A) and of the porphyrins TPP (B), pTCPP (C) and mTCPP (D).

urea, dicyandiamide, cyanamide, thiourea and melamine [12,15]. Although it presents some absorption in the visible region, its band gap (~ 2.7 eV) largely restricts its solar light application. Moreover, the high degree of recombination between photoinduced electrons (e^-) and holes (h^+) also hampers its practical application. Therefore, it is mandatory to find alternatives for overcoming these disadvantages. Some of the methods proposed to increase the photocatalytic activity of g-C₃N₄ include heteroatom doping [16], metal loading [17], coupling with carbon materials such as carbon nanotubes [18] and graphene derivatives [19] and sensitization with organic dyes [20]. Among these strategies, dye sensitization is considered an efficient route, not only to extend the spectral response region of wide band gap semiconductors, enabling more efficient visible light harvesting, but also to enhance the separation and transport of photogenerated electrons and holes at the semiconductor dye interface [21,22], a key factor to obtain better photocatalytic activity. The efficiency of these systems depends on both the properties of the sensitizers and semiconductor, and their interaction upon photoexcitation [20]. Porphyrins and phthalocyanines [23] have merited much attention as dye sensitizers owing to their physical-chemical properties, enabling their use in diverse fields such as in dye sensitized solar cells (DSSCs) [23], medicine (e.g. photodynamic therapy of cancer [24,25] and photoinactivation of microorganisms [26]), photoelectronic devices [27], sensors [28–30], environmental remediation [31], CO₂ reduction [32] and photocatalytic H₂ generation [33,34]. These coloured organic macrocycles exhibit high absorption coefficient in the visible and near IR region (where the maximum of the solar photon flux occurs), that is necessary for efficient photon harvesting, rich redox properties, good chemical stability when compared with other dyes and photoinduced electron transfer and semiconducting capabilities [35]. Indeed, the metalloporphyrin derivative chlorophyll is the paradigm for solar to chemical energy conversion [36]. The ability to tune the photophysical properties of synthetic porphyrins, by modifying the electronic distribution on the aromatic ring via peripheral substitution, led to the design and understanding of numerous porphyrin photonic assemblies which mimic photosynthetic solar energy transduction by converting solar energy into chemical potential in the form of long-lived charge separation states [37]. The sensitization of g-C₃N₄ has been reported using dyes such Erythrosin [38], Eosin Y [39], phthalocyanines [39–41] and porphyrins [42,43].

For instance, Chen *et al.* [42] reported a simple method to assemble Cu(II) *meso*-tetra(4-carboxyphenyl)porphyrin (CuTCPP) on the surface of g-C₃N₄ through a non covalent approach, which promotes visible-light harvesting and enhances the visible light photocatalytic activity towards phenol degradation. Another study carried out by Wang and co-workers [43] reported the synthesis of a pure organic heterostructure of g-C₃N₄/(FeTPP)₂O, in which the porphyrin (FeTPP)₂O acted not just as a photosensitizer but also played the role of charge promoter, inhibiting the e^-/h^+ pair recombination, and leading to an outstanding photocatalytic H₂ production efficiency under solar light irradiation without using any co-catalysts (52.9 μ mol H₂, 4 h). Zhang *et al.* [41] reported the sensitization of g-C₃N₄ by combining an asymmetric zinc phthalocyanine derivative with an organic dye for the photocatalytic H₂ production in the visible/near-infrared region. That work puts in evidence the added value of combining two photosensitizers over one semiconductor for the photocatalytic generation of H₂. Zhu *et al.* [44] reported the non-covalent immobilization via π - π^* stacking interactions of porphyrin over reduced graphene oxide (RGO) nanosheets to obtain the porphyrin/RGO nanocomposite. Porphyrin moiety in the nanocomposite acts as a photosensitizer harvesting light. This composite shows remarkable photocatalytic activity under UV-vis light irradiation attributed to the fast electron transfer from the photoexcited porphyrin molecules to RGO sheets.

Herein, we report the preparation and characterization of g-C₃N₄ (henceforth abbreviated as CN) sensitized with *free-base* porphyrins for the efficient photocatalytic H₂ generation through water splitting. Although these materials present interesting characteristics for photocatalytic applications, porphyrin-sensitized CN has not yet received wide attention, which boosted our interest in exploring this theme. In fact, and to the best of our knowledge, this is the first study using *free-base* porphyrins as CN dye sensitizers for photocatalytic H₂ production. Three different porphyrins were used in the present work (Fig. 1): *meso*-tetraphenylporphyrin (TPP), *meso*-tetrakis(*meta*-carboxyphenyl)porphyrin (mTCPP) and *meso*-tetrakis(*para*-carboxyphenyl)porphyrin (pTCPP).

The porphyrins were immobilized over CN by a simple impregnation method in order to obtain hybrid photocatalysts of TPP-CN, mTCPP-CN and pTCPP-CN. Furthermore, the electron transfer process from the excited state porphyrin to the CB of CN was investigated by

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