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Melem: A metal-free unit for photocatalytic hydrogen evolution

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ABSTRACT

Melem, the building unit of g-C_3N_4, is reported for the first time as a metal-free photocatalyst for hydrogen evolution from methanol aqueous solution. Melem is synthesized via a facile thermal condensation of melamine at 425 °C. Its chemical structure is verified by the combination of Fourier transform infrared spectroscopy (FTIR), solid-state ^{13}C nuclear magnetic resonance (NMR) and elemental analysis. Density functional theory (DFT) calculations reveal that melem possesses frontier orbitals quite similar to those of g-C_3N_4. By conjugating melem with dianhydride monomer, an extended polyimide network with greatly enhanced visible-light absorption is formed. Consequently, the visible-light activity for hydrogen evolution is enhanced by six times and reaches to a rate of 13.1 μmol/h. This work may open up new opportunity to develop efficient metal-free photocatalysts based on melem unit.

Introduction

The search for active photocatalysts that split of water into hydrogen fuel has attracted great attention for its promising potential to settle intractable energy issues using abundant solar energy [1]. Over the past several decades, extensive studies have been centered on metal-containing materials, mainly including inorganic solids (e.g., metal oxides, nitrides, sulfides, phosphates) [2–5] and organic metal complex (e.g. Ru or Pt complex) [6,7]. Recently, Wang et al. reported that a polymer semiconductor, graphitic carbon nitride (g-C_3N_4), can function as a metal-free photocatalyst for H_2 evolution from water in the presence of a sacrificial donor [8]. g-C_3N_4 has many advantages, such as being cheap and abundant, high thermal and chemical stability (stable in air up to 550 °C), which make this material a promising candidate for solar-energy conversion. Moreover, the organic nature of g-C_3N_4 enables plentiful choices to chemically modify the skeleton for enhancing photocatalytic performance, which is well documented in recent reviews [9,10]. To date, g-C_3N_4 has been widely studied as a

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metal-free photocatalyst, however, the investigation of photocatalytic property of melem, the building unit of g-C_3N_4, has not yet been reported to our knowledge.

Melem was one of the oldest synthetic organic materials and first studied by Liebig as early as 1834 [11]. Owing to the insolubility, its molecular structure containing the heptazine ring remained unidentified for more than a century. It was until 1937 did its formula was postulated by Pauling and Sturdivant [12]. In 2003, Schnick and coworkers reported its crystal structure and spectroscopic details, and proved its existence as an important intermediate during the thermal condensation of melamine (MA) to g-C_3N_4 [13], as depicted in Scheme 1. Melem is formed around 400 °C and stable up to 450 °C, at which temperature melon is formed [14,15]. Due to the nucleophilicity of NH_2-groups, melem can react with electrophiles to form various melem derivatives for innovative functions [16].

Herein, we first report that melem is a metal-free photocatalyst for H_2 evolution from methanol aqueous solution, in which methanol roles as a sacrificial agent to consume the photo-induced holes in the valence band of the photocatalyst, while the photo-induced electrons reduce hydrogen ions to product H_2 in aqueous solution. Moreover, by utilizing the rich chemistry of melem, a few polyimide photocatalytic materials based on melem unit are synthesized for solar hydrogen production.

Experimental section

Sample preparation

MA was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd with chemical purity. All dianhydride monomers were purchased from TCI Shanghai Chemical Reagent Co., Ltd.

Melem was synthesized by heating 5 g MA at 425 °C for 4 h into a porcelain crucible with a cover (semi-closed system) by referring to the reported procedures [17,18]. Melem was obtained as a white-beige powder with a yield of 2.85 g.

g-C_3N_4 was synthesized by heating 5 g MA at 550 °C for 4 h in a semi-closed system according to the literature [19]. g-C_3N_4 was obtained as a yellow powder with a yield of 2.38 g.

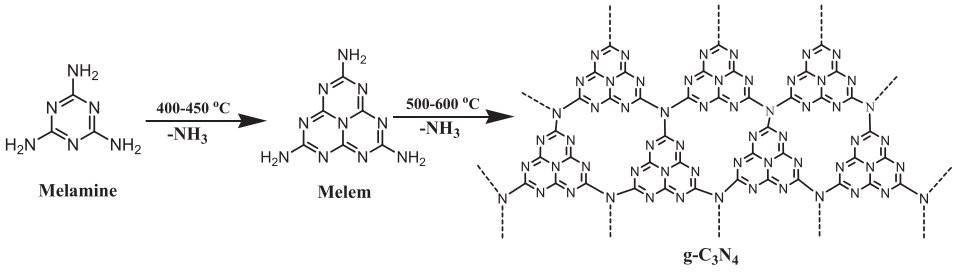
Three kinds of Polyimide (PI) photocatalysts were synthesized in the following procedure: melem (10 mmol) and dianhydride monomers [pyromellitic dianhydride (PMDA); 4,4-biphthalic dianhydride (BPDA) and naphthalene-1,4,5,8-tetracar boxylic dianhydride (NTDA)] with equal molar ratio (10 mmol) were mixed uniformly in an agate mortar, respectively. Then the mixture was put into a porcelain crucible with a cover and heated at 7 °C/min up to 350 °C for 4 h. The resultant deep yellow solid was ground into powder and washed with water at 50 °C to remove any residual monomers if exist. Finally, the solid was filtered and dried at 100 °C overnight. The sample was denoted as PI-1, PI-2 and PI-3 corresponding to the used dianhydride monomers PMDA, BPDA and NTDA. For comparison, a polyimide sample was prepared by thermal condensation of g-C_3N_4 and PDMA using the same synthesis procedure and denoted to PI-g-C_3N_4.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet NEXUS870 spectrometer. Solid-state ^{13}C nuclear magnetic resonance (NMR) was performed on a Bruker Advance III 400WB spectrometer equipped with a 9.4 T magnet. The chemical shift was referenced to adamantane. Elemental analysis was determined by Elementar vario EL analyzer. X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima III X-ray diffractometer using CuKα radiation. TG (Thermogravimetric) analysis was carried out using Netzsch STA 449C equipment with a heating rate of 10 °C/min under a nitrogen atmosphere. UV–Vis spectra were collected by Shimadzu UV-2550 spectrometer. Specific surface area was measured using Micromeritics Tristar-3000 equipment.

Photocatalytic hydrogen evolution

Photocatalytic reactions were carried out in a closed gas-circulation system, as depicted in supporting information (SI, Fig. S1). A 300 W Xenon lamp was used as the light source, and visible light irradiation was realized by attaching a 420 nm cutoff filter. The cooling water for the reactor was set at 10 °C. 0.2 g catalyst was dispersed in an aqueous solution (400 mL) containing methanol (10 vol%) as the sacrificial electron donor and 1 wt% Pt as the cocatalyst by referring to the amount of catalyst. Pt was photo-deposited on the catalyst by using H_2PtCl_6 dissolved in the reactant solution. The reactant solution was first irradiated under full arc light ($\lambda > 300$ nm) for 1 h to facilitate the deposition of Pt. Then, the system was evacuated several times prior to irradiation. The evolved H_2 was analyzed by an online gas chromatography (GC-14C, Shimadzu, TCD, Ar carrier).



Scheme 1 – Formation of melem and g-C_3N_4 during the thermal condensation of melamine.