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Article

Immobilization of metal-organic molecular cage on g-C₃N₄ semiconductor for enhancement of photocatalytic H₂ generation

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ABSTRACT

A new compound based on immobilizing of Pd₆(RuL₃)₈(BF₄)₂₈ (L=2-(pyridin-3-yl)-1H-imidazo [4,5-f][1,10]-phenanthroline) cage (MOC-16) on g-C₃N₄ was synthesized. Infrared spectrum and powder X-ray diffraction were used to characterize structure of hybrid MOC-16/g-C₃N₄, as well as UV-vis absorption spectrum and X-ray photoelectron spectroscopy were carried out to unveil photocatalytic mechanism. With the introduction of MOC-16, the absorption edge of MOC-16/g-C₃N₄ in UV-vis spectrum extended apparently to long-wavelength region compared with pristine g-C₃N₄. H₂ evolution yielded with MOC-16/g-C₃N₄ in aqueous solution containing TEOA was much higher than that with RuL₃/g-C₃N₄, Pd/RuL₃/g-C₃N₄ and mixture of MOC-16 and g-C₃N₄, showing that the octahedral cage structure with high-efficient electron transfer and the interface interaction between MOC-16 and g-C₃N₄ were significant for improvement of H₂ evolution.

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1. Introduction

Visible light-driven photocatalytic hydrogen production from water is an attractive strategy towards solar energy conversion and storage. Various heterogenous-semiconductor [1–6] and homogenous-molecule assemblies [7,8] have experienced intensive exploration, and great progress has been achieved [9,10]. A hydrogen-evolving photochemical molecular device self-assembled Pd₆(RuL₃)₈(BF₄)₂₈ (L=2-(pyridin-3-yl)-1H-imidazo [4,5-f][1,10]-phenanthroline) cage (MOC-16) [11], incorporating multiple photo- and catalytic metal centers, had

been developed in our previous report [7]. Although the directional electron transfers through multiple but independent channels led to efficient hydrogen production, MOC-16 suffer from the typical drawbacks of homogeneous catalysis, primarily catalyst deactivation to colloidal Pd nanoparticles. To circumvent the vulnerability of molecular catalysts under photocatalytic conditions, a plethora of approaches have been pursued to immobilize them onto a suitable matrix as heterogeneous systems. For example, anchoring molecular catalysts on surfaces with multiple binding motifs is a usual strategy, especially in electrode, albeit cleavage or deactivation of the catalyst

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is inevitable [12–14].

Graphitic carbon nitride (g-C₃N₄) is a fascinating conjugated polymer in solar fuel generation through water splitting and CO₂ photoreduction [15–21]. The special layer structure with π -conjugated electrons and abundant edge termination to form H bonds engender an ideal platform for C₃N₄ to construct hybrid systems with various components. So far, a plenty of heterostructured g-C₃N₄ with second even third components, including metal, semiconductor, graphilic carbon, sensitizer et al., had been constructed to remedy its imperfection of wide bandgap, severe charge recombination, and lack of surface-active sites [18,22–25].

Inspired by preceding heterostructured g-C₃N₄ photocatalysts, immobilizing molecule-MOC-16 on C₃N₄ is a compelling and feasible approach to heterogenize MOC-16. The opened-up 2D flat morphology of C₃N₄ could provide a platform to isolate MOC-16, which is expected to promote the photocatalytic performance comparing with homogenous MOC-16. From perspective of g-C₃N₄, the high-efficient electron transfers and multiple photo- and catalytic metal centers within MOC-16 are also anticipated to advance the performance of g-C₃N₄, in terms of expanding light absorption, promoting charge separation, and accelerating surface kinetics. Hereinafter, hybrid nanocomposite of MOC-16/g-C₃N₄ was constructed, and the influences of MOC-16 content and the comparison systems, such as RuL₃/g-C₃N₄, Pd/RuL₃/g-C₃N₄ and mixture of MOC-16 and g-C₃N₄, on photocatalytic H₂ evolution (PHE) was evaluated and discussed. The optimized PHE rate of 10 wt% MOC-16/g-C₃N₄ was 2021 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which was higher than those with the comparison catalysts. Moreover, the catalysts 10 wt% MOC-16/g-C₃N₄ could be repeatedly utilized 3 times with slight loss in hydrogen production activity, giving an enhanced turnover number of 517 for 15 h compared with homogenous MOC-16 system (638 in 48 h).

2. Experimental

2.1. Preparation of MOC-16/g-C₃N₄

MOC-16 was synthesized according to the reported procedure. g-C₃N₄ was prepared as following. 10 g urea was placed in a 50 mL crucible, calcinated in the muffle furnace with a heating rate of 10 °C/min to reach the temperature of 550 °C, then held at this temperature for 2 h. After grinded, the resulting powder underwent a heat treatment at the rate of 10 °C/min to reach 500 °C, holding for 2 h. The resulting g-C₃N₄ powder was then stirring overnight in H₂O and CH₃CN mixed solvent (v:v=1:1) dissolving a series calculated amount of MOC-16 (5.0/7.5/10.0/12.5/15.0 wt%), followed by withdrawing solvent with rotary evaporation. The product underwent washing and filtrating with H₂O several times, which stayed colorless during the washing procedure. The samples were denoted as *X* wt% MOC-16/g-C₃N₄.

As controls, equivalent RuL₃ with 10 wt% MOC-16/g-C₃N₄ was immobilized on g-C₃N₄ with same procedure to get RuL₃/g-C₃N₄. Following that, equivalent Pd with 10 wt% MOC-16/g-C₃N₄ was co-immobilized on RuL₃/g-C₃N₄ via pho-

to-deposition under Xenon lamp irradiating for 1 h with H₂PdCl₄ as Pd source. The resulting Pd-RuL₃/g-C₃N₄ powder was collected and washed with H₂O, and then dried under 40 °C. In addition, equivalent MOC-16 and g-C₃N₄ with 10 wt% MOC-16/g-C₃N₄ were physical mixture to contrast with 10 wt% MOC-16/g-C₃N₄.

2.2. Photocatalysis

The photocatalytic H₂ evolution experiments were carried out in a closed gas circulation and evacuation system equipped online GC (Agilent 7820A) for H₂ detection. In detail, 10 mg photocatalyst was dispersed in 20 mL solvent containing 18 mL distilled water and 2 mL TEOA as sacrificial reagent. The reaction was carried out under visible light ($\lambda > 420 \text{ nm}$) irradiation with 300 W Xenon lamp (PLS-SXE-300C, Beijing Perfectlight). The apparent quantum yields (AQYs) were tested by online GC (Agilent 7820A) and Zolix LED ($\lambda > 420 \text{ nm}$, lighting area was 0.8 cm²), using 5 mg photocatalyst in 10 mL solvent containing 9 mL distilled water and 1 mL TEOA.

2.3. Characterization

UV-vis absorption spectrum (UV-Vis) was measured by UV-3600 spectrometer. The fluorescence spectra were measured by Edinburgh FLS980 combined fluorescence spectrometer. Powder X-ray diffraction (PXRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-K α_1 radiation, $\lambda = 1.54056 \text{ \AA}$). The Fourier transform infrared (FT-IR) spectra were obtained by KBr tablet in Nicolet avatar 330 FT-IR spectrometer with the unit of cm⁻¹. Scanning electron microscopy (SEM) micrographs were measured by Hitachi ultra-high resolution FE-SEM SU8010 microscope. Transmission electron microscopy (TEM) images and EDX elemental mapping were obtained on FEI Tecnai G2F20S-TWIN (US) 200 KV transmission electron microscope. The specific surface area of 0.25 cm² was measured by the Cantal-automatic adsorption-iQ2-MP analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an XR6 monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) with a 900 mm spot size in an ultrahigh vacuum chamber (ESCALAB 250Xi). The pass energy was 20 eV. The amounts of MOC-16 loaded on samples were detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (spectra range: 120–800 nm, holographic grating, 2924 line/mm, SPECTRO CIROS VISION). The photocurrent-time (*i-t*) curve was conducted on ChengHua CHI660E workstation with 0.1 M Na₂SO₄, FTO working electrode, glassy carbon electrode and Ag/AgCl as reference electrode.

3. Results and discussion

Prior to photocatalytic test, the composition and structure of hybrid compounds were determined by ICP-AES, PXRD and FT-IR spectra. The percentage compositions of a serial of *X* wt% MOC-16/g-C₃N₄ samples were 3.9, 6.0, 8.4, 9.0, and 10.5, respectively, listed in Table 1, and all of them were slightly lower

Table 1

Percentage compositions, H₂ evolution rates and surface areas of a series of *X* wt% MOC-16/g-C₃N₄ hybrid compounds.

Content-original feeding (wt%)	Content-ICP (wt%)	H ₂ evolution rate (μmol g ⁻¹ h ⁻¹)
0	—	79
5.0	3.9	1105
7.5	6.0	1644
10.0	8.4	2021
12.5	9.0	1000
15.0	10.5	515
100	—	354

than original feeding. Fig. 1(a) gives XRD patterns of MOC-16/g-C₃N₄ composites with different MOC-16 content. All samples showed two distinct diffraction peaks at 27.7° and 13.0° related to (002) and (100) planes of g-C₃N₄ respectively, indicating g-C₃N₄ remained intact during hybrid process. Due to molecular feature of MOC-16, XRD is blind for MOC-16. Instead, FT-IR is sensitive to molecular MOC-16 and is used to confirm the presence of MOC-16 in hybrid composition. As shown in Fig. 1(b), pristine g-C₃N₄ exhibited characteristic IR bands of CN heterocycles at 1251, 1325, 1419, 1571, 1639 cm⁻¹, apart from broad peaks between 3000 and 3500 cm⁻¹ contributed to the N-H bond and breathing mode of triazine units at 810 cm⁻¹ [26]. The characteristic bands of MOC-16 were observed at 1000–1200 and 1400–1660 cm⁻¹ regions, accompanying with two broad bands at 3100–3500 cm⁻¹ region. For hybrid composite of 10 wt% MOC-16/g-C₃N₄, the IR features of g-C₃N₄ retained and overlapped with those of MOC-16. No obvious shifts were observed in composite of MOC-16/g-C₃N₄.

To further disclose distribution of MOC-16 on g-C₃N₄, HRTEM and EDX elemental mapping were recorded and images were shown in Fig. 2. In Fig. 2(a) and (b), laminar morphology with bending edges was observed, and no features related to MOC-16 were observed due to its molecular nature. In elemental mapping in Fig. 2(c)–(h), all elements were uniformly distributed in the measured domain, including noble metals of Pd and Ru, which evidenced that MOC-16 was homogeneously dispersed on g-C₃N₄.

Photocatalytic H₂ evolution in MOC-16/g-C₃N₄ with differ-

Fig. 2. (a) HRTEM image of g-C₃N₄; HRTEM image (b) and elemental mapping images (c–h) of 10 wt% MOC-16/g-C₃N₄.

ent MOC-16 contents were shown in Fig. 3(a), and the corresponding evolution rates were listed in Table 1. It can be seen that H₂ evolution was significantly enhanced in hybrid catalysts comparing with pristine g-C₃N₄, and the improvement was strongly correlated with MOC-16 content. When MOC-16 content increased from 5 to 10 wt%, the H₂ evolution rate increased from 1105 μmol g⁻¹ h⁻¹ to the maximum of 2021 μmol g⁻¹ h⁻¹, further increasing MOC-16 content, the rate declined, instead further improvement. That is, there existed an optimum MOC-16 content of 10 wt% for H₂ evolution. As controls, pristine g-C₃N₄, RuL₃/g-C₃N₄, Pd/RuL₃/g-C₃N₄ and physical mixture of MOC-16 and g-C₃N₄ were tested for H₂ generation and compared with the optimized sample in Fig. 3(b). The negligible H₂ evolution was observed in pristine g-C₃N₄, and the hybrid of RuL₃ with g-C₃N₄ did not lead to activity increase as expected, although optical absorption was also extended to longer wavelength with RuL₃. Further loading Pd metal on the surface of RuL₃/g-C₃N₄, the activity was significantly improved several magnitudes, but lower than the optimized 10 wt% MOC-16/g-C₃N₄. It indicated that metal Pd as an active site was important for activity promoting, and the linkage of RuL₃ and Pd in MOC-16 assembly with high-efficient electron transfer was favorable for H₂ evolution. The activity of physical mixture of MOC-16 and g-C₃N₄ was inferior to that of 10 wt% MOC-16/g-C₃N₄, exemplified the interaction (*vide infra*) between MOC-16 and g-C₃N₄ was inevitable. The stability of 10

Fig. 1. (a) XRD patterns of pure g-C₃N₄ and MOC-16/g-C₃N₄; (b) FT-IR spectra of pure g-C₃N₄, MOC-16 and 10 wt% MOC-16/g-C₃N₄.

Fig. 3. (a) H₂ evolution on MOC-16/g-C₃N₄ with different MOC-16 content; (b) H₂ evolution on RuL₃/g-C₃N₄, Pd/RuL₃/g-C₃N₄ and physical mixture of MOC-16 and g-C₃N₄; (c) Three cycles tests for 10 wt% MOC-16/g-C₃N₄; (d) accumulated TON and TOF based on Pd-center for 10 wt% MOC-16/g-C₃N₄ in 15 h.

wt% MOC-16/g-C₃N₄ was also test in three cycles as shown in Fig. 3(c). In the following two cycles, the rate slightly declined but still sustained 1731 μmol g⁻¹ h⁻¹. The accumulated turn over number (TON) and turn over frequency (TOF) based on Pd was calculated and shown in Fig. 3(d). The TON achieved 517 within 15 h, significantly improved comparing with homogenous MOC-16 system of 638 (48 h) [7]. Its TOF value of ~35 h⁻¹ was comparable with that of ~30 h⁻¹ for homogenous MOC-16. The apparent quantum yield of 10 wt% MOC-16/g-C₃N₄ was 0.29%, while that of homogenous MOC-16 was 0.01% under the same condition, in agreement with the results in photocatalytic hydrogen production experiments.

In order to unveil the reason for activity improvement in hybrid compounds, optical absorption of a serial of MOC-16/g-C₃N₄ samples were measured, and relevant results were shown in Fig. 4(a). The pristine g-C₃N₄ exhibited a typical feature of semiconductor absorption with onset band edge at about 460 nm. For solid-state MOC-16, a broad absorption band at 300–400 nm UV region and a visible absorption peak centered at 460 nm were observed along with a tail till to 700 nm, partly inconsistent in UV region with that dissolved in solvent [7] due to different condensed states. For hybrid compounds of MOC-16/g-C₃N₄, absorption bands showed the overlapped features of MOC-16 and g-C₃N₄, the sharp band edge absorption of g-C₃N₄ plus the visible absorption band of MOC-16. In other words, the optical absorption of g-C₃N₄ was extremely extended from 460 to 700 nm after combining with MOC-16, allowing a more efficient utilization of solar light to

create photogenerated electrons and holes. Moreover, the loading amount of MOC-16 increased in the MOC-16/g-C₃N₄ hybrid, the absorbance intensities of the hybrids was enhanced. The optimum loading content was always reported in a plenty of composites related to g-C₃N₄ due to shielding effect existence [22]. In our case, it is reasonable that lower content MOC-16 could be isolated on the surface of g-C₃N₄, corresponding to smaller amounts of active sites, on the contrary, excessive MOC-16 could engender aggregation on 2D surface and the following decline of activity.

To further confirm the enhanced photoresponse, photocurrent-time (*i-t*) curves of 10 wt% MOC-16/g-C₃N₄ and MOC-16 electrode have been measured under illumination with several on/off switches (Fig. 4(b)). The MOC-16/g-C₃N₄ electrode showed higher photocurrent than MOC-16, hinting that effective interfacial electron transfer between MOC-16 and g-C₃N₄ in the hybrid.

Although H₂ evolution was significant improved as expected, the activity still declined in sequence reaction cycles (Fig. 3(c)). XPS was carried out to disclose the deactivated reason and results were shown in Fig. 4(c). The double peaks of Pd²⁺ species corresponding to 3d_{5/2} and 3d_{3/2} are observed in both MOC-16 and 10 wt% MOC-16/g-C₃N₄ with comparable binding energy at 338.0 and 343.1 eV. For the recycled sample after three cycles, the preceding peaks moved to 337.3 and 342.6 eV, accompanying with the appearance of zero valent Pd with binding energy at 335.0 and 340.0 eV. It is indicated that MOC-16 immobilized on the surface of g-C₃N₄ went through

Fig. 4. (a) UV-Vis absorption of MOC-16/g-C₃N₄ with different percentage composition of MOC-16; (b) photocurrent-time (*i*-*t*) curves of 10 wt% MOC-16/g-C₃N₄ and MOC-16; (c) XPS spectra of MOC-16, pristine, and recycled 10 wt% MOC-16/g-C₃N₄.

dissociation of Pd-N bonds during photocatalytic process. The photogenerated electron continuously flowed to Pd active sites for H₂ generation, and the sluggish dynamic of consumption of electrons engendered part reduction of Pd²⁺ and then breakage of Pd-N.

As mentioned in preceding text, the interaction between MOC-16 and g-C₃N₄ was essential to the highest activity observed in 10 wt% MOC-16/g-C₃N₄, apart from the optical absorption extending. In previous reports [21], negative polarity surface on 2D g-C₃N₄ was evidenced by Z-potential measurement, on the contrary, MOC-16 with Pd₆(RuL₃)₈(BF₄)₂₈ composition possessed +28 charges in solvent [11]. It is supposed that electrostatic attraction were the main driving force to immobilize MOC-16 on g-C₃N₄. The location of MOC-16 on the surface defects of g-C₃N₄ via electrostatic and π - π stacking interaction and on the edge of g-C₃N₄ through hydrogen bonding were favorable. Thus, an interface between MOC-16 molecule and g-C₃N₄ semiconductor was constructed. A possible reaction mechanism based on band edge alignment of MOC-16 and g-C₃N₄ with respect to standard water redox potential was proposed in Fig. 5. The HOMO and LUMO energy levels of MOC-16 were respectively determined from the oxidation and reduction peaks of cyclic voltammogram, 1.55 and -0.95 V vs. NHE [7]. The energy band position of pristine g-C₃N₄ was slightly different in previous reported references [22,27]. The conductive band (CB) changed from -1.09 to -1.3 V, concomitantly, valence band (VB) altered from 1.53 to 1.4. Anyway, the photogenerated electron transfer from g-C₃N₄ to MOC-16 was thermodynamically feasible. The destination of photoelectrons

were active sites of Pd to be consumed for H₂ evolution, meantime, photo holes were consumed by sacrificial reagent of TEOA.

4. Conclusions

In summary, MOC-16 was immobilized on g-C₃N₄ with open-up 2D flat morphology to fulfill the heterogenization of molecular catalyst and the high-efficient electron transfer in MOC-16 with photosensitized RuL₃ centers to catalytic Pd centers was inherited in hybrid MOC-16/g-C₃N₄. A significantly-promoted H₂ evolution with TON (517) was obtained comparing with pristine MOC-16 and g-C₃N₄. In addition to the support function, g-C₃N₄ also possessed thermodynamic electron donating ability to facilitate activity enhancement. This work provides a promising strategy to promote H₂ evolution via constructing molecule and semiconductor interface.

Acknowledgments

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Fig. 5. A proposed reaction mechanism of the photochemical process.

Graphical Abstract

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A new compound based on immobilizing of metal-organic molecular cage on g-C₃N₄ has been synthesized and a significant leap in photocatalytic H₂ evolution under visible light was observed.

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金属-有机分子笼在g-C₃N₄半导体上的固定以提高光催化产氢性能

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摘要: 可见光驱动的光催化水制氢是一种太阳能转化策略, 各种异质结半导体和均相分子器件在光催化领域取得了很大的进展. 本课题组曾开发了一种含多个吸光中心和催化中心的金属-有机自组装分子笼Pd₆(RuL₃)₈(BF₄)₂₈(MOC-16), 并研究了其光催化分解水产氢性能. 尽管该笼子定向电子通过多个独立的通道转移实现了高效制氢, 但仍存在均相催化剂的典型缺点, 即在光催化过程中, 笼子分解后钯纳米颗粒团聚致使催化剂失活. 而二维片层结构的石墨相氮化碳(g-C₃N₄)具有大量的共轭π电子和终止边缘以构成氢键, 是构建杂化材料的理想基底. 在此基础上, 本文采用简单的制备方法将MOC-16分立固定在g-C₃N₄基质上, 得到异质体系MOC-16/g-C₃N₄. 相比其均相组分, 该新型催化剂具有更优良的光催化分解水产氢性能. 本文设计了空白的催化产氢实验, 比较了MOC-16中各部分及分子笼在催化产氢体系中的作用, 并采用X射线衍射(XRD), 傅里叶红外光谱, 透射电镜, 紫外可见光谱(UV-Vis), 瞬态光电流响应(*i-t*), X射线光电子能谱(XPS)等手段研究了MOC-16和g-C₃N₄之间的相互作用和杂化材料MOC-16/g-C₃N₄的光催化产氢机理.

10 wt% MOC-16/g-C₃N₄表现出最高的产氢速率2021 μmol g⁻¹ h⁻¹, 并优于空白对照组的产氢效果, 循环15 h时的

TON(Pd)为517, TOF(Pd)值约 36 h^{-1} , 与MOC-16均相催化剂相比, 催化剂MOC-16/g-C₃N₄在产氢效率和稳定性上有明显提升. 形貌结构表征显示, MOC-16不与g-C₃N₄形成新的共价键, 也不改变g-C₃N₄原有形貌结构, MOC-16以配合物形式均匀分散在g-C₃N₄基底材料上. UV-Vis结果表明, MOC-16/g-C₃N₄的紫外-可见吸收峰结合了两种组分的吸收峰, 杂化材料的可见光区的吸收峰延伸至700 nm左右. 随着MOC-16负载量增大, 杂化材料MOC-16/g-C₃N₄的吸光范围越大. *i-t*结果进一步表明, MOC-16和g-C₃N₄之间存在有效的电子转移. XPS结果显示, 杂化前后, MOC-16中Pd价态未发生改变, 但峰位置发生位移, Pd 3d的电子结合能分别从343.1和338.0移动到342.6和337.3 eV, 进一步表明杂化后MOC-16和g-C₃N₄间存在相互作用. 然而经过三轮连续循环产氢后, 部分二价钯被还原为零价, 表明固定在g-C₃N₄表面的MOC-16在光催化过程中光生电子不断流向Pd, 电子消耗缓慢导致Pd-N键的断裂.

我们提出了MOC-16/C₃N₄复合光催化剂可能的光催化产氢机制. MOC-16的LUMO和HOMO能级分别为-0.95和1.55 V (vs.NHE), g-C₃N₄的导带在-1.09至-1.3 V, 价带在1.53至1.4 V之间, 所以光生电子从g-C₃N₄转移到MOC-16在热力学上是可行的. 光生电子转移到MOC-16分子的Pd上, Pd作为助催化剂为H₂的产生提供活性位点, 而TEOA作为牺牲试剂, 则在g-C₃N₄表面消耗光生空穴.

关键词: g-C₃N₄; 金属-有机笼; 光催化产氢; 可见光; 稳定性

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