



Short communication

Hybrid carbon dot/Ni₃S₂ architecture supported on nickel foam for effective light collection and conversion

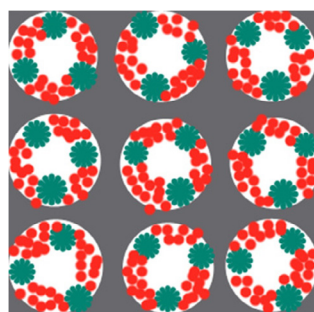
Shengliang Hu ^{a,*}, Xuejun Han ^a, Yufeng Zhou ^a, Chaorui Xue ^a, Qing Chang ^{a,*}, Jinlong Yang ^{a,b}^a School of Material Science and Engineering, North University of China, Taiyuan 030051, PR China^b State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- Use of carbon dot/Ni₃S₂ hybrid supported on Ni foam as a recyclable photocatalyst.
- Carbon dot/Ni₃S₂ hybrid exhibited broad and strong light absorption and excellent photooxidation activities.
- The different roles of CDs and Ni₃S₂ played in energy conversion process.

GRAPHICAL ABSTRACT

The obtained hybrid of CDs and Ni₃S₂ shows broad absorption and excellent photocatalytic activities without incurring the burden of hard separation.



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ABSTRACT

We offer a powerful strategy that makes use of in-situ Ni₃S₂ formation on porous wall of Ni foam to enhance light capture and energy conversion of carbon dots (CDs). The obtained hybrid of CDs and Ni₃S₂ is well characterized and shows broad and strong light absorption and excellent photooxidation activities. In this hybrid, both CDs and Ni₃S₂ play different roles in energy conversion process and their combined architectures determine efficiency of light harvesting. Not only could our presented product be particularly promising for oxidation and degradation of organic species, but also show more competitive advantage in separation and recovery from the reaction system than the powder as a photocatalyst.

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1. Introduction

As a green and low cost material, carbon dots (CDs) have attracted extensive attention increasingly because they have potential to capture, transfer and store light energy besides for application in fluorescence imaging and sensing [1–4]. Because the CDs generally exhibit strong optical absorption in the ultraviolet

region and a high number of recombination centers [4–7], the CDs confront two challenging issues, i.e. lower absorptivity in visible light region and the difficulty in charge transfer. To improve the effective capture of visible light and the conversion of excitation energy, the nanocomposite and hybrid systems comprising CDs in conjunction with another photosensitizer have been developed. For instance, Sun et al. and Kim et al. demonstrated the significant advantage of visible absorption by coupling noble metals (Au, Ag, Pt) with CDs due to surface plasmon resonance effects [8,9]. Reisner et al. reported the CDs in combination with molecu-

* Corresponding authors.

E-mail addresses: hsliang@yeah.net (S. Hu), changneu@gmail.com (Q. Chang).

lar Ni showing effective light-harvesting and H₂ production under solar irradiation [10]. Due to relatively low cost, carbon-dot-sensitized compounds including of Fe₂O₃, TiO₂, Cu₂O, Ag₃PO₄, C₃N₄, Bi₂SiO₅, Bi₂WO₆, Bi₂MoO₆, BiOX and TaOH (or NaTaOH) were studied extensively and they exhibited the efficient capture of visible light as well as the better energy conversion [2,11–18]. However, separation and recovery of these products from the reaction system is cumbersome because of their extremely small sizes [19].

Ni foam (NF) is relatively cheap and has a hierarchically porous structure. In physics, the porous architecture remarkably favors light capture due to low surface reflectivity of light and light multiple scattering and absorption in the pores as well as a large density of surface reactive/catalytic sites exposed to reactants [20–22]. Therefore, the absorptivity of CDs for visible light could be enhanced after they are attached on the porous walls of NF, resulting in high surface chemical reactions. In this work, the CDs were firstly coupled with the porous wall of NF by electrostatic interaction and then their contact on NF was reinforced through Ni₃S₂ formation between them. As an environmentally friendly and earth abundant material, Ni₃S₂ has been widely used in electrochemical capacitors and electrocatalysis [23–26], but few reported the application in photocatalysis. Not only did we first demonstrate here that it facilitated charge separation and transfer, but also it showed the good capacity of hole reservoir. Hereby, the formed hybrid of CDs and Ni₃S₂ (CDs@Ni₃S₂) on NF presented the effective light harvesting and excellent photooxidation performance, and particularly facile separation and recovery from reaction mixture since it is supported on NF.

2. Experimental section

Firstly, a piece of fresh NF (10 × 15 × 1.5 mm) was obtained by ultrasonically cleaning the NF in 3 M HCl solution for 15 min and then washing in ethanol for several times. Secondly the fresh NF was put into the suspension of CDs prepared by the method reported previously [27], and subsequently was treated by ultrasonication for 30 min. Thirdly, after drying at 50 °C in vacuum oven the resulting NF was submerged into a Teflon-lined stainless autoclave (25 mL volume) containing 10 mL of 1.35 mM thiourea solution, then the covered autoclave was kept at 150 °C for 3 h. Finally, the obtained sample was washed with ethanol two times and dried in vacuum at room temperature, giving S1. For comparison, the sample S2 was prepared using the same recipe and process as those above except for without performing second step; the samples (S3 and S4) were also prepared at reaction time of 2 h and 5 h, respectively, without changing other conditions. See the supporting information for more details.

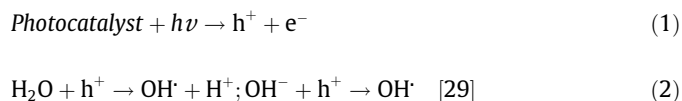
3. Results and discussion

More dangling bonds were created on the porous walls of NF after it was treated with HCl solution, thus resulting in easy adsorption of CDs on NF by electrostatic interaction. Besides, according to the Brunauer–Emmett–Teller (BET) measurements, many mesopores were present on the wall of NF (Fig. S1), which also offered ideal locations for trapping CDs under ultrasonic wave. For S1, the loading amount of CDs on NF is 1.18 mg under our presented conditions. As shown in Fig. 1a, the exposed surfaces without adsorption of CDs react with thiourea molecules, forming Ni₃S₂ between CDs. The NF color turns from grey white to black after S1 formation (the inset of Fig. 1a). The scanning electron microscope (SEM) image of S1 reveals that the three dimensional (3D) macroporous structure of NF remains intact (Fig. 1b). The whole surfaces of NF wall are inhomogeneously covered by the hybrids, forming a large number of void spaces (Fig. 1c and d). The Ar adsorption/desorption isotherms indicate that the S1 possesses much larger total pore volume (1.452 cm³/g) and BET specific surface area (1331.41 m²/g) than those of NF (1.273 cm³/g and 1075.72 m²/g, respectively); and its pore size distribution presents a new peak at around 6 nm (Fig. S1), suggesting hierarchically porous microstructures of the hybrids formed on the NF. The corresponding energy dispersive X-ray spectroscopy (EDS) analysis implies that such hybrid is made of the elements of C, O, S and Ni (Fig. 1e). The chemical bonding states of each element were also confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The Ni 2p, C 1s and S 2p spectra indicate the presence of Ni-S, C-C and C-O bonds, which originate from Ni₃S₂ and CDs in the formed hybrid (Fig. S2).

Further X-ray diffraction (XRD) pattern of S1 (Fig. 2a) reveals clear phase peaks at 21.7°, 31.1°, 37.8°, 49.7° and 55.2° assigning to (101), (110), (003), (211, or 113), and (122, or 300) planes of the hexagonal phase of Ni₃S₂, respectively (PDF#44-1418) [23–25]. Moreover, there is a broader peak centered at ca. 25°, which is attributed to the diffraction of CDs (Fig. 2a) [6]. Note that three strong peaks at 44.5°, 51.8°, and 76.3° in the XRD spectrum originate from the NF [24,25]. The formation of CDs@Ni₃S₂ was further confirmed by Raman spectrum (Fig. 2b). Five peaks at 201, 223, 304, 324, and 350 cm⁻¹ are in agreement with previous reports of Raman measurement of Ni₃S₂ crystals while the peaks at 1358 and 1550 cm⁻¹ are ascribed to D and G bands of CDs, respectively [28]. As shown in Fig. 2c, high-resolution transmission electron microscopy (HRTEM) image of S1 powder presents carbon-dot-embedded Ni₃S₂ nanolayer and two lattice spacings of 0.408 and 0.22 nm that correspond to the (101) plane of Ni₃S₂ and (100) diffraction facets of graphite carbon, respectively. For comparison, Fig. 2d shows HRTEM image of only Ni₃S₂ in the S2, which is clearly different from that in Fig. 2c. Accordingly, all the above results demonstrate the formation of CDs@Ni₃S₂ supported on NF.

Fig. 3a shows the ultraviolet-visible (UV–Vis) absorption spectra of both S1 and CDs. The CDs (Photoluminescence behavior and TEM result shown in Figs. S3 and S4) display strong UV absorption due to high density π-electron system, but weak absorption in visible region [4]. In contrast, the light absorption of S1 increases significantly and covers the entire UV–Vis range. This should be ascribed to 3D macroporous structures of NF as shown in Fig. 1b. The multiple reflections and scattering of visible light occur inside their pores and then remarkably enhance light harvesting efficiency of CDs@Ni₃S₂ supported on NF.

Photocatalyst + $h\nu \rightarrow h^+ + e^-$ (1)



In photochemical system shown in Eq. (1), the role of photocatalysts is to accelerate/initiate redox reaction by producing the reductive excited-state electrons (e⁻) and oxidative ground-state holes (h⁺). The holes react with the surface-adsorbed H₂O and OH⁻ to generate active OH[·] radicals while the electrons are scavenged by O₂ to produce active O₂^{·-} (Eqs. (2) and (3)) [29,30]. These active oxygen species are usually involved in directly activating the reactants, reducing energy barrier of their chemical transformation. Because the OH[·] radicals can react with terephthalic acid (TA) to yield 2-Hydroxy-terephthalic acid (TAOH) with a fluorescence peak at ca. 426 nm, TA has been widely used to detect the production of OH[·] in the photocatalysis reaction [29,31,32]. Fig. 3b shows the fluorescence spectra collected from 1 mM TA solution in the presence of S1 under the visible light irradiation. It can be seen that the fluorescence signals from TAOH increase significantly with

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