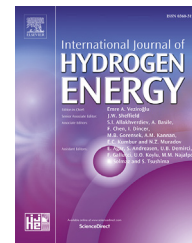




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Single Pt atoms deposition on g-C₃N₄ nanosheets for photocatalytic H₂ evolution or NO oxidation under visible light

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ABSTRACT

Generally, the outstanding photoactivity of the semiconductor photocatalyst often attributes to the loaded Pt or H₂PtCl₆ solution. However, the utilization efficiency of Pt is relatively low due to the agglomeration during the loading or photocatalytic reaction process. Here, we have successfully synthesized the single Pt atoms supported on g-C₃N₄ nanosheets (Pt-SA-CN) with dilute amounts of Pt (<0.3 wt% Pt) by a facile incipient wetness impregnation. The single Pt atoms are uniformly embedded into the g-C₃N₄ nanosheets via Pt–N coordination bonds. Surprisingly, with the introduction of single Pt atoms, the Pt-SA-CN photocatalysts exhibit both higher photocatalytic H₂ evolution and photo-oxidation of NO to NO₃. Especially, the Pt_{0.2}-SA-CN photocatalyst displays the most excellent photocatalytic performance in the series of Pt-SA-CN samples, and even higher than that of the g-C₃N₄ nanosheets in H₂PtCl₆ (1 wt% Pt) solution and the Pt loaded on g-C₃N₄ surface by photodeposition method. The utilization efficiency of Pt has a considerable enhancement and the photoactivity is also improved. The reasons for the enhanced photocatalytic performance of Pt-SA-CN samples are also further discussed.

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Introduction

With the development of rapid population growth and industrialization, energy crisis and natural environments deterioration are the topic of concern all over the world [1,2]. Among various green and environmental technology underway, semiconductor heterogeneous photocatalysis has been received keen interest because of their wide application in solving energy shortages and environmental pollution [3–5].

In the meantime, the production of sustainable clean energy source (H₂) and the removal of hazardous gas NO by photocatalysis have been the hot spot in studying [6–8]. In recent years, we have been devoted to developing high-efficiency photocatalytic H₂ evolution and NO removal, but photocatalysts still suffer from low efficiency due to high photo-generated electron-hole recombination ratio, crystal structure, morphology, size and so on [9,10]. Thus, the development of highly active photocatalysts remains a huge undertaking.

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Graphite carbon nitride ($g\text{-C}_3\text{N}_4$) with the properties of nontoxic, highly stable and low cost exhibits excellent visible light absorption property ($E_g = 2.7$ eV) and thus attracting extensive attention in the field of photocatalysis [11–13]. Band structure majorization for appropriate conduction and valence band positions is a major factor for the reduction or oxidation reaction in the photocatalytic reaction system [14]. The porous $g\text{-C}_3\text{N}_4$ modified by a simple co-pyrolyzation of precursors melamine and NH_4HCO_3 not only unfolded a remarkably improved photocatalytic H_2 evolution but also displayed a highly photo-oxidation activity. Therein, the conduction band up shifted [14]. Wang reported that $g\text{-C}_3\text{N}_4$ modified by a monomer with a phenyl end showed a negative shift of the conduction band, and then exhibited superior photocatalytic H_2 evolution [15]. The photocatalytic performance also mainly depends on the effective separation of photogenerated charge carriers [16–18]. Specifically, the high separation and transportation ratio of photogenerated charge carriers can produce more active electrons and holes, which will react with H^+ for H_2 or adsorbed substance (O_2 or H_2O_2) for oxidation process [14,19]. Previously, we reported that $g\text{-C}_3\text{N}_4$ prepared by copolymerization displayed relatively strong photo-oxidation properties, which could efficiently oxidize high concentration NO (~400 ppm) with the help of H_2O_2 under visible light irradiation. The strong oxidation of $g\text{-C}_3\text{N}_4$ is ascribed to its high photogenerated charge carriers [20]. The particular excellent property triggers us to investigate the band structure and photogenerated charge carriers of $g\text{-C}_3\text{N}_4$ for its reduction and oxidation reaction under visible light irradiation, so as to make the material possess versatility.

Up to now, a large number of modified $g\text{-C}_3\text{N}_4$ revealed superior photocatalytic H_2 evolution performance, while the photocatalyst was conducted with a cocatalyst (1 wt% or 3 wt% Pt) not only to effectively separate the electron-hole pairs but also provide more proton reduction sites [21–23]. However, Pt is a rare and expensive noble metal. Therefore, it is necessary to reduce the amount of Pt in the case of the photocatalytic performance is not declined. As reported that size effect of metal particles had a great influence on catalytic performance. Subnanometer-sized metal clusters always performed superior catalytic efficiency than the nanometer-sized ones [24]. The single atom catalysts with smallest size were considered to contain well-defined, atomically distributed metal active centers, which were dramatically conducive to the improvement of catalytic performance [24]. It is an effective and efficient way to downsize the noble metals to clusters or even single atoms to improve the atom utilization efficiency of noble metals. Recently, many researchers have been committing themselves to the single Pt atoms system, such as photocatalytic H_2 evolution, photocatalytic reduction of CO_2 and so on [25,26]. And it has also been reported that the $g\text{-C}_3\text{N}_4$ could be as a substrate to support the Pt single atom [27].

Herein, the single Pt atoms supported on $g\text{-C}_3\text{N}_4$ nanosheets was synthesized by a facile two steps method: copolymerization and incipient wetness impregnation. The sheetlike structure of $g\text{-C}_3\text{N}_4$ and the size of the noble metal Pt in $\text{Pt}_{0.2}\text{-SA-CN}$ sample are confirmed by SEM, TEM and STEM. The single Pt atoms supported on $g\text{-C}_3\text{N}_4$ nanosheets photocatalysts are investigated by the structure, electronic

environment and optical properties. The photocatalytic performance of the Pt-SA-CN system is evaluated in photocatalytic H_2 evolution and oxidation gaseous NO to NO_3^- . The improvement of the photocatalytic performance is remarkable, and reasons are will further discussed.

Experimental

Preparation of $g\text{-C}_3\text{N}_4$ nanosheets, Pt-SA-CN and Pt-VL-CN photocatalysts

All chemicals were in chemical purity grade. The $g\text{-C}_3\text{N}_4$ nanosheets were synthesized by copolymerization of cyanuric acid (C), melamine (M) and 2,4-diamino-6-methyl-1,3,5-triazine (Me). Typically, 1.0332 g C, 0.5103 g M and 0.5032 g Me were mixed in 100 ml deionized water, and vigorously stirred for 12 h to form a milky suspension. Then the mixture was centrifuged and dried at 80 °C overnight under vacuum conditions and heated at 2 °C \cdot min⁻¹ under N_2 atmosphere up to 550 °C for 4 h.

A series of Pt-SA-CN photocatalysts with different Pt content were prepared by incipient wetness impregnation method: an appropriate amount H_2PtCl_6 (10 mg mL⁻¹) was added into the $g\text{-C}_3\text{N}_4$ aqueous dispersion (50 mg $g\text{-C}_3\text{N}_4$ dispersed in 20 mL of distilled water) with ultrasound for 5 min and then kept stirring at 70 °C water bath for 5 h. The resulting product was centrifuged and subsequently dried in vacuum at 80 °C overnight. Then the sample was in the activation treatment in Ar at 125 °C for 1 h. All the samples are denoted as $\text{Pt}_x\text{-SA-CN}$, with x referring to the nominal Pt/ $g\text{-C}_3\text{N}_4$ mass ratio. Samples with nominal 0.1 wt%, 0.2 wt% and 0.3 wt% Pt loading were obtained. As a reference, the $\text{Pt}_{0.2}\text{-VL-CN}$ photocatalyst was prepared by adding the H_2PtCl_6 solution into the $g\text{-C}_3\text{N}_4$ aqueous dispersion and then visible light (VL) irradiated by 300 W Xe lamp for 5 h.

Characterizations

The structural and chemical information for prepared samples were measured by X-ray diffraction (XRD, Cu $K\alpha$, Purkinjie XD-3); Field-emission scanning electron microscope (SEM, FEI Quanta 250F); High-resolution transmission electron microscope (HRTEM), high-angle annular dark field TEM (HAADF-STEM) and energy dispersive X-ray (EDX) (FEI Tecnai G2 F30S-TWIN); X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA); Electron paramagnetic resonance (EPR, Bruker EMX-10/12-type spectrometer); UV–vis diffuse reflectance spectra (DRS, Shimadzu UV-2600), Brunauer-Emmett-Teller (BET, Quantachrome, autosorb IQ), and Photoluminescence spectra (PL, He-Cd laser, Labram-HR800).

The Photoelectrochemical experiments were conducted on a CHI 760E electrochemical workstation (Shanghai Chenhua, China) with a standard three-electrode cell. A Pt wire was used as the counter electrode, and a standard Ag/AgCl in saturated KCl as reference electrode. The working electrode was prepared by dip-coating: 5 mg of photocatalyst was suspended in 1 mL ethanol and 50 μL naphthol solution to form a slurry, and then dip-coated onto a fluorine-tin oxide (FTO) glass electrode, on which edge it was carefully covered with insulating tape

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