Agglomeration of Pt nanoparticles on the g-C₃N₄ surface dominated by oriented attachment mechanism and way of inhibition

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Abstract

0.3 mol% platinum loaded g-C₃N₄ sample was prepared by photoreduction method to study the long-term stability of photocatalysts. For the first time, we have discovered the oriented attachment (OA) mechanism growth of Pt nanoparticles on g-C₃N₄ solid surface, which is completely different from Ostwald ripening (OR) or particle migration and coalescence (PMC) that previously reported. The Pt nanoparticles perform Brownian motion on the surface of g-C₃N₄ support under the collision of liquid molecules, then two or more nanoparticles attach together via the crystallographic orientation to construct larger ones. Al₂O₃ film prepared by atomic layer deposition was introduced to inhibit the Brownian motion of Pt nanoparticles. It is found that as the increase of the Al₂O₃ growth cycles, the photocatalytic hydrogen production of Pt/g-C₃N₄ coated by Al₂O₃ increase from 1.14 mmolg⁻¹h⁻¹ to 2.08 mmolg⁻¹h⁻¹ and then decrease to 1.4 mmolg⁻¹h⁻¹, and the apparent quantum efficiency (QE) also increase from 1.2% to 2.1% and then decrease to 1.4%. Meanwhile, the long-term stability of photocatalyst always increases. This work has revealed new pathway of photocatalytic nanoparticle growth on solid surface and proposed the method to prevent it.

1. Introduction

As a semiconductor photocatalysts for the photocatalytic hydrogen evolution, graphitic carbon nitride (g-C₃N₄) has become a superstar material because of its proper band structure, high stability, easy preparation and low cost [1]. However, due to the rapid recombination of photogenerated charges, enormous efforts should be continued commitment to further enhance the photocatalytic performance of g-C₃N₄ [2]. Therefore, the development of efficient g-C₃N₄-based photocatalysts with better separation efficiency of photogenerated carriers has become an urgent demand [3, 4]. Kinds of metal oxides, metal sulfides, halides, multicomponent compound semiconductors, and metals have been used for developing g-C₃N₄-based heterojunctions to accelerate the separation of photogenerated charge carriers [3, 5, 6]. Among these possible options, noble-metals having large work function and low H₂O molecular activation energy ability are suitable to establish a larger built-in electric field between interface of metals and C₃N₄ to assist carriers’ separation and lower overpotential for splitting water [7], which would be a potential direction to remarkably improve the photocatalytic hydrogen production activity of g-C₃N₄ [8].

The long-term stability of photocatalysts is of the utmost importance for industrial applications. It is generally believed that metal nanoparticles in heterogeneous catalysts are regarded as active sites and the photogenerated carriers participate in reactions of substances adsorbed on the active sites of photocatalysts [3, 9]. When a catalyst is used in a reaction environment, the nanoparticles will grow, leading to the change in particle size of metal co-catalysts, which is termed agglomeration [10, 11]. As shown in Schemes 1(a) and (b), the agglomeration of metal nanoparticles, which occur through an Ostwald ripening (OR) or particle migration and coalescence (PMC) mechanism, means a decrease in the density of surface active sites thereby a significant reduction in photocatalytic activity. Due to thermodynamic environment at high temperatures, such
agglomeration of loaded active metals nanoparticles is reported be inevitable in thermal driven heterogeneous catalysis [11, 12]. Scheme 1 (c) shows the oriented attachment (OA) mechanism, which is related to the direct self-organization of two particles into a single crystal by sharing a common crystallographic orientation, is only found in aqueous solutions where nanoparticles can freely migrate and collide according to the available literature [13, 14]. For photocatalytic hydrogen production, the reaction is carried out near room temperature, therefore the agglomeration of metal nanoparticles on semiconductors has been considered to be negligible. Nevertheless, it is found that the activity of photocatalyst decreases after certain reaction time or number of recyclings in our experiments.

To overcome agglomeration of metal nanoparticles, different entrapment methods were used to protect catalysts in both liquid and gas reaction media, such as chemical vapor deposition, atomic layer deposition (ALD) and nonhydrolytic sol-gel method [15]. Among these methods, ALD has generated increasing interest because it allows for precise control of the thickness and composition of the layer overcoating the catalysts [15]. In this study, the Pt/g-C₃N₄ heterostructure photocatalysts were prepared by photoreduction method to study the long-term stability of photocatalysts. TEM results show Pt nanoparticles attached together via OA mechanism, generating larger nanocrystals with irregular shapes and abrupt edges after three weeks of standing still in solution in the dark. This is the first time that the agglomeration of nanoparticles mediated by OA mechanism has been discovered on the solid surface. Therefore, Al₂O₃ thin films with different growth cycles were fabricated by ALD on the surface of Pt/g-C₃N₄ to inhibit the agglomeration of Pt nanoparticles. The results can help to reassess the growth mechanism of nanoparticles on solid surfaces and create a new pathway to prepare efficient catalysts and photocatalysts.

2. Experimental procedure

2.1. Materials Synthetic

2.1.1. The Fabrication of samples g-C₃N₄ and Pt/g-C₃N₄

The g-C₃N₄ powder was prepared by the thermal polycondensation of organic precursors urea, and the metal loaded g-C₃N₄ samples were synthesized by a solution method. Briefly, 25–30 g urea was ground thoroughly in a mortar and poured into corundum crucible. The organic precursors was put into a tube furnace in a 5% hydrogen-nitrogenous atmosphere and heated to 550 degrees in 100 min and kept for two hours. The light yellow solid product was ground with a mortar into a powder sample for later use. Pt/g-C₃N₄ sample was prepared by photodeposition, 0.05 g g-C₃N₄ powder was dispersed in mixed solution of 40 ml water and 10 ml methanol and then sonicated and stirred for 10 min, respectively. Next, the mixed solution was bubbled with N₂ for 20 min to remove the O₂ inside. Afterwards, an aqueous solution of H₂PtCl₆·6H₂O were added and
irradiated by xenon lamp under visible-light illumination (λ ≥ 420 nm) for 1 h. All the samples were collected by centrifugation, washed with deionized water for three times, and dried by freezing dryer.

2.1.2. The Fabrication of 3 weeks samples
To further study the long-term stability of the photocatalysts, 0.05 g Pt/g-C3N4 powder with different Pt loads was dispersed in mixed solution of 40 ml water and 10 ml methanol and then sonicated and stirred for 10 min. Next, the mixed solution was bubbled with N2 for 20 min to remove the O2 inside, and then irradiated by xenon lamp under 25°C circulating water cooling (300 W, λ ≥ 420 nm). After 3 h of the first photocatalytic hydrogen production tests, the reaction solutions including the photocatalyst were poured into sealed plastic bottles. The plastic bottles were completely individually wrapped in tin foil to keep them from irradiation and let stand still at room temperature. After 3 weeks of standing still, the samples (denoted as Pt/g-C3N4−3w) were poured into the photocatalytic reactor again, and a second test of photocatalytic experiment was performed.

2.1.3. The Fabrication of the
Al2O3/Pt/g-C3N4, The Al2O3 thin films loaded on the surface of Pt/g-C3N4 were fabricated by ALD (denoted as Al2O3/Pt/g-C3N4). Al2O3 films were fabricated using H2O and trimethylaluminum (TMA) as precursors at 100 °C. Nitrogen (N2, 99.999%) was used as a carrier gas on the TMA and as the purge gas. The process pressure of ALD was 50 Pa. Al2O3 films were deposited using 60 ms of TMA pulse, 60 s of N2 purge time, 60 ms of H2O pulse and 60 s of purge. The thickness of the Al2O3 films grown on the Si (111) single crystal substrate under the same conditions is about 0.11 nm per cycle.

All chemicals were of analytical grade and used without further purification in this work. Urea, H2PtCl6, 6H2O and methanol were received from Aladdin (Shanghai, China). Distilled water was made by Milli-Q Direct16.

2.2. Characterization
The photocatalytic hydrogen production experiments were performed in a 100 ml commercial glass reactor with optical quartz window at ambient temperature and atmospheric pressure. A 300 W xenon lamp PLS-SXE300(Perfectlight, Beijing, China), which was positioned 16.5 cm away from the reactor, was used as a light source to trigger the photocatalytic reaction. In a typical photocatalytic experiment, 50 mg of catalyst was dispersed by a constant stirring in mixed aqueous solution containing 40 ml deionized water and 10 ml methanol, and then irradiated by xenon lamp under 25 °C circulating water cooling (300 W, λ ≥ 420 nm). The focused intensity on the reactor was about 510 mW cm−2. Before irradiation, the system was bubbled with N2 for 30 min to remove the dissolved oxygen and ensured that the reaction system was under an anaerobic condition. A 1 ml portion of gas at the center of reactor was sampled through the septum, and hydrogen was analyzed by gas chromatograph GC2060 (Ramiin, Shanghai, China) (nitrogen as a carrier gas and 5 Å molecular-sieve column).

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition. A 300 W xenon lamp CEL-HXF300-T3 (China Education Au-Light, Beijing, China) with a narrow-band band-pass filter (central wavelength 420 nm, full width at half maxima 15 nm) was used as the irradiation light source. The focused intensity on the reactor was ca. 161 mW cm−2 (position of spot center). A mask with a center circular hole of 1.5 cm in diameter was covered on the reactor to reduce the influence of uneven light intensity. The QE was calculated according to equation (1):

$$\text{QE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}}$$

$$\text{number of incident photons} \times 100$$

XRD test was carried by Miniflex300 (Rigaku, Japan) and TEM/HRTEM and HAADF-STEM images were performed by Tecnai F20 (FEI, Hillsboro, OR, USA).

3. Results and discussion
The morphological and structural features of samples, including the pristine Pt/g-C3N4 and the Pt/g-C3N4−3w, were examined by XRD and TEM. Figure S1 (available online at stacks.iop.org/MRX/8/055504/mmedia) show XRD pattern of pristine Pt/g-C3N4 sample. Due to the low platinum loading, no diffraction peak of Pt can be seen in the pattern. The weak peak located at 13.1° is associated with the (100) crystalline plane, while the sharp peak at 27.4° corresponding to (002) crystalline plane is a characteristic interplanar stacking peak of conjugated aromatic system. Figures 1(a) and (b) shows the TEM/HRTEM images of pristine Pt/g-C3N4 sample. As seen in
Figure 1(a), the g-C₃N₄ showed a typical lamellar structure [16]. HRTEM observations indicate that the distances between the adjacent lattice fringes in figure 1(b) were approximately 0.23 nm, in agreement with the (111) d spacing of Pt, confirming successive loading of Pt nanoparticles on g-C₃N₄. Figures 1(c) and (d) display the morphological and structural features of the Pt/g-C₃N₄-3w. Figure 1(d) exhibits many agglomerates of larger Pt nanoparticles binding on the surface of g-C₃N₄. Moreover, the typical HRTEM observation in figure 1(d) indicate that the larger Pt particles are built up by smaller nanoparticles attached via different crystalline directions, rather than form a single crystals. The results of photocatalytic H₂ production activities of the two samples are shown in figure 1(e). In the first photocatalytic H₂ production test, the pristine Pt/g-C₃N₄ exhibited a hydrogen production rate of 1139 μmol h⁻¹ g⁻¹; in the second test after 3 weeks, the hydrogen production rate of Pt/g-C₃N₄-3w dramatically decline to 151 μmol h⁻¹ g⁻¹. Obviously, the sharp decrease in photocatalytic H₂ production activities is due to a decrease in the density of active surface sites caused by agglomeration of Pt nanoparticles.

Further studying the HRTEM of the sample Pt/g-C₃N₄-3w is presented in figure 2, it can be frequently observed that small particles attached together via the same crystallographic orientation, generating larger nanocrystals with irregular shapes and abrupt edges and displaying traces of coalescence of primary particles. More examples are shown in figure 3. The larger nanoparticles produced by small ‘building blocks’ which sizes are mostly 3–5 nm display the microstructural features of defects. On the contrary, the agglomeration of metal nanoparticles on the support surface that mediated by an OR or PMC mechanism showing regular spheroidal morphology [17, 18]. Moreover, the OR and PMC process require certain thermodynamic conditions, such as saturated ion concentration or vapor pressure for equilibrium, which is generally occurred at high temperature [19, 20]. As an example of low temperature reaction, Finke et al have studied the stability of zeolite-supported mononuclear Ir complex under the reaction conditions for liquid-phase hydrogenation of cyclohexene at 22°C, and found no agglomeration of Ir single atoms into clusters or nanoparticles at this condition [10].
Time course of photocatalytic H₂ production for Pt/g-C₃N₄ was shown in figure 4. It is found that no significant decrease of photocatalytic hydrogen production of Pt/g-C₃N₄ was observed after 9 h of photocatalytic reaction, indicating the agglomeration and growth of Pt nanoparticles should be a very slow process. Meanwhile, there is no external energy supply during the following three weeks of standing still in the dark. In this case, the agglomeration of Pt nanoparticles in our experiments could not be dominated by OR and PMC mechanism associated with photo irradiation or thermodynamic environment. Therefore, we suggest that OA mechanism growth actually exist in the agglomerate of Pt on the solid surface of g-C₃N₄. The Pt nanoparticles perform Brownian motion on the surface of C₃N₄ support under the collision of liquid molecules, then two or more nanoparticles attach together via the crystallographic orientation to construct larger ones.

To overcome the OA agglomeration of Pt nanoparticles, Al₂O₃ thin films with different growth cycles were fabricated by ALD to overcoat the surface of Pt/g-C₃N₄, which was named Al₂O₃/Pt/g-C₃N₄. The thickness of the Al₂O₃ layer grown on the Si (111) single crystal substrate is about 0.11 nm per cycle in our experimental condition. The schematic and process of the fabrication of the Al₂O₃/Pt/g-C₃N₄ by ALD are shown in figure S2. The photocatalytic H₂ productions of the Al₂O₃/Pt/g-C₃N₄ samples with different Al₂O₃ growth cycles were shown in figure 5(a). It was found that with the increase of the growth cycles of Al₂O₃ layer from 0 to 25 cycles, the hydrogen production rate of Al₂O₃/Pt/g-C₃N₄ firstly increased and then decreased. When the growth cycles of Al₂O₃ layer was increased to 20 cycles, the hydrogen production rate reaches the maximum. Despite the existence of thin films, the photogenerated carriers can still reach to the surface by tunneling effect and participate in redox reactions [21–23]. The surface recombination was suppressed by the passivation effect of Al₂O₃ thin film, resulting in the enhancement of the photocatalytic H₂ productions. The hydrogen production efficiency decreased when the growth cycles of Al₂O₃ exceeds 20, probably due to that the thickness of the Al₂O₃...
Figure 3. Bigger nanoparticles have irregular shapes and abrupt edges, which are widespread on the surface of g-C$_3$N$_4$. Scale bars: 5 nm.

Figure 4. Time course of photocatalytic H$_2$ production for Pt/g-C$_3$N$_4$. The reaction system was bubbled with N$_2$ for 30 min every 3 h to remove the H$_2$. After three recycles, no significant decrease was observed in the H$_2$ production rate, indicating the good stability of the catalyst during the photocatalytic reaction.
layer have exceeded the length of the charge tunneling path, and thereby, photogenerated carriers could not migrate to the surface by tunneling effect [22].

The second tests after 3 weeks of standing still in figure 3(a) also show that the larger the growth cycles of Al2O3 layer, the smaller the attenuation of photocatalytic activity. The detailed of hydrogen production rate and QE of samples in the first and second photocatalytic hydrogen production tests and the attenuation between two tests were listed in table 1. It could be seen that as the increase of the Al2O3 growth cycles, the photocatalytic hydrogen production of Al2O3/Pt/g-C3N4 coated by increase from 1.14 mmolg⁻¹h⁻¹ to 2.08 mmolg⁻¹h⁻¹ and then decrease to 1.4 mmolg⁻¹h⁻¹, and the apparent quantum efficiency (QE) also increase from 1.2% to 2.1% and then decrease to 1.4%. Meanwhile, the long-term stability of photocatalyst always increases with the increase of the growth cycles of Al2O3 layer. The hydrogen production rate of the second photocatalytic H₂ productions test of pristine Pt/g-C3N4 have been reduced by 86.8%, while 25-cycles Al2O3/Pt/g-C3N4 sample only by 15.3%.

![Figure 5](image_url)

**Figure 5.** (a) The hydrogen production rate of the first and second photocatalytic hydrogen production test of Pt/g-C3N4 with different growth cycles of Al2O3: 0, 5, 10, 15, 20 and 25 cycles; (b) TEM and (c) HAADF-STEM images of 20-cycles Al2O3 overcoated Pt/g-C3N4 after 3 weeks of standing still and (d) the elemental mapping images of C, N, Al, O and Pt elements, and a superimposition of the distributions. Scale bars: 50 nm.

**Table 1.** Comparison of hydrogen production rate and QE of the first and second photocatalytic hydrogen production tests for Al2O3/Pt/g-C3N4 loaded with different growth cycles of Al2O3. The attenuation between two tests was also given.

| Al2O3 growth cycles | 0   | 5   | 10  | 15  | 20  | 25  |
|---------------------|-----|-----|-----|-----|-----|-----|
| First test (mmolg⁻¹h⁻¹) | 1.14 | 1.4 | 1.25 | 1.65 | 2.08 | 1.31 |
| QE                  | 1.2 | 1.4 | 1.3 | 1.7 | 2.1 | 1.4 |
| Second test (mmolg⁻¹h⁻¹) | 0.15 | 0.85 | 0.89 | 1.21 | 1.56 | 1.11 |
| attenuation         | 86.8% | 39.3% | 28.8% | 26.7% | 25.0% | 15.3% |
The TEM of 20-cycles Al2O3/Pt/g-C3N4 after 3 weeks of standing still in figure 5(b) shows that no agglomerates of Pt nanoparticles could be found in contrast to figure 1(c). The HAADF-STEM and elemental mapping images in figures 5(c) and (d) also show that elements Al, O and Pt homogeneously dispersed on the surface of g-C3N4, which confirms that the Al2O3 thin films exactly overcoated on the surface of Pt/g-C3N4. Despite the existence of thin films, the photogenerated carriers can still reach to the surface by tunneling effect and participate in redox reactions [21, 22]. The surface recombination was suppressed by the passivation effect of overcoated Al2O3 thin film, resulting in the enhancement of the photocatalytic H2 productions. The hydrogen production efficiency decreased when the growth cycles of Al2O3 exceeds 20 cycles, probably due to that the thickness of the Al2O3 layer have exceeded the length of the charge tunneling path, and thereby, photogenerated carriers could not migrate to the surface by tunneling effect [22]. On the one hand, the surface recombination can be suppressed by the passivation effect of Al2O3 thin film, thereby improving the photocatalytic performance; on the other hand, the agglomeration of Pt nanoparticles through an OA mechanism can be inhibited by the fixed effect of Al2O3 thin film. Follow this method, we can find a balance between photocatalytic efficiency and stability, so as to obtain a photocatalyst with both photocatalytic hydrogen production efficiency and stability.

4. Conclusions

In conclusion, Pt/g-C3N4 sample was prepared by photoreduction to study the long-term stability of photocatalysts. The TEM study found that the Pt nanoparticles of pristine Pt/g-C3N4 sample are well dispersed on the surface of C3N4. After 3 weeks of standing still, the Pt nanoparticles form larger agglomerates on the surface of g-C3N4 through an oriented attachment mechanism, which has never been observed on the solid surface before. Al2O3 thin films were grown by ALD on the surface of Pt/g-C3N4 to inhibit the OA agglomeration of Pt nanoparticles. It is found the long-term stability of Pt/g-C3N4 photocatalyst increases with the increase of the thickness of Al2O3 layer. These results can help the research community to reassess the growth mechanism of nanoparticles on solid surfaces and find alternative ways to prepare efficient and stable catalysts and photocatalysts.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of Interest

The authors declare no conflict of interest.

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