Photocatalysts Fabricated by Depositing Ag on Co-g-C$_3$N$_4$ and Its Enhanced Visible-Light Photocatalytic Performance

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Abstract: A novel photocatalyst, Ag/Co-g-C$_3$N$_4$, was synthesized by a simple photodeposition method successfully to increase visible-light absorption efficiency and the separation rate of the photogenerated electron hole pairs. A series of characterization analysis were conducted including XRD, SEM, EDS, FT-IR, DRS and PL. The result of DRS shows that there was much visible-light absorption in Co-g-C$_3$N$_4$ compared with pristine g-C$_3$N$_4$. Co-g-C$_3$N$_4$ and Co-g-C$_3$N$_4$ loaded with Ag showed a much lower photo-reduced carriers recombination rate according the data of PL. And the different contents of Ag were investigated in detail. The experiment of RhB visible-light degradation indicated the sequence of photocatalytic performances was: Ag/Co-g-C$_3$N$_4$> Co-g-C$_3$N$_4$> pure g-C$_3$N$_4$. The Ag/Co-g-C$_3$N$_4$ in this work would be quite useful for removal of organic pollutants.

1. Introduction
Nowadays, energy shortage and environmental pollution have become one of the most significant issues throughout the world, which threatened sustainable development of human beings and were taken seriously by more and more people [1-2]. In detail, discharging hazardous wastewater containing hazardous organic dyes is an important part in environmental contamination [3-4]. Photocatalytic technology as a chemical catalytic oxidation has great potential for friendly environmental remediation and energy conversion, which has many advantages including utilization of solar energy, low cost and mild reaction conditions, especially semiconductor-based photocatalysis [5-7]. Therefore, photocatalysts have been studied by more and more researchers in the field of organic pollutants degradation and utilization of solar energy.

TiO$_2$ is in widespread known as one of promising photocatalysts since it was made use to the photocatalytic hydrogen evolution by Fujishima et al. in 1972 [8]. But its applications in photocatalysis field are limited by utilization no more than ultraviolet light for broad-band gap. Then an increasing number of photocatalysts have been investigated like ZnO [9], BiVO$_4$ [10], CdS [11] and graphitic carbon nitride (g-C$_3$N$_4$) [12]. G-C$_3$N$_4$ has allured considerate attention as a fascinating visible-light photocatalyst owing to its proper band gap structure, low cost, mild conditions and absorption in visible-light region [12-14]. However, its practical applications were restricted by low quantum yield owing to high combination of photogenerated elections and holes and insufficient visible-light absorption. To popularize the application of g-C$_3$N$_4$, there are a number of functionalizations for g-C$_3$N$_4$ have been accomplished, including deposition of noble metal, introducing non-precious elements and constructing heterojunctions with other semiconductors [15-17].
The noble metal Ag, because of its surface plasmon resonance (SPR), has been applied in enhancing photocatalytic activities of semiconductors. In recent years, many studies have shown that Ag-loaded g-C₃N₄ with improving visible-light catalytic performance. For example, Yanjuan Sun et al. studied improving NOx removal for g-C₃N₄ by Ag nanoparticles decoration [18]. Wen-Da Oh et al. reported Ag-decorated S-doped g-C₃N₄ has enhanced photocatalytic degradation of bisphenol A under solar irradiation [19]. Visible-light-driven H₂ production from water splitting of Ag quantum dots/g-C₃N₄ photocatalysts were investigated by Tianjun Chen et al. [20]. In Ag/g-C₃N₄, Ag can store electric charge carries to restrain its combination, and then enhance its photocatalytic performance. In addition, the absorption in visible-light range of g-C₃N₄ has been broadened owing to introduction of Co in accordance with the studies by Liang Zhou et al. [21].

Here, we synthesized Ag/Co-g-C₃N₄ photocatalyst successfully by a simple method. To our knowledge, there are rarely reported about Ag/Co-g-C₃N₄. In the photocatalyst of Ag/Co-g-C₃N₄, the improved visible photocatalytic performance for degradation of RhB was likely to contribute to two sides as follows. On the one hand, the successful introduction of Co made its visible absorption range widen. On the other hand, the deposition of Ag made its capacity of charge storage strengthen greatly. Moreover, the fabrication and characterization were conducted in detail.

2. Experimental

2.1. Preparation of Co-g-C₃N₄

The Co-g-C₃N₄ was prepared by calcining mixture of dicyandiamide and cobalt acetate. 2 g dicyandiamide and cobalt acetate were blended with deionized (DI) water in a beaker under vigorous stirring conditions. After stirring for another 1 h, the mixture was dried at 60 °C to obtain Purplish red sample, and then was transferred into a covered crucible and heated at 520 °C for 1 h in a muffle with a heating rate of 2 °C/min. After being ground, the powder was denoted as CoCN. The pure g-C₃N₄ was prepared in the same procedure mentioned above without addition of cobalt acetate and written as CN. All reagents are analytically pure and the DI water was made from FBZ1002-UP-P water purification system (Flom, P.R. China).

2.2. Photo-deposition of Ag on Co-g-C₃N₄

0.5g CoCN was put into 15 ml DI water and then was dealt with ultrasound for 30 min until well dispersed. Later, 5 mL different concentrations of silver nitrate aqueous solutions were added by dropwise into that while stirring, followed by further photo-deposition treatment in the condition of 350W Xe lamp irradiation. Subsequently, the mixtures were washed with DI water 3 times and dehydrated at 60 °C for about 24h. Table 1 presented different Ag content samples. All reagents are analytically pure.

| Samples | CoCN [g] | silver nitrate [g/L] | Ag [%] |
|---------|---------|----------------------|--------|
| SAg-1   | 0.50    | 0.79                 | 0.5    |
| SAg-2   | 0.50    | 1.57                 | 1.0    |
| SAg-3   | 0.50    | 4.72                 | 3.0    |

2.3. The characterization of as-synthesized hybrids

The crystal structure, morphologies and optional properties of as-synthesized composites were measured by X-ray diffraction (XRD, Shimadzu XRD-6100, Cu Kα, 40 kV, 30 mA, Japan), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectrograph (EDX)(Zeiss, Sigma, Germany), transform infrared spectra (FT-IR, PerkinElmer Spectrometer, America), ultraviolet visible diffuse reflectance spectrum (UV-Vis DRS, PerkinElmer UV/Vis...
Spectrometer lambda 750, United Kingdom) and photofluorescence spectrometer with a Xe lamp (PL, Zolix, China), respectively.

2.4. Evaluation of visible-light photocatalytic activity of as-synthesized hybrids

The experiment for organic pollutants degradation was carried out on XPA-Photochemical Reactor (Xujiang Electromechanical Plant, Nanjing, China). Rhodamine B aqueous solution (10mg/L) was selected as reactant. Typically, 50 mg as-prepared catalysts were dispersed in 50 mL RhB solution, which was magnetically stirred in dark for 1 h to reach the adsorption–desorption equilibrium. Then the mixed solution was exposed to 500W Xe lamp with a 420 nm cut filter. At certain time intervals, ∼4 mL was taken out by centrifugation and then was measured on UV–Vis spectrophotometer (PerkinElmer UV/Vis Spectrometer lambda 35, United Kingdom). As a result, the variation concentration was recorded to gain degradation efficiency according to the maximal absorption of RhB, whose characteristic absorption peak is at 553nm.

![Figure 1](image)

**Figure 1.** The XRD spectra of CN, CoCN and SAg-1~3 samples (a); the FT-IR spectra of CN, CoCN and SAg-1~3 samples (b).

3. Results and discussion

3.1. Characterization of the as-synthesized catalysts

Figure 1a shows the XRD data of CN, CoCN and SAg-1~3 samples. There are two diffraction peaks at 13.1º and 27.4º, which belong to in-plane structural packing motif of (100) plane and interlayer-stacking of (002) plane, respectively. After introduced Co into g-C$_3$N$_4$, the peak at 27.4º looks depressed obviously and broadened compared to that of CN, and the peak at 13.1º was disappeared, ultimately [22]. As a result, it is indicative of that Co ions are embedded into in-planes of carbon nitride sheets [23]. Furthermore, the patterns of CoCN loading with Ag decreased with increased contents of Ag, suggesting the crystallinity is gradually lower. The diffraction peaks corresponding to Ag could not be observed, which may be caused by its poor particle size and low amount. Previous studies have reported the similar results [24]. There are scarcely any impurities in as-synthesized g-C$_3$N$_4$, Co-g-C$_3$N$_4$ and Ag/Co-g-C$_3$N$_4$ samples.

The composition, structure and functional groups of as-prepared photocatalysts could be revealed in FT-IR spectra. As displayed in Figure 1b, the peaks at 1641, 1570, 1409, 1320 and 1243 cm$^{-1}$ could be ascribed to the typical stretching vibration modes of g-C$_3$N$_4$ heterocycles. And the peak located at 808 cm$^{-1}$ could be assigned to the typical breathing mode of the tri-s-triazine units in g-C$_3$N$_4$ [22]. Both Co-g-C$_3$N$_4$ spectra and Ag/Co-g-C$_3$N$_4$ spectra remains mainly unchanged peaks of original g-C$_3$N$_4$ without other impure peaks, which is similar to former reports [23-25].
As depicted in Figure 2, all of Co-g-C$_3$N$_4$ (Figure 2b) and Ag/Co-g-C$_3$N$_4$ (Figure 2c) exhibit tremella-like structure and form graphitic-like planes, which are similar to morphology feature of pure g-C$_3$N$_4$ (Figure 2a). The elements contents of Ag and Co were determined with energy dispersive X-ray spectroscopy (EDX) in Table 2. The results indicated Co was introduced in g-C$_3$N$_4$ and Ag was loaded successfully on surface of Co-g-C$_3$N$_4$. In fact, the ratio of Co is basically similar. The actual loading ratios of Ag are 0.27 w.t.% 0.50 w.t.% and 1.31 w.t.% corresponding to 0.5 w.t., 1.0 w.t.% and 3.0 w.t.% in theory.

| Samples   | Co[w.t.%] | Ag [w.t.%] |
|-----------|-----------|------------|
| CN        | 0         | 0          |
| CoCN      | 0.60      | 0          |
| SAg-1     | 0.50      | 0.27       |
| SAg-2     | 0.44      | 0.50       |
| SAg-3     | 0.54      | 1.31       |

UV-Vis diffuse reflection spectroscopy of as-fabricated samples was conducted as shown in Figure 3. It can be observed in Figure 3a that all of as-prepared samples exhibit visible-light absorption. And absorption is increased evidently when doped Co into g-C$_3$N$_4$ in the range of visible light. Furthermore, after loaded with Ag, the absorptive intensity of visible-light region is decreased but still higher than pure g-C$_3$N$_4$ in Figure 3b. Compared with pure Co-g-C$_3$N$_4$, the absorption edge of the Ag/Co-g-C$_3$N$_4$
is dramatically blue shifted from 450nm, which was consistent with the reported literatures [25]. And the order of absorption is: CoCN > SAg-3 > SAg-2 > SAg-1 > CN, which confirms that Co and Ag exist in g-C₃N₄ in keeping with the results of EDX.

Figure 3. The diffuse reflectance spectra of CN, CoCN and SAg-1~3 samples (a); clear view of the absorption edges for the samples (b).

Figure 4. The photoluminescence spectra of CN, CoCN and SAg-1~3 samples (the excitation wavelength is 325 nm).

The recombination of photoexcited carriers of as-obtained photocatalysts were employed by PL spectra in Figure 4 in the condition of 325 nm exciting wavelength. Obviously, the PL intensity order is as follows: CN > CoCN > SAg-1 > SAg-2 > SAg-3. Therefore, it can be easily concluded that the order of photogenerated carries recombination is: CN > CoCN > SAg-1 > SAg-2 > SAg-3. Particularly, the separation rate of photogenerated conductors and holes in Co-g-C₃N₄ increased in contrast with g-C₃N₄. After deposited with Ag, the spectra show much lower PL intensity, which means the lower combination of photogenerated electrons and holes pairs. And the SAg-3 has the lowest recombination of photoexcited carriers. And it may behave the best photocatalytic performance among as-fabricated samples.
3.2. The evaluation of visible photocatalic removal of dye
Under irradiation of Xe lamp with cut-off filters of 420nm, the 10 mg/L RhB was selected as the substrate to assess the photocatalytic performance. As is depicted in Figure 5, after irradiated for 140 min, the RhB degradation rate of 10mg/L RhB with nothing, CN, CoCN, SAg-1, SAg-2, SAg-3 is 1.1155%, 30.114%, 48.344%, 67.146%, 68.122% and 68.651%, respectively. It can be simply concluded that the degradation efficiency of dye increases 18.230% within 140 min compared with pure g-C3N4, when introduced Co element into g-C3N4. Moreover, with the increasing of Ag contents, the degradation efficiency of dye increases. And when loading Ag with 3 w.t.% in theory, the visible-light photocatalytic performance is better than others. Furthermore, the results of the evaluation of visible photocatalytic removal of RhB are in agreement with the data of PL spectra.

Figure 5. The as-prepared samples removal of 10 mg/L RhB under irradiation of Xe lamp (λ ≥ 420 nm).

4. Conclusion
In conclusion, the Ag/Co-g-C3N4 photocatalysts were successfully fabricated by a simple photodeposition method. A number of characterizations and photocatalytic degradation of RhB experiments for pure g-C3N4, Co-g-C3N4 and Ag/Co-g-C3N4 photocatalysts manifest that Ag/Co-g-C3N4 photocatalysts have a broad absorption in visible-light region and higher separation of photoexcited carriers compared with pure g-C3N4, and have an enhanced visible-light photocatalytic removal of RhB. Furthermore, the photocatalytic activities improve gradually with increasing of Ag contents. In detail, it exhibits superior photocatalytic activities as Ag was deposited 3 w.t.% in theory. The 10 mg/L RhB photodegradation efficiency of Ag/Co-g-C3N4 photocatalysts with 3 w.t.% in theory is 68.651%, which is increased 38.537% and 18.230% correspondingly compared with pure g-C3N4 and Co-g-C3N4. The studies in this work not only provided a new g-C3N4-based photocatalyst, but also may motivate more g-C3N4-based photocatalysts for practical and eco-friendly environmental remediation.

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