



# *In-situ* photocalorimetry-fluorescence spectroscopy studies of RhB photocatalysis over Z-scheme g-C<sub>3</sub>N<sub>4</sub>@Ag@Ag<sub>3</sub>PO<sub>4</sub> nanocomposites: A pseudo-zero-order rather than a first-order process

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## ABSTRACT

Much effort has been expended recently to apply photocatalysis to address the environmental crises and energy shortage crises. However, it is controversial to demonstrate that photocatalytic kinetics follows a pseudo-first-order process by common spectroscopy, because it only reflects the variation of chromophoric groups vs. time in the initiating photocatalysis, ignoring the subsequent intermediates oxidation. In this study, we used a photocalorimetry-fluorescence spectrum, coupling of a photocalorimeter and a laser-induced fluorescence spectroscopy, to demonstrate it is a pseudo-zero-order rather than a first-order process. It shows the feasibility to investigate not only photocatalytic kinetics but also reaction pathway and rate-determining step. During RhB photocatalysis over g-C<sub>3</sub>N<sub>4</sub>@Ag@Ag<sub>3</sub>PO<sub>4</sub>, three main heat changes occurred: (ab) the photoresponse of Rhodamine B molecules and the photocatalyst, consequently generating both hydroxyl and superoxide radicals, (bc) the balance between endothermic photoresponse and exothermic RhB photodegradation by O<sub>2</sub><sup>•-</sup>/<sup>•</sup>OH and finally (cd) a stable exothermic period of RhB photodegradation. Specifically, the photocatalysis underwent an initial endothermic reaction and a subsequent exothermic stage, and eventually maintained a stable exothermic rate of  $-(0.2345 \pm 0.0971) \text{ mJ s}^{-1}$  with a pseudo-zero-order process. With Ag NPs working as a bridge, the g-C<sub>3</sub>N<sub>4</sub>@Ag@Ag<sub>3</sub>PO<sub>4</sub> system followed a Z-scheme mechanism, simultaneously generating both hydroxyl and superoxide radicals. Therefore, N-demethylation and chromophore cleavage rapidly occurred within 10 min. Then the ring cleavage and the oxidation of intermediates which were the rate-determining step eventually dominated, corresponding to the cd stage with a pseudo-zero-order process, and resulting in a pseudo-zero-order rather than a first-order process in RhB photocatalysis over g-C<sub>3</sub>N<sub>4</sub>@Ag@Ag<sub>3</sub>PO<sub>4</sub>.

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## 1. Introduction

Current progress in heterogeneous photocatalysis is highlighted in solar energy conversion and storage, including water splitting, organic synthesis, environmental remediation, CO<sub>2</sub> photoreduction and antibacterial applications [1,2]. Up to now, the development of photocatalysts with high efficiency, long-term stability and eco-friendliness for practical applications is always receiving considerable attention [2–5]. On the other hand, understanding of the photocatalytic mechanism has struggled to keep up because most

of these photocatalysis involve multiple reactions that are difficult to characterize with current analytical techniques, which is one of the indispensable factors for making substantial breakthroughs for practical application of photocatalysts [6]. Hence, an alternative method or instrument for *in situ* characterization of the photocatalytic mechanism is really needed [7].

Significant progress has been made in studying *in-situ* catalytic processes, including the use of *in-situ* spectroscopy [8,9], *in-situ* X-Ray absorption techniques [10] and *in-situ* small-angle X-ray scattering [11]. By taking advantage of the measurement of heat changes and thermokinetics with simultaneous sample irradiation [12,13], photocalorimetry (PC) provides an alternative approach to thermodynamically study *in-situ* photoreactions and has been used extensively for the determination of quantum

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efficiency in complicated photoreactions [14–23], photostability evaluation of light-sensitive substances [22–26], and photopolymerization kinetics [27–29]. LED-photocalorimetry (LED-PC) was designed in our laboratory by introducing LED light into an RD496L microcalorimeter using optical fibers, which was used to study *in situ* photocatalysis thermodynamically by tracing thermodynamics and kinetics in real-time [7]. The work principle of LED-PC is based on a heat-conduction principle, in which sample cell and reference cell are surrounded by a heat-sink [12,13]. Any heat variation is exchanged quantitatively with the heat-sink, and the temperature difference between the sample and the reference is converted to a power signal and recorded [7]. However, heat changes measured by a photocalorimeter in the beginning of photocatalysis were macroscopical and the sum of multiple reactions, in which mainly occurred photoresponse of photocatalyst and then balance between endothermic photoresponse and pollutant photodegradation [7]. Besides, thermokinetics of photocatalysis derived from heat releases were lagged behind its heat changes. Herein, to overcome the relaxation effects of thermokinetics and obtain sophisticated information of photoreaction, we report the coupling of a photocalorimeter and an *in-situ* fluorescence spectroscopy to incorporate analysis of photoreaction.

Recently, fluorescence spectroscopy has been widely used as a rapid and effective method to assess wastewater quality in tracking sources of pollution and treatment processes [30]. In general, compared to natural waters, wastewater presents higher fluorescence intensity for the components containing cellular material and their exudates or fluorescence compounds. Compared with expensive or time-consuming techniques which offered only snapshots of moments in time [31,32], such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC), fluorescence spectroscopy has multiple advantages: it is fast, inexpensive, reagentless, requires little sample preparation, is highly sensitive and non-invasive [33–35]. Meanwhile, fluorescence monitoring could provide rapid feedback, allowing dynamic, high spatial and temporal resolution studies [36]. Thus, it makes fluorescence spectroscopy suitable for online monitoring in wastewater treatments. Therefore, we coupled of the photocalorimeter and an *in-situ* fluorescence spectroscopy to incorporate analysis of photocatalysis thermodynamically by tracing thermodynamics and kinetics in real-time.

In this work, first, Z-scheme  $g\text{-C}_3\text{N}_4\text{@Ag@Ag}_3\text{PO}_4$  nanojunctions with Ag NPs embedded in the interface of  $g\text{-C}_3\text{N}_4$  and  $\text{Ag}_3\text{PO}_4$  are synthesized via the etching of  $g\text{-C}_3\text{N}_4\text{@Ag}$  by aqueous solutions of  $\text{Fe}^{3+}$  containing a certain amount of  $\text{H}_2\text{PO}_4^-$ , in which Ag NPs, with a large work function, work as a bridge for fabricating the recombination of  $h^+$  in the VB of  $g\text{-C}_3\text{N}_4$  and  $e^-$  in the CB of  $\text{Ag}_3\text{PO}_4$ . Secondly, to better understand the photocatalytic pathway, active species and degradation intermediates were determined by electron paramagnetic resonance (EPR) and ultrahigh performance liquid chromatography-mass spectrometry (UPLC-MS), respectively, and we use the photocalorimeter-fluorescence spectrum to investigate photocatalytic kinetics and degradation pathway of RhB photocatalysis by tracing thermodynamics and kinetics in real-time.

## 2. Construction of a novel photocalorimeter-fluorescence spectrum (PC-PL)

Based on the previous LED-PC [7], we designed a novel photocalorimetry-fluorescence spectrum, which includes a photocalorimeter and a laser-induced fluorescence spectroscopy with 405-nm laser. Specifically, monochromatic light (405-nm laser with 1-nm half peak width) was introduced into both sample cell and reference cell of the microcalorimeter by fiber optics in Fig. 1a,

meanwhile, another parallel fiber optic installed in the sample cell was applied to transmit the photoinduced fluorescence originating from the photocatalysis to a spectrometer (USB4000-FL, Ocean Optics, Florida, USA). Specifically, the incident 405 nm-laser passes a lens and converted to parallel light, going through a dichroic and band-pass filter, finally focusing on the sample cell by a convex lens; While the photoinduced fluorescence is transmitted to the spectrometer through the scattering path and two consecutive reflexes by a mirror and the dichroic, respectively, finally collecting to the spectrometer, as shown in Fig. 1b. The reason for choosing this laser as a source is that it has the features of good brightness, monochromaticity, anti-jamming, coherence, penetrability, and it is highly efficient with minimal energy burned off as heat with a cold light wavelength. A 405 nm-laser with a tunable intensity was used as an excitation light source of both photocatalysis and the fluorescence spectrum.

The incident light intensity in Fig. S1a of two cells were adjusted roughly outside of the photocalorimeter and determined 20 times using a solar power meter (TES-1333, TES Electrical Electronic Corp., Taiwan, China), which was  $19.15 \pm 0.14 \text{ W m}^{-2}$  for the reference cell and  $19.53 \pm 0.20 \text{ W m}^{-2}$  for the sample cell. The baseline was adjusted to zero by fine tuning of light intensity and is shown in Fig. S1b. To offset the baseline shift because of the trace heat deviation produced by the differential intensity of two cells, a blank was used to record the heat changes generated by irradiation of the reference and the sample cell charged with 1.0 mL deionized water under identical conditions. Prior to using the integrated system, the laser-photocalorimeter was calibrated by determination of standard molar reaction enthalpy of the photolysis of potassium ferrioxalate at 298.15 K, which is  $-(59.9425 \pm 2.7298) \text{ kJ mol}^{-1}$  and is very close to the value in the literature [7,15], which indicates that the instrument is reasonable and reliable (please see Fig. S2 and the Supporting information for more details).

## 3. Results and discussion

### 3.1. Synthesis and characterization of $g\text{-C}_3\text{N}_4\text{@Ag@Ag}_3\text{PO}_4$

3D tremella-like  $g\text{-C}_3\text{N}_4$  (denoted as CN) was prepared via a facile thermal polymerization method. The XRD image of the as-prepared  $g\text{-C}_3\text{N}_4$  in Fig. S3 show two peaks at  $13.2^\circ$  and  $27.5^\circ$ , corresponding to the (100) and (002) planes the graphite-like carbon nitride [37]. The SEM images of the  $g\text{-C}_3\text{N}_4$  in Fig. 2a show essentially the tremella-like morphology composing of irregularly assembled nanosheets with a thickness of less than 10 nm. The TEM analysis in Fig. 2b find that 3D tremella-like  $g\text{-C}_3\text{N}_4$  is consisted of nanosheets and crosswise nanowires with a diameter of about 30 nm. The zeta potential of the  $g\text{-C}_3\text{N}_4$  suspension in Fig. S4 ranges from  $-15.56$  to  $-25.79$  mV when the pH changes from 5 to 7, indicating that its surface possesses a negative charge which could interact well with the  $\text{Ag}^+$ , facilitating the uniform decomposition of Ag NPs on the surface of  $g\text{-C}_3\text{N}_4$ . Consequently, the SEM image of  $g\text{-C}_3\text{N}_4\text{@Ag}$  with a 12% Ag NPs content (denoted as CNA12%) in Fig. S5a show that the Ag NPs with a diameter of about 10 nm are uniformly deposited on the surface of  $g\text{-C}_3\text{N}_4$ , whose actual Ag NPs content eventually turned out to be 0.57%. Its XRD images in Fig. S3 show two peaks at  $13.2$  and  $27.5^\circ$ , corresponding to the (100) and (002) planes of the graphite-like carbon nitride [37], and three peaks at  $38.2$ ,  $44.2$ , and  $64.5^\circ$ , corresponding to the (111), (200), and (220) planes of Ag (JCPDS No. 04-0783) [27], respectively.

The Z-scheme  $g\text{-C}_3\text{N}_4\text{@Ag@Ag}_3\text{PO}_4$  (denoted as CNAAP) with Ag NPs embedded in the interface of  $g\text{-C}_3\text{N}_4$  and  $\text{Ag}_3\text{PO}_4$  were synthesized via the etching of  $g\text{-C}_3\text{N}_4\text{@Ag}$  by aqueous solutions of  $\text{Fe}^{3+}$  containing a certain amount of  $\text{H}_2\text{PO}_4^-$ . In view of the generation of possible precipitation in the mixture solution, the optimum con-

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