

Research Paper

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Optimization of P25/CaTiO₃nanorod Composite Photocatalysts for High Organic Matter Degradation Performance

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Abstract

Wastewater is discharged into rivers and oceans without any treatment, causing significant damage to animal health and destroying ecosystems. Semiconductor photocatalysts are attracting attention as an effective means for solving this problem. Among them, titanium-based perovskite semiconductors are expected to be the next-generation photocatalysts because of their wide range of properties, including chemical and optical stability. CaTiO₃, in particular, has attracted attention because of its excellent corrosion resistance, low cost, and ease of material synthesis. In this study, CaTiO₃ nanorods (CaTiO₃NR) were prepared by hydrothermal synthesis. The photocatalytic activity was improved by forming a heterostructure between TiO₂ particles (P25) and CaTiO₃nanorods (CaTiO₃NR) and by optimizing the mass ratio of P25 to CaTiO₃NR. Methylene blue (MB) solution was used as a pollutant model to simulate the degradation performance of photocatalysts under UV irradiation. The results show that controlling the mass ratio of P25 /CaTiO₃NR can significantly improve the photocatalytic performance and has better degradation than P25/CaTiO₃nanocuboids (CaTiO₃NC) composite photocatalysts. The highest photocatalytic performance was achieved by the P25 /CaTiO₃NR=3:1 composite photocatalyst, which had about 60% decomposition performance compared to P25.

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Keywords

CaTiO₃ nanorod; P25; Ratio; Photocatalysis; Organic degradation

1. Introduction

Wastewater is discharged into rivers and oceans without any treatment, causing significant damage to animal health and destroying ecosystems (Pei et al., 2020). A simple, low-cost, and environmentally friendly technology is needed to treat this organic pollutant (Dong et al., 2015). Semiconductor photocatalysts are expected to be applied to various wastewater treatment technologies (Yan et al., 2015). Among them, perovskite-type oxide semiconductors have attracted the attention of many researchers because of their conductive, photovoltaic, and piezoelectric properties (Shi et al., 2018). Because of these properties, perovskite oxides are used in a variety of applications, including ferroelectrics, superconductors, and photocatalysts. (Lu et al., 2022), (Yan et al., 2019). In particular, calcium titanate (CaTiO₃) has applications in the decomposition of organic pollutants and solar cells because it is activated by UV light, is light corrosion resistant, non-toxic, low-cost, and easy to synthesize (Gao et al., 2021), (Simsek & Tuna., 2022). However, the problem is that CaTiO₃ alone does not have very high photocatalytic activity (Genki et al., 2023).

Therefore, a possible means of improving photocatalytic activity is to form a Z-scheme heterostructure between two materials with well-matched band structures (Jiang et al., 2020). Among the various photocatalysts, anatase TiO₂ is known to be the most effective due to its excellent stability, low cost, non-toxicity, and availability (Gupta et al., 2021). Here, the conductor band and valence band of CaTiO₃ are misaligned with the conductor band of TiO₂, and the coupling of TiO₂ and CaTiO₃ introduces a strong BIEF effect (in the direction from CaTiO₃ to TiO₂). This facilitates the transport and separation of photogenerated charge and improves photocatalytic activity (Yang et al., 2022).

In this study, the heterostructure between CaTiO₃nanorods (CaTiO₃NR) and P25 was formed, and the mass ratio was controlled to improve the photocatalytic activity. CaTiO₃NR with P25 as a precursor was prepared by hydrothermal synthesis. Methylene blue (MB) solution was used as a pollutant model to simulate the degradation performance of the photocatalyst under UV irradiation.

2. Methods and Analysis

2.1 Preparation of CaTiO₃NR

2 g of P25 (JAPAN, AEROJIL) were dissolved in 80 ml of NaOH solution (10 M) at room temperature. Then, it was transferred to a Teflon-lined stainless steel autoclave and heat-treated at 180°C for 24 h. After hydrothermal synthesis, the product was washed several times with HCl solution (0.1M) and purified water to lower the pH to 7 and then dried at 80°C to obtain TiO₂ nanorods (TiO₂NR) (Guo et al.,2010). 0.5 g of prepared TiO₂NR was dissolved in 80 ml of saturated Ca(OH)₂ solution at room temperature. It was then transferred to a Teflon-lined stainless-steel autoclave and heat-treated at 120°C for 12 h (Shi et al., 2018). After hydrothermal synthesis, the products were washed twice with deionized water and once with ethanol and dried at 80°C.

2.2 Preparation of CaTiO₃NC

0.2396 g of P25 was dissolved in CaCl₂ (0.15 M) and NaOH (5 M) at room temperature. It was then transferred to a Teflon-lined stainless-steel autoclave and heat-treated at 200°C for 24 h. After hydrothermal synthesis, the products were washed twice with deionized water and once with ethanol and dried at 80°C (Genki et al., 2023).

2.3 Photocatalytic Test

To evaluate photocatalytic activity, MB solution was simulated under UV irradiation as a model of the contaminant. 0.05 g of photocatalyst was added to 20 ml of MB solution. The eleven types of photocatalysts were prepared for addition, as shown in Table 1. The P25 and CaTiO₃ composite photocatalyst was sonicated with 30 ml of methanol for 30 min. It was then stirred at 100°C until the methanol evaporated and prepared. UV light was provided by a 20 W black light (NEC, FL20SBL-B), and the temperature was kept at room temperature (25°C) to decompose the MB solution. After 0.5 h of adsorption in the dark, the solution was irradiated with UV light for 4 h. The degradation rate of methylene blue is expressed by the following equation.

$$\frac{C_0 - C_t}{C_0} \times 100 \quad [\%] \quad (1)$$

Where C_0 is the initial concentration of methylene blue and C_t is the residual concentration of methylene blue. The optical concentration of the methylene blue solution with an initial concentration of C_0 is set to 1.0. The photocatalyst was removed by centrifugation prior to optical density measurement (Genki et al., 2023).

Table. 1. Photocatalyst and mass ratio.

Name of photocatalyst	Mass ratios (P25:CaTiO ₃)
CaTiO ₃ NR	0:1
P25/CaTiO ₃ NR(1/3)	1:3
P25/CaTiO ₃ NR(1/2)	1:2
P25/CaTiO ₃ NR(1)	1:1
P25/CaTiO ₃ NR(2)	2:1
P25/CaTiO ₃ NR(3)	3:1
P25/CaTiO ₃ NR(4)	4:1
P25/CaTiO ₃ NR(5)	5:1
P25	1:0
CaTiO ₃ NC	0:1
P25/CaTiO ₃ NC	1:1

3. Results and discussions

3.1 Characterization of crystal structure and morphology

The crystal structure of the prepared samples was measured by XRD (Fig. 1). CaTiO₃NC showed high agreement with CaTiO₃ (PDF # 00-022-0153). CaTiO₃NR was observed to be a mixture of CaTiO₃ and TiO₂ (PDF # 00-022-0153). This confirms that the hydrothermal synthesis of TiO₂NR transforms them into CaTiO₃NR.

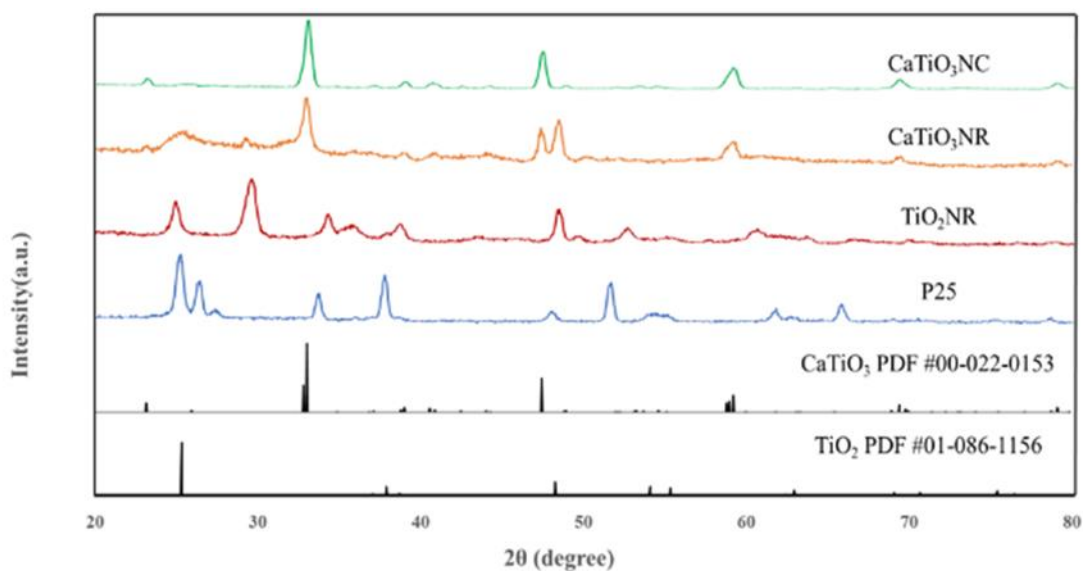


Fig. 1. XRD patterns of P25, TiO₂NR, CaTiO₃NR, and CaTiO₃NC.

The surface structure of the prepared samples was observed by SEM (Fig. 2). TiO_2NR was grown by hydrothermal synthesis of P25 in an aqueous solution with 10M NaOH concentration (Fig. 2 (a)). CaTiO_3NR was obtained by hydrothermally synthesizing TiO_2NR in a saturated aqueous solution of $\text{Ca}(\text{OH})_2$, but both the diameter and length remained unchanged (Fig. 2 (a) and (b)). The following chemical reaction equation shows the process of changing TiO_2NR to CaTiO_3NR .

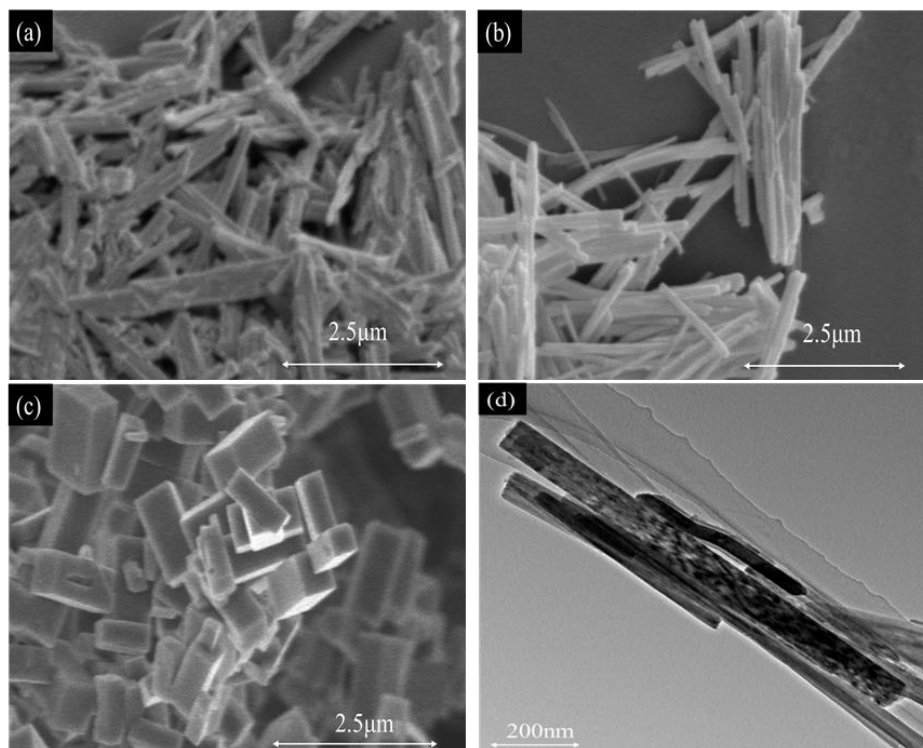
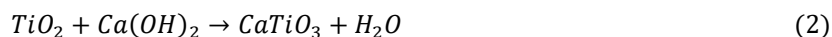


Fig. 2. SEM image of (a) TiO_2NR , (b) CaTiO_3NR , (c) CaTiO_3NC . TEM image of CaTiO_3NR (d).

Fig. 2 (c) shows the fabricated CaTiO_3NCs , where cubic structures with a width of about $0.4\ \mu\text{m}$ and a length of $0.8\ \mu\text{m}$ were observed. The process of conversion of P25 to CaTiO_3NC is shown by the following chemical reaction equation.

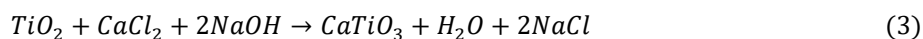


Fig. 2 (d) is a TEM image of CaTiO_3NR . CaTiO_3NR is found to be a prismatic nanorod structure with a diameter of about $50\ \text{nm}$ and a length of about $1\ \mu\text{m}$.

Fig. 3 shows the surface structure of synthetic samples with different mass ratios of P25/ CaTiO_3NR observed by SEM. All samples were gold sputtering before observation. It was observed that P25 was clearly adhered around the surface of CaTiO_3NR by methanol treatment. The ability to form Z-scheme heterostructures is believed to improve photocatalytic performance.

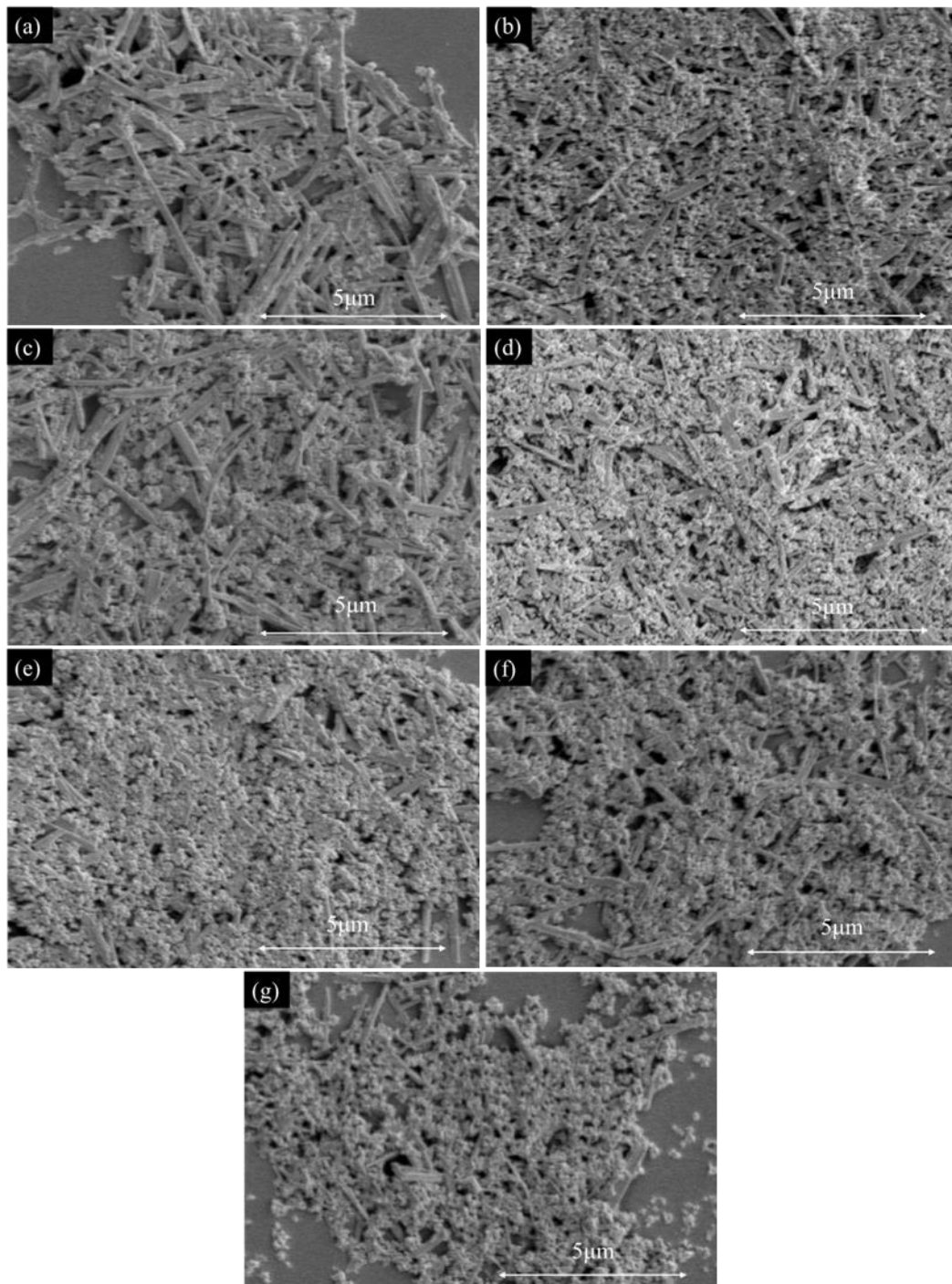


Fig. 3. SEM image of (a) P25/CaTiO₃NR(1/3), (b) P25/CaTiO₃NR(1/2), (c) P25/CaTiO₃NR(1), (d) P25/CaTiO₃NR(2), (e) P25/CaTiO₃NR(3), (f) P25/CaTiO₃NR(4), and (g) P25/CaTiO₃NR(5)

3.2 Photocatalyst degradation performance

The decomposition performance of organic matter was evaluated under simulated UV irradiation using MB solution as a model for organic contaminants. As shown in Fig. 4, the P25/CaTiO₃NR composite photocatalyst resulted in the highest degradation performance. CaTiO₃ alone cannot decompose most organic matter, but the addition of P25 significantly improves decomposition performance. The P25/CaTiO₃NR composite photocatalyst showed about 30% better degradation performance compared to P25. The heterostructure formation facilitates the separation of carriers excited by UV light and the transport of electrons, which is thought to enhance photocatalytic activity (Lu et al., 2022) (Jiang et al., 2020). The degradation performance was improved compared to the P25/CaTiO₃NC composite photocatalyst. The increased specific surface area is thought to have improved light absorption and electron transport (Gupta et al., 2021).

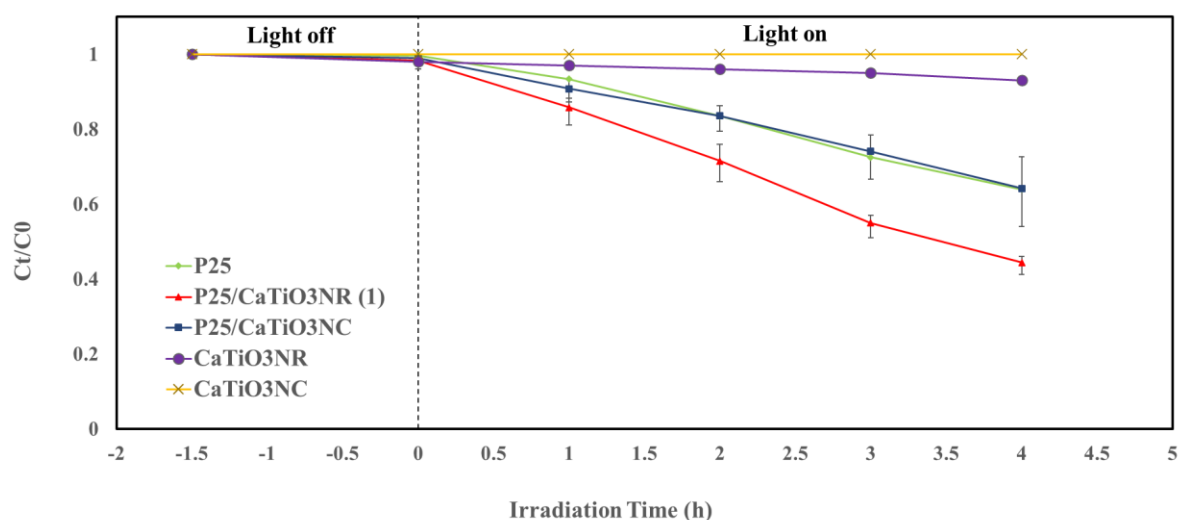


Fig. 4. Degradation performance of five photocatalysts in the degradation of methylene blue under UV irradiation.

As shown in Fig. 5, the P25 /CaTiO₃NR(3) composite photocatalyst had higher photocatalytic performance than the other P25 /CaTiO₃NR weight ratio samples, with about 60% better degradation performance than P25. Since CaTiO₃ alone is not very active as a photocatalyst, the lower the ratio of P25, the lower the photocatalytic performance, and the higher the ratio of P25, the lower the light irradiation to CaTiO₃NR and the lower the photocatalytic performance.

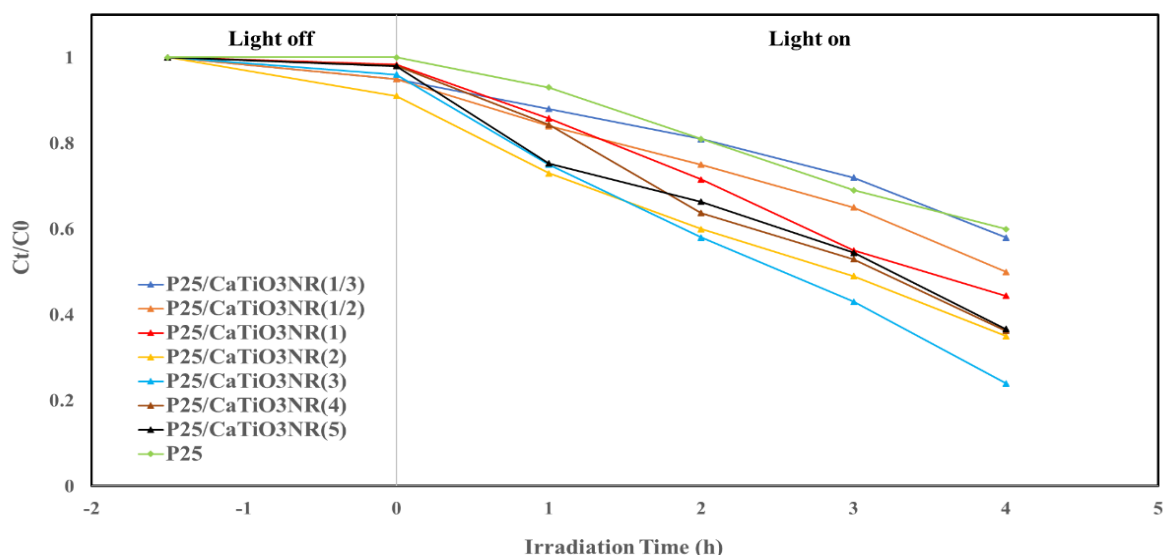


Fig. 5. Degradation performance of P25/CaTiO₃NR mass ratio in the degradation of methylene blue under UV irradiation.

4. Conclusion

In summary, using P25 as a precursor, CaTiO₃NR with a diameter of about 50 nm and a length of about 1 µm were prepared by hydrothermal synthesis. Then, the heterostructure was formed between CaTiO₃NR and P25, and the mass ratio was controlled to improve the photocatalytic activity by about 60% over P25. The heterostructure formation is thought to have enhanced the separation of photogenerated carriers and the transport of electrons, resulting in improved photocatalytic activity. The P25/CaTiO₃NR composite photocatalyst was found to be a better photocatalyst than the P25/CaTiO₃NC composite photocatalyst. The improved specific surface area may have improved the light absorption and electron transport properties of the P25/CaTiO₃NR photocatalyst. P25/CaTiO₃NR mass ratio was an important factor in improving photocatalytic performance, with P25/CaTiO₃NR=3:1 composite photocatalyst having the highest photocatalytic performance. These results indicate that the P25/CaTiO₃NR composite photocatalyst is an excellent photocatalyst, albeit under UV irradiation and limited conditions. In the future, we hope to use the P25/CaTiO₃NR composite photocatalyst to decompose organic matter under visible light irradiation.

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Ethics approval:

Not applicable.

Conflict of interest:

The authors declare that there is no competing interest.

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