Novel composite architectures made up of graphitic carbon nitride quantum dots/bismuth phosphate nanocrystals have been synthesized as a visible light-induced photocatalyst for efficient degradation of methyl orange.

The development of photocatalysts with high catalytic activity and good stability under sunlight is a key issue in photocatalysis science, and is also important in solving present environment and energy problems.\(^1\) The creation of efficient photocatalysts utilizing visible light (~43% of the solar irradiance) instead of UV light (~4% of the solar irradiance) seems greatly significant for practical applications.\(^2\) Recently, there has been a great deal of research focused on the synthesis of quantum dots (QDs)-based composite semiconductor architectures, such as carbon QDs/Ag\(_3\)PO\(_4\),\(^3\) carbon QDs/Cu\(_2\)O,\(^4\) CdS QDs/carbon nitride\(^5\) and CdS QDs/graphene,\(^6\) due to their outstanding dimensional effects, interfacial properties as well as multipurpose functionalities. As a result, the design of QDs-based composite is effective strategy to enhance the catalytic efficiency of photocatalysts under visible light irradiation.

Graphitic carbon nitride (g-C\(_3\)N\(_4\)) was found to be a stable and effective photocatalysts under solar light irradiation due to their remarkable electronic properties.\(^7\) The catalytic applications of g-C\(_3\)N\(_4\) include degradation of organic dyes, NO decomposition, Friedel–Crafts reactions, CO\(_2\) reduction, and water splitting, etc.\(^8\) Recently, many works presented that g-C\(_3\)N\(_4\) as one commonly available and promising photocatalyst with visible light response has particular superiority for environmental application.\(^9\) However, there are still some limitations in the bulk g-C\(_3\)N\(_4\) photocatalytic system, such as its low specific surface area and poor quantum yield.\(^10\) Generally, several approaches including dimension reduction\(^11\) and heterostructures\(^12\) can be used to deal with these problems, because the nanostructures can endow with maximum specific surface area of active component, and the heterostructures can effectively decrease the recombination of photo-generated electrons and holes,\(^13\) thus increasing the quantum efficiency of catalytic system. However, most of the reported g-C\(_3\)N\(_4\) nanostructures are composed of stacked 2-D nanosheets,\(^14\) and very few available examples concentrated on 0-D quantum dots exist,\(^15\) especially on QD-based heterostructures.

Bismuth phosphate (BiPO\(_4\)), as a new type of oxy-acid salt photocatalyst, has proved to be of more superior photocatalytic activity than that of TiO\(_2\) (P25) photocatalyst for the degradation of organic dye.\(^16\) It is found that both the wider band gap (3.85 eV) and higher separation efficiency of electron–hole pairs contributed to the high photocatalytic activity of BiPO\(_4\) photocatalyst.\(^17\) Expressly, the inductive effect of PO\(_4\) helps the e\(^-\)/h\(^+\) separation, which plays an important role in its excellent photocatalytic activity.\(^18\) Up to now, the most of previous applications of BiPO\(_4\)-based photocatalysts were limited to UV light.\(^19\) To obtain a more efficient utilization of sunlight therefore, it is of great significance to develop efficient visible light (\(\lambda > 420\) nm) induced photocatalysts for organic dye photodegradation.

In this communication, we demonstrate the creation of novel g-C\(_3\)N\(_4\) quantum dots/BiPO\(_4\) nanocrystals (g-C\(_3\)N\(_4\) QDs/BiPO\(_4\) NCs) composite architectures with significantly enhanced photocatalytic activity for degradation of methyl orange (MO) under visible light irradiation. For this composite system, three features have become apparent in previous reports: (i) unique g-C\(_3\)N\(_4\) QDs in size of ~5 nm are successfully synthesized; (ii) spherical BiPO\(_4\) NCs in diameter of ~60 nm are also achieved and (iii) novel heterostructures on the base of g-C\(_3\)N\(_4\) QDs and BiPO\(_4\) NCs are firstly created by a facile synthesis procedure. With these merits, we investigated that the MO photo-degradation with excellent performances, including...
high activity and stability, could be designed on the basis of such composite architectures.

For the synthesis (see ESI† for details) of g-C₃N₄ QDs/BiPO₄ NCs composite architectures, a associated sonochemical and heat-treating synthesis was introduced, by using CH₂N₂, NaH₂PO₄ and Bi(NO₃)₃·5H₂O as precursor materials. The integrated synthesis process of g-C₃N₄ QDs/BiPO₄ NCs composite and synthetic mechanism of g-C₃N₄ are schematically shown in Fig. 1. Firstly, the precursor ions of Bi³⁺ could be easily combined with PO₄³⁻ to form deposited BiPO₄ NCs. Meanwhile, the CH₂N₂ precursor can be evenly adsorbed on to the surface of BiPO₄ NCs under ultrasonic dispersion. Afterward, g-C₃N₄ QDs were formed and assembled on the surface of BiPO₄ NCs via a bottom-up growth from CH₂N₂ precursor,⁷ at the elevated temperature in subsequent procedure. Generally, the condensation pathway from amino cyanide to dicyandiamide and later to melamine and melem was seen as a receivable synthetic mechanism to generate the slightly defect polymeric species of carbon nitride.⁸ It is noteworthy that all these NCs growth and QDs assemble processes can be accomplished by the facile sonochemical synthesis and heat-treatment procedure.

In order to confirm the crystalline and atomic structures of the as-prepared g-C₃N₄ QDs/BiPO₄ NCs composite, the XRD and XPS analysis were carried out, respectively. Fig. 2(A) shows the XRD patterns of g-C₃N₄ QDs/BiPO₄ NCs (green) and single BiPO₄ NCs (blue). Evidently, for the both samples, the same diffraction peaks of BiPO₄ (JCPDS 15-0766) have been detected, in which the peaks at 2θ ≈ 14.6°, 20.1°, 25.5°, 29.5°, 31.3°, 41.9° and 48.7° are corresponding to the diffraction peaks of (100), (101), (110), (200), (102), (211) and (212) crystal planes of BiPO₄,⁹ The XRD pattern of g-C₃N₄ QDs/BiPO₄ NCs composite have an additional peak at 2θ ≈ 27.5° (as labelled by *), corresponding to the inter-planar distance of d = 0.324 nm, can be indexed as the (002) peak of the stacking of the conjugated aromatic system in g-C₃N₄.⁷ The XRD pattern of g-C₃N₄ QDs/BiPO₄ NCs composite have an additional peak at 2θ ≈ 27.5° (as labelled by *), corresponding to the inter-planar distance of d = 0.324 nm, can be indexed as the (002) peak of the stacking of the conjugated aromatic system in g-C₃N₄.⁷ The XRD pattern of the single g-C₃N₄ sample are shown in Fig. S1(A) and (B).† Respectively, the results demonstrate that the single technique, with the results shown in Fig. 3. Fig. 3(A) and (B) display the typical TEM images of the single BiPO₄ NCs in different magnification, which indicate that the sample has an approximate spherical nanostructures. The diameter of BiPO₄ NCs ranges from 40 nm to 80 nm, and the dominant diameter would be about 60 nm (see Fig. 4(A)). On the other hand, the detailed microstructures of g-C₃N₄ QDs/BiPO₄ NCs have been demonstrated in Fig. 3(C) and (D). Obviously, multitudinous g-C₃N₄ QDs have been synthesized and uniformly distributed on the surface of BiPO₄ NCs. The diameter of g-C₃N₄ QDs ranges from 3 nm to 7 nm, and the dominant diameter would be about 5 nm (see Fig. 4(B)). Remarkably, despite that the size of g-C₃N₄ QDs is very small, no secondary particle aggregation can be observed on the surface of BiPO₄ NCs, suggesting a good compatibility of the heterogeneous components of BiPO₄ and g-C₃N₄. For comparison, the single g-C₃N₄ sample was also achieved at the absence of bismuth nitrate while keeping other conditions unchanged in the synthesis. The TEM image and XRD pattern of the single g-C₃N₄ sample are shown in Fig. S1(A) and (B),† respectively. The results demonstrate that the single

![Fig. 1 Schematic processes for the formation of g-C₃N₄ QDs/BiPO₄ NCs composite by associated sonochemical and heat treating synthesis.](image1)

![Fig. 2] A) XRD patterns of g-C₃N₄ QDs/BiPO₄ NCs (green) and single BiPO₄ NCs (blue); B) XPS spectrum (N 1s) of g-C₃N₄ QDs/BiPO₄ NCs. (A) XRD patterns of g-C₃N₄ QDs/BiPO₄ NCs (green) and single BiPO₄ NCs composite architectures, a associated sonochemical and heat-treating synthesis was introduced, by using CH₂N₂, NaH₂PO₄ and Bi(NO₃)₃·5H₂O as precursor materials. The integrated synthesis process of g-C₃N₄ QDs/BiPO₄ NCs composite and synthetic mechanism of g-C₃N₄ are schematically shown in Fig. 1. Firstly, the precursor ions of Bi³⁺ could be easily combined with PO₄³⁻ to form deposited BiPO₄ NCs. Meanwhile, the CH₂N₂ precursor can be evenly adsorbed on to the surface of BiPO₄ NCs under ultrasonic dispersion. Afterward, g-C₃N₄ QDs were formed and assembled on the surface of BiPO₄ NCs via a bottom-up growth from CH₂N₂ precursor,⁷ at the elevated temperature in subsequent procedure. Generally, the condensation pathway from amino cyanide to dicyandiamide and later to melamine and melem was seen as a receivable synthetic mechanism to generate the slightly defect polymeric species of carbon nitride.⁸ It is noteworthy that all these NCs growth and QDs assemble processes can be accomplished by the facile sonochemical synthesis and heat-treatment procedure.

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![Fig. 3 Typical TEM images of the as-prepared samples: (A and B) single BiPO₄ NCs and (C and D) g-C₃N₄ QDs/BiPO₄ NCs.](image2)
The g-C3N4 sample has the same crystallographic structure (with a characteristic peak at 2θ ≈ 27.5°) as compared with g-C3N4 QDs, whereas the morphological structure of the single g-C3N4 sample is entirely different (with a porous fibre structure in size of 100 nm). It could be deduced that the BiPO4 solid surface might play an important role in the formation of smaller g-C3N4 QDs, and the further studies toward the detailed growth mechanism are now underway. On the whole, it would be a promising innovation for the present study, as far as the quantum dot architecture concerned, relative to the previously reported g-C3N4 2-D nanostructures.

As one important factor that may influence the photocatalytic properties, the BET specific surface area has been determined through the nitrogen adsorption/desorption measurements. The BET specific surface area of the single BiPO4 NCs, g-C3N4 QDs/BiPO4 NCs and single g-C3N4 samples is 8.3, 39.4 and 62.8 m² g⁻¹, respectively. The higher surface area of single g-C3N4 sample should be derived from the lower density than the single BiPO4 NCs sample. In addition, the mass content of BiPO4 in the g-C3N4 QDs/BiPO4 NCs is estimated to be 87.4 wt% based on the lower density of g-C3N4 (namely 12.6 wt%). It can be calculated that the potential specific surface area of g-C3N4 QDs is as high as 255 m² g⁻¹, in which the specific surface area is beneficial for building photocatalysts with high activity.

The visible light-induced photocatalytic activities of the as-prepared samples were evaluated by degradation of methylene orange (MO), a hazardous dye as well as a representative model to test the photodegradation capability of nanoarchitectures. Fig. 5 shows the photocatalytic activities and kinetics of the as-prepared photocatalysts including the single BiPO4 NCs, single g-C3N4 and g-C3N4 QDs/BiPO4 NCs (based on the composite) samples, for the degradation of MO dye in aqueous solution under visible-light irradiation. Obviously, the g-C3N4 QDs/BiPO4 NCs composite photocatalyst exhibits a higher photocatalytic activity than the single g-C3N4 photocatalyst, where the MO can be decolorized with about 92% in 180 min for g-C3N4 QDs/BiPO4 NCs, whereas the decolorization rate of single g-C3N4 was only about 75% (see Fig. 5A). The first-order reaction rate constant can be calculated by the plots of the ln (C/C0) vs. radiation time (t). The obtained rate law may be ln (C/C0) = -kt, where C is the concentration of dye, C0 the initial concentration of dye, k the reaction rate constant, and t the irradiation time. The degradation rate constant k of g-C3N4 QDs/BiPO4 NCs was estimated to be 0.0135 min⁻¹, which was 1.7 times as high as that of single g-C3N4 (0.0079 min⁻¹) (see Fig. 5B). A contrast degradation experiment over single BiPO4 NCs was also achieved, and the result showed that single BiPO4 there is no obvious photocatalytic activity under visible-light irradiation, which is similar to the case without the use of catalyst.

In an attempt to learn about the potential activity of g-C3N4 component in the g-C3N4 QDs/BiPO4 NCs composite, the photocatalytic activity was normalized on the base of component mass (see Fig. 6A). Remarkably, the photocatalytic activity on the base of g-C3N4 QDs in g-C3N4 QDs/BiPO4 NCs under visible irradiation can be estimated to be 13.5 times as high as that of single g-C3N4 sample. Understandably, the high activity of g-C3N4 QDs mainly originates from the high specific surface area of g-C3N4 QDs and the potential promoted effect from BiPO4 NCs. Furthermore, the photocatalytic activity was further normalized on the S BET of g-C3N4 component, from which one can conclude the promoted effect of BiPO4 component (see Fig. 6B). Fortunately, the S BET normalized photocatalytic activity was still 3.3 times that of single g-C3N4 sample, which clearly demonstrates that introducing BiPO4 into g-C3N4 photocatalyst system can effectively enhance their photocatalytic activity.

The stability of photocatalysts is another important issue for their assessment and application. Therefore, the cycling runs for the degradation of MO on the single g-C3N4 and g-C3N4 QDs/BiPO4 NCs samples were further performed to evaluate the photocatalytic stability (see Fig. 7). After every 180 min of photodegradation, the photocatalysts were separated and washed with deionized water. The stability testing results illustrated that both the degradation rates of the two samples showed slightly decrease after the continuous four-run repeated irradiation within 720 min. The above mentioned results demonstrate that the obtained g-C3N4 QDs/BiPO4 NCs composite can be used as a promising photocatalyst with excellent activity and

**Fig. 4** Histograms of diameter distribution for (A) BiPO4 NCs and (B) g-C3N4 QDs by TEM measurement.

**Fig. 5** Photocatalytic activities (A) and corresponding rate constant k (B) of MO degradation for the as-prepared photocatalysts.

**Fig. 6** Normalized photocatalytic activity based on the mass (A) and S BET (B) of the designated component.
BiPO₄ may capture the adsorbed O₂ on the composite catalyst resulting in enhanced photocatalytic activity and stabilization. The CB of g-C₃N₄ to that of BiPO₄. Meanwhile, the photo-generated electron–hole pairs at the g-C₃N₄/BiPO₄ interface. 

For a possible degradation process, the electrons on the BiPO₄ can capture the adsorbed O₂ on the composite catalyst surface and reduce it to ‘O₂’ . The hydrogen ions ionized from water molecular might be combined with the moderate ‘O₂’ to form H₂O₂ molecular. H₂O₂ can then be further activated to the most reactive ‘OH by accepting a third photo-generated electron and cause the formation of ‘OH groups. On the other hand, the holes on the g-C₃N₄ can also bond with water to generate more ‘OH groups. Under the action of substantial strong oxidizing species, the structure of MO was destroyed and finally decomposed into degradation products. All these processes could be described as follows:¹⁹

\[
\begin{align*}
\text{e}^- + \text{O}_2 & \rightarrow \text{‘O}_2^- \\
\text{‘O}_2^- + \text{e}^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{e}^- & \rightarrow \text{‘OH} + \text{OH}^- \\
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \text{‘OH} + \text{H}^+ \\
\text{‘OH} + \text{MO} & \rightarrow \text{degradation products}
\end{align*}
\]

In conclusion, for the first time we demonstrated the synthesis of g-C₃N₄ QDs/BiPO₄ NCs composite photocatalysts for the advanced application of photodegradation water purification. The as-prepared g-C₃N₄ QDs has uniform and ultrathin nanostructures, which are well assembled on the surface of BiPO₄ NCs without the extraneous adhesive agents. Due to the potential high specific surface area and favorable hetero-structures, the g-C₃N₄ QDs/BiPO₄ NCs composite photocatalyst exhibited significantly enhanced photocatalytic activity for the degradation of methylene orange under visible-light irradiation. The decolorization rate of can reach 92% for the g-C₃N₄ QDs/BiPO₄ NCs, while that of single g-C₃N₄ was only about 75%. The photocatalytic activity on the base of g-C₃N₄ QDs in g-C₃N₄ QDs/BiPO₄ NCs can be estimated to be 13.5 times as high as that of single g-C₃N₄. The present findings suggest that this novel g-C₃N₄ QDs/BiPO₄ NCs composite architecture could be used as one of promising visible light-induced photocatalysts for the degradation of organic dyes.

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**Notes and references**


