纳米片自组装的(BiO)₂CO₃单分散微米绒球的 绿色可控合成及其光催化性能

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摘要: 采用水为溶剂, Bi(NO₃)₃·5H₂O为Bi源, C₆H₅Na₃O₇·2H₂O (TCD)为配体构筑了前驱配合物Bi-TCD, 通过配合物分解实现了由纳米片自组装的碳酸氧铋(BS)微米绒球的绿色可控合成, 例如, BS的结构和形貌可由改变反应物浓度和反应时间来调控。我们发现, 一方面, TCD的配位作用可致BiO⁺离子缓慢释出从而调控BS的形成速率; 另一方面, 尿素在BS材料的形成过程中起碳源、碱源、形貌调控剂和晶体成长控制剂的多重作用, 通过调控尿素的浓度制备了三种分别沿着[001]、[110]和[013]优势生长方向的BS晶体。这种合成方法成本低, 不需要有机溶剂、模板、表面活性剂、高温和很长的反应时间; 产物分散性好; 产率高; 且拥有可控的形貌和优势生长方向。特别是由纳米片自组装的BS微米绒球对罗丹明B展现出优异的光催化性能。我们相信当前工作将是绿色可控合成和无机微纳材料应用方面的一个重要进展。

关键词: 碳酸氧铋; 绿色可控合成; 光催化性能; 微米绒球; 二水合柠檬酸三钠
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Facile Green Synthesis of Highly Monodisperse Bismuth Subcarbonate Micropompons Self-assembled by Nanosheets: Improved Photocatalytic Performance

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Abstract: This work reports a controlled green synthesis of highly monodisperse bismuth subcarbonate (BS) micropompons self-assembled by nanosheets using a simple and facile hydrothermal route in which deionized water, bismuth nitrate pentahydrate (BNP), and urea were used as the solvent, bismuth source, and carbon source respectively. Trisodium citrate dihydrate (TCD) was used as a coordination agent to fabricate a complex precursor. The structure and morphology of the BS materials can be finely modulated by adjusting the initial concentration ratios of the reactants or the reaction time. The presence of TCD decreased the formation rate of BS due to a direct competitive interaction for the BiO⁺ ions between a coordination equilibrium and a precipitation equilibrium. Urea played a crucial role (e.g., carbon source, alkaline source, morphology control agent, and crystal growth control agent) in the formation of the BS microstructures. We obtained three kinds of BS crystals with preferred orientations along [001], [110], and [013] by adjusting the concentration of urea. Our synthesis approach has the advantages of low cost, high reaction yields, monodisperse particles, controlled morphologies and orientations, and not requiring the use of organic solvents, templates, surfactants, high

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temperatures, and long reaction times. Particularly, when compared with those reported by other investigators, the micropompon material exhibited improved photocatalytic performance for Rhodamine B due to a unique microstructure (large specific surface area, high efficiency of photoelectric conversion, small interfacial charge-transfer resistance, and active {001} exposed facets). These results indicate a major advance in the controlled green synthesis and the application of inorganic micro- and nano-materials.

Key Words: Bismuth subcarbonate; Controlled green synthesis; Photocatalytic performance; Micropompons; Trisodium citrate dihydrate

1 Introduction

Photocatalytic technology has attracted wide attention toward designing novel photocatalysts with excellent activity to mitigate the global energy crisis and environmental pollution^{1,2}. Among the photocatalysts investigated, micro- and nano-materials with layered structures have been a subject of increasing interest, because their anisotropic crystal structure and internal static electric field effect can efficiently improve photoinduced charge separation and transfer³. It has been reported that the $5d^{10}6s^2$ valence orbits of Bi (III) ions can hybridize with the O-2p valence orbits to form a hybridized valence band, thereby allowing oxide semiconductors of the ions to exhibit a specific absorption in visible light range⁴, for example, high photocatalytic performance of bismuth oxyhalides⁵. Bismuth subcarbonate $[(\text{BiO})_2\text{CO}_3, \text{BS}]$, a newcomer of Sillen-type semiconductors, with alternating layers of $(\text{BiO})_2^{2+}$ and CO_3^{2-} ions, bears close resemblance to those seen in bismuth oxyhalides⁵.

In the last years, BS has drawn considerable attention because of its strong antibacterial activity, good photoelectric property, and high photocatalytic performance, becoming a very active research area^{6–12}. Several groups have an interest in designing and synthesizing BS micro- and nano-structures with different morphologies^{8–19}. For example, Dong and co-workers^{14b} successfully synthesized monodisperse BS microspheres using ammonia bismuth citrate and urea as reactants through a hydrothermal process at 453 K for 12 h. The as-obtained BS microspheres exhibited efficient photocatalytic removal of NO in indoor air under UV light or visible irradiation. Chen and his coagents^{8,17} obtained nanotube, nanoplate, and nanocube-like structures of BS by a simple reflux or solvothermal synthesis using ethylene glycol or mannitol as a solvent. They found that the solvent ethylene glycol or mannitol played an important role in controlling the morphology of BS. Cao and his colleagues⁹ successfully prepared persimmon-like BS microstructures using polyacrylamide as a template *via* a simple hydrothermal process at 453 K. Moreover, Liu's group^{14a} reported the synthesis of novel hierarchical rose-like BS microstructures using ammonia bismuth citrate as bismuth source in the presence of polyvinylpyrrolidone through a hydrothermal treatment at 453 K for 12 h. The BS microstructures assembled by 2D single-crystalline nanosheets with dominant {001} facets exhibited good photocatalytic performance. Recently, Qian's group¹⁵ synthesized sponge-like BS structures at 453 K for 18 h, and found that the morphology and Brunauer-Emmett-Teller (BET) specific surface area of the obtained BS materials could be

easily adjusted by changing the concentration of reactants.

There is no doubt that the results of these authors were qualitatively representative, but it is well to note that in most instances the synthesis techniques either required a high temperature and/or a long reaction time to be applied^{15,18,19}, or tended to use organic solvents or templates^{8,15,17}, which do not satisfy the requirements of green synthesis due to the creation of organic waste and pollutants. Therefore, a green, mild and controllable synthesis method needs to be developed. This is one objective of the present work (Scheme 1).

In this study, a simple one-pot hydrothermal synthesis was carried out in a sealed Teflon-lined stainless steel autoclave at 413 K for 10 h using deionized water, bismuth nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}, \text{BNP}]$, and urea as solvent, bismuth source and carbon source respectively, when trisodium citrate dihydrate $[\text{Na}_3\text{Cit} \cdot 2\text{H}_2\text{O}, \text{TCD}]$ was used as a coordination agent to fabricate the citrate complex Bi-Cit as a precursor^{20,21}. White crystals of BS with spherical-shape were successfully obtained. The main advantages of this method, when compared to previously available synthesis methods^{2,3,9,10}, are its simplicity (comes from simple inorganic salts rather than expensive Bi-Cit) and the absence of polymer ligands.

The other objective of the present work is to improve photo-

Scheme 1 Objective one is achieved by the coordination of Bi(III) ions with Cit^{3-} and the slow hydrolysis of urea; objective two is met very satisfactorily due to very large specific surface area and exposed {001} facets of the as-obtained BS material

catalytic performance of BS by the analysis of the relation between the structure and photocatalytic performance of BS (Scheme 1). The as-prepared BS materials were characterized by various techniques. Our results provide new insights in understanding the catalytic capabilities of BS and how they might be enhanced by controlled crystal-facet synthesis. We believe that these results are significant milestones towards the controllable fabrication of Bi-based photocatalysts based on the concept of green synthesis.

2 Experimental

2.1 Materials

Citric acid, BNP, TCD, sodium tartrate dehydrate, urea, sodium hydroxide and sodium sulfate were purchased from Shanghai Chemical Reagent Company. Rhodamine B (RhB) was obtained from Aladdin Chemistry Co. Ltd. Lead. All other reagents were the best available commercial products, used without further purification. Water used in the preparation of solutions for measurements was distilled and deionized carefully before use.

2.2 Preparation of the BS materials

The BS-1 was synthesized by a facile hydrothermal process. First, TCD of 0.882 g (3 mmol) and BNP of 0.484 g (1 mmol) were dissolved in 40 mL of deionized water at room temperature under vigorous stirring for 0.5 h, and then urea of 0.301 g (5 mmol) was added to the solution. This solution was stirred for another 0.5 h. Subsequently, the solution was removed to a Teflon-lined stainless autoclave (50 mL). The autoclave was maintained at 413 K for 10 h, and then cooled gradually to ambient temperature. Finally, a white precipitate was collected *via* centrifugation, and washed with deionized water and absolute ethanol several times and dried in vacuum. All of the other samples including the BS-2 and BS-3 were synthesized in a similar fashion.

2.3 Material characterization

The X-ray diffraction (XRD) measurements were recorded on a Philips X'Pert Pro X-ray diffractometer equipped with monochromatized Cu K_α ($\lambda = 0.15418$ nm) radiation operated at 40 kV and 40 mA in the range: $10^\circ \leq 2\theta \leq 65^\circ$. The field emission scanning electron microscope (FE-SEM) images were performed by using a Supra 40 FE-SEM. The transmission electron microscopy (TEM), high-resolution (HR-TEM) images, and selected-area electron diffraction (SAED) patterns were taken on JEF 2100F microscope performing at 200 kV. The UV-Vis diffuse-reflectance spectrum (DRS) of the BS-1 was recorded employing a Shimadzu DUV-3700 spectrophotometer in the wavelength between 220 and 1000 nm. Barium sulfate powder was used as the reflectance standard material to adjust baseline parameters. UV-Vis spectra were done with a Shimadzu UV 3600 spectrometer in the range of 200–800 nm. X-ray photoelectron spectroscopy (XPS) measurements were done using an ESCALAB 250 spectrometer with Al K_α radiation (1486.6 eV) in ultra-high vacuum (2.67×10^{-7} Pa). And all of the values of binding energy were referenced to C 1s peak (284.8 eV) with an energy resolution of 0.16 eV. Nitrogen adsorption/desorption isotherms were acquired

using Micromeritics ASAP-2000 at 77 K. The photoluminescence (PL) measurements were performed on a Perkin Elmer Luminescence spectrometer L550B at room temperature (excited at 280 nm).

2.4 Photocatalytic measurements

The photocatalytic activities of the BS materials were evaluated by the degradation of RhB in aqueous solution under visible light irradiation. Metal halide lamp (Shanghai Yaming Lighting Co. Ltd., XY73, 220 V, 150 W) was used as the light source. In a typical experiment, 25 mg of the BS-1 sample was added to a solution of RhB (50 mL, $10 \text{ mg} \cdot \text{L}^{-1}$). Before being irradiated, the solution was stirred in the dark for 60 min at room temperature to establish the adsorption equilibrium between the solution and the photocatalyst. Subsequently, the solution was irradiated under metal halide lamp for 70 min. Finally, the BS catalyst was separated by centrifugation and the supernatant solution was analyzed using an UV-Vis spectrophotometer.

2.5 Photoelectrochemical measurements

The BS-1 material was coated on the indium-tin oxide electrode. The electrode was immersed in Na_2SO_4 solution ($0.5 \text{ mol} \cdot \text{L}^{-1}$). Current-time curves were obtained by an electrochemical analyzer system, CHI760 (Chenhua, Shanghai, China) in a three-compartment cell with a working electrode, a platinum plate counter electrode and a Ag/AgCl reference electrode under a bias voltage of 0.5 V using the excitation light of Xe lamp (PLS-SXE300, 300 W) as the light source. Electrochemical impedance spectroscopy (EIS) experiments were carried out under visible light irradiation in $0.1 \text{ mol} \cdot \text{L}^{-1}$ KCl solution containing $5.0 \text{ mmol} \cdot \text{L}^{-1}$ $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1 : 1, molar ratio) mixture as a redox probe in the frequency range of 10^{-2} to 10^5 Hz with a perturbation signal of 10 mV.

3 Results and discussion

3.1 Structure and morphology of the BS-1 and BS-2

Fig. 1a shows the XRD pattern of the BS-1. All of the diffraction peaks are in perfect agreement with the tetragonal phase of BS [JCPDS 41-1488; space group $I4/mmm$ #139; $a = 0.3865$ nm and $c = 1.367$ nm]^{22,23}. No impurity phase was detected. The (002), (004) and (006) diffraction peaks are much sharper and stronger in intensity than those of the others, suggesting that the crystals preferentially grow along the [001] crystallographic direction^{13,24,25}.

The FE-SEM of the BS-1 in Fig. 1b indicates a large scale feature over the entire image, stressing high monodispersity and uniform size of about 1.6 μm . The magnified images in Figs. 1c and 1d exhibit that the BS-1 particles have a pompon-like morphology assembled by a side-by-side arrangement of nanosheets (side length, 200 nm; thickness, 40 nm). The TEM image (Fig. 1e) of a single micropompon reveals a regular spherical particle shape. The HR-TEM image (Fig. 1f) from an edge of the micropompon illustrates that the interplanar spacing of lattice fringes is 0.275 nm, which is indexed with the (110) plane in XRD pattern. This is demonstrated by the fact that the intersection angle between the (110) planes is 90° . The SAED pattern (the inset of Fig. 1f) taken

Fig.1 XRD patterns of the BS-1 and -2 (a), FE-SEM images (b–d), TEM image (e), and HR-TEM image (f) of the BS-1; FE-SEM images (g and h), TEM image (i), and HR-TEM image (j) of the BS-2

The inset in Fig.1f is the SAED pattern of the same place as shown in Fig.1f. The inset in Fig.1j is the SAED pattern of the same place as shown in Fig.1j.

from the edge of the same micropompon as the HR-TEM pattern shown in Fig.1f confirms the single-crystallinity of the nanosheet.

3.2 Formation process of the monodisperse BS-1 micropompoms

Initially, BNP was easily hydrolyzed into insoluble BiONO_3 (Eq. (1))²⁶, resulting in the release of H^+ ions into the solution ($\text{pH} \sim 2.8$), and then the BiONO_3 was reacted with the ligand Cit^{3-} to produce the Bi-Cit precursor complex^{20,21} ($\text{pH} \sim 6.0$, Eq.(2)). Clearly, the transfer between the two forms of Bi (III) is markedly dependent on the acidity of the medium. Thereafter, urea in the solution was hydrolyzed to OH^- ($\text{pH} \sim 9.5$) and CO_3^{2-} ions^{9,27}, and the Bi-Cit precursor in the alkaline solution was hydrolyzed into BiO^+ ^{9,14b}, when heated (Eqs.(3–6)). Finally, the CO_3^{2-} ions were reacted with the BiO^+ ions to form the BS-1 (Eq.(7))^{14b,19}.

In order to further understand the formation mechanism of BS, we examined the effect of reaction parameters including the reactant concentration, reaction time and temperature. There were several interesting findings.

First, the effect of the concentration of TCD on the morphology of a group of BS was investigated by changing the molar ratio of TCD and BNP from 3 : 1 to 0 : 1, 1 : 1, 2 : 1, and 5 : 1. As shown in Fig.S1 (Supporting Information (SI)), no appreciable difference was detected in their XRD patterns, and all the diffraction peaks belong to the tetragonal phase of BS. Fig.S2 (SI) shows that the creation of BS microparticles as well as the uniformity and dispersity of the particles was strongly dependent on the molar ratio. An adequate molar ratio to form regular spherical particles seemed to be between 2 : 1 and 3 : 1, and a higher or lower ratio led to either the formation of irregular particles or the appearance of clusters. These results provide a significant clue regarding the role of TCD. Although TCD might not act as a carbon source, it did play an important part in affecting the morphology of BS, namely, acting as a morphology control agent. This can be understood if we consider that the role of TCD is to form a precursor complex

(Eq.(2)), thus decreasing the formation rate of BS due to a direct competitive interaction for the BiO^+ ions between the coordination equilibrium (Eq.(6)) and the precipitation equilibrium (Eq.(7)).

Second, the effect of the concentration of urea on the formation of BS was studied by a series of similar syntheses with BNP (1 mmol) and urea of 0.420 g (7 mmol), 0.180 g (3 mmol), 0.060 g (1 mmol), 0.030 g (0.5 mmol) and 0 g (0 mmol) to get the materials: BS-2, -3, -4, -5 and -6, respectively. The XRD analysis (Fig.1a and Fig.2) reveals that the particles are pure and homogeneous, having the same tetragonal structure as their sister compound BS-1. The particle size increases, and especially the increase in the degree of crystallinity becomes more pronounced with the increase of the concentration of urea as can be seen from Fig.1(a, c, g), and Fig.2. Moreover, the relative intensity of the (110) diffraction peak in the BS-3 and -4 is significantly higher than that of the other three, indicating that the two crystals have a preferred orientation along the [110], which differs from the [001] orientation of the BS-1. Upon increase (BS-2) or decrease (BS-5) of the concentration of urea from this level, the preferred growth orientation is along the [013]. These findings highly suggest a potential role of urea in the regulation of BS crystal growth direction and thereby in the modulation of the BS structure. The control experiments supported the presence of the structural difference between the BS materials. As shown in Fig.1 (g, h), the BS-2 formed a nest-like structure (diameter, $\sim 1.3 \mu\text{m}$), with an internal hollow (Fig.1i), which was self-assembled by single crystal nanosheets (see the inset in Fig.1j). The spacing of

Fig.2 FE-SEM images and XRD patterns of the BS-1, -2, -3, -4 and -5

lattice fringes observed is 0.372 nm, corresponding to lattice spacing of (011) plane (Fig.1j). Further, we found that only Bi_2O_3 (BS-6) was formed in the absence of urea (Fig.S3 (SI)).

In light of the above observations, we think that the role of urea merits greater emphasis. On the one hand, it was used as the only carbon source for the formation of CO_3^{2-} . This was verified by the fact that TCD did not decompose at this temperature (Fig.S4 (SI)), though it could be used as a carbon source at higher temperatures^{15,19}. On the other hand, the presence of OH^- ions from the hydrolysis of urea^{28,29} contributed to the hydrolysis reaction of the Bi-Cit complex to generate BiO^+ (Eq.(6)). In other words, higher pH in this system was required to promote the hydrolysis of the complex. A simple experiment demonstrated this. A lower yield (42.0%) of BS was obtained when TCD was replaced by citric acid (pH ~ 6.3 in the system) while sodium tartrate (pH ~ 8.7 in the system) afforded a high yield (80.4%, Fig.S5 (SI)). In the other experiment (Fig.S6 (SI)), when urea was substituted by NaOH to create the same alkaline conditions (i.e., the molar ratio of NaOH to urea is 2 : 1), only Bi_2O_3 was observed. The results not only verified a synergistic effect of the combination of citrate and urea on the formation of BS, but also highlighted that a slow supply of OH^- ions^{7,8,16} was required for decreasing the formation rate of BS, perhaps by the competitive interaction between the two equilibria (Eqs.(6) and (7)).

It should be noted that the materials (BS-1–5) were constructed at the condition of excessive urea. As seen from Eq.(5), the increase of CO_3^{2-} ions signifies the decrease of OH^- ions. Thus, the relative concentrations of CO_3^{2-} and OH^- ions change with changing the initial concentration of urea. Recent reports showed that excessive CO_3^{2-} ions can cause a preferred growth orientation of BS^{9,10}, while a suitable pH may facilitate the oriented growth^{30,31}. Therefore, we have good reason to speculate the difference in the

crystal structure of the BS materials may be attributed to the difference in the concentrations of CO_3^{2-} and OH^- ions induced by the initial concentration of urea.

Based on these results, we conclude that urea acts not only as a carbon source and an appropriate alkaline source but also as a morphology control agent and especially a crystal growth control agent. This is an interesting result. The role of urea in many synthetic strategies was well established^{32–35}, but this is the first example in which it can exert so many functions for inorganic synthesis, i.e., acting as a multifunction reagent. Therefore, we expect that this result can be extended to other inorganic materials and more complex inorganic structures.

Finally, we performed several time-dependent experiments to elucidate the crystal formation process of BS. Fig.S7 (SI) displays the morphological evolution of the BS materials obtained at the identical pathway used for Fig.1c but at different growth stages: 2, 4, 6, 8 and 12 h. At an early stage of 2 h, irregular nanoparticles (diameter, ~ 120 nm) were formed. Subsequently (4 h), some of the nanoparticles were changed into nanosheets (thickness, ~ 30 nm) by spontaneous organization, and a few spherical structures constructed by the nanosheets appeared. When the reaction time was prolonged to 6 h, almost all the nanoparticles were changed into nanosheet structures, and more self-assembled microspheres were observed. With increasing the reaction time to 8 h, the nanosheets almost disappeared, and the self-assembled microspheres grew larger, but having different sizes. The larger particles grew at the cost of the small ones as described by the Gibbs-Thomson law³⁶. After the reaction continued for two more hours (10 h), the uniform pompon-like microstructures were formed (Fig.1c). When the reaction time was further increased to 12 h, the size of the micropompons was increased (Fig.S7). It is worth stressing that the crystallinity of the BS materials increases with increasing reaction time (Fig.S8 (SI)). Since this crystallinity increase was accompanied by a steady sharpening of the crystalline diffraction peaks, we consider that the crystallinity increase may be related to an improvement in the quality of the crystals. Furthermore, we found that temperatures can influence the size and uniformity of the BS particles formed (Figs.S9 and S10 (SI)). The proper temperature is about 413 K (Fig.1b), because a lower (393 K) or higher (433 K) led to nonuniform spherical structures. These observations convincingly demonstrate that the crystal growth of the microsphere-like BS was controlled by an Ostwald ripening process³⁷.

On the basis of the above results, a possible five-step growth process is presented in Fig.3. Initially, the precursor complex Bi-Cit was formed (Step I) in water. Then, with the aid of hydrolysis of urea to produce OH^- and CO_3^{2-} ions (Step II), the complex was hydrolyzed to release free BiO^+ ions (Step III). Subsequently, the CO_3^{2-} ions were reacted with the BiO^+ ions to produce BS crystal nuclei (Step IV). With the increase of reaction time, the crystal nuclei gradually grew up to form nanosheets. Finally, the nanosheets were stacked together, and self-assembled into BS microspheres (Step V). The optimal conditions for the micro-

Fig.3 Schematic illustration describing the formation process of the BS materials

pompon-like BS were determined to be as follows: TCD/BNP molar ratio, 3/1; urea/BNP, 5/1; temperature, 413 K; and time, 10 h.

Although some existing synthetic methods can obtain uniform size and good morphology of BS materials^{8,9,17}, but there are many problems in these methods such as the use of organic solvents, polymer additives or expensive complexes of bismuth (Table S1 (SI)), which is not conducive to the realization of large-scale production. Especially, the organic solvents and polymer additives are likely to cause pollution to the environment. Recently, some researchers tried to synthesize BS materials at room temperature or in the absence of coordination agents^{16b}, but they were unable to achieve the controllable synthesis of BS. Moreover, the synthesized materials usually have either large sizes or disordered layer structures^{16b}. Also, there were some attempts to improve the synthesis methods of BS, such as the use of citrate as a coordination agent or using urea as carbon source to control the reaction process^{6b,15}, but the improved methods still have some problems, such as long reaction time, high temperature or poor product morphology. To the best of our knowledge, our work provides the first example in which the formation mechanism of BS has been associated with the synergistic effect of the concentration combination of citrate and urea, thereby not only overcoming the problems of current concern in the synthetic field of BS, but also achieving a substantial progress to the controlled growth of BS nanostructures. We believe that the method can be extended to a wide range of carbonate materials.

3.3 Photocatalytic performance of the monodisperse BS micropompons

The specific surface area and porous structure of the BS-1–3 were explored by gas adsorption/desorption measurements in liquid nitrogen (Figs.S11–S13 (SI)). The sorption isotherms of the three materials exhibit a similar profile categorized as type IV³⁸ with a small hysteresis loop observed at relative pressures of 0.45–0.97, showing mesoporous characteristics (2–50 nm). It is worthy of remark that the BS-1 has a much larger BET³⁹ specific surface area ($36.65 \text{ m}^2 \cdot \text{g}^{-1}$) and a much narrower average pore diameter (8.94 nm) not only than the BS-2 ($10.79 \text{ m}^2 \cdot \text{g}^{-1}$, 31.95 nm) and BS-3 ($27.96 \text{ m}^2 \cdot \text{g}^{-1}$, 13.27 nm), but also than those reported by most investigators^{10,14,16,40}, further highlighting the advantage of the present synthesis method. There is a decreasing order of specific

surface areas: BS-1 > BS-3 > BS-2. Undoubtedly, this difference reflects dissimilar surface features. The fact that the surface of the BS-1 was loosely covered by numberless interconnecting nanosheets may be a major part of the reason for the increase in BET specific surface area and the decrease in average pore diameter.

Such a large difference in specific surface areas and pore diameters allow us to estimate whether there is a similar trend in their photocatalytic activity. Fig.4A displays the UV-Vis absorption spectra of RhB ($10 \text{ mg} \cdot \text{L}^{-1}$) in water after being treated by the BS-1 (25 mg) under a metal halide lamp ($0.26 \text{ W} \cdot \text{cm}^{-2}$). Clearly, the maximum absorption peak of RhB at 554 nm was gradually decreased with increasing irradiation time. Finally, the peak almost completely disappeared at 70 min of irradiation. The photodegradation degree (ζ , %) of RhB was determined by Eq.(8)⁴¹. In this equation, C_0 and C are the initial concentration of RhB and its equilibrium concentration after irradiation, respectively.

Our data indicate that the ζ value for the BS-1 at 70 min is up to 99.6%, but they are dramatically decreased to 64.7% for the BS-2 (Fig.4B, 75.3% at 100 min) and 85.8% for the BS-3 (Fig.4B, 98.2% at 100 min). Importantly, the values of ζ can still reach up to 98% for the BS-1 at 70 min over the first three cycles (Fig.S14 (SI)). Also, no change in crystal structure and surface morphology was observed after the consecutive cycles (Fig.S15 (SI)), emphasizing that the BS-1 catalyst possesses a good structural stability.

Thus, these results give a strong indication that the BS-1 has a high photocatalytic activity, stability and sustainability for the degradation of RhB. Furthermore, we noticed that the order of photocatalytic efficiency observed for the materials (BS-1 > BS-3 > BS-2) agrees with the order of decreasing specific surface area established above. Further, the density of O atoms on the {001} facets of the BS-1 is much higher than on the {013} facets for the BS-2 and the {110} facets for the BS-3⁴². It is known that the more oxygen atoms were exposed on the surface, not only resulting in more photo-induced oxygen vacancies but also enhancing the ability in separating the electron-hole pairs^{3,36}. This comparison suggests that control of crystal growth direction may be important in improving photocatalytic activity, which is in accordance with other studies^{6a,43}.

Fig.4 UV-Vis absorption spectra of the RhB solutions ($10 \text{ mg} \cdot \text{L}^{-1}$) after being treated by the BS-1 after 0, 10, 20, 30, 40, 50, 60 and 70 min of visible light irradiation (A), the photodegradation degree of RhB at different time points after treated by BS-1, -2 and -3 (B)

$$\zeta = [(C_0 - C)/C_0] \times 100\% \quad (8)$$

It is worth noting that the ζ value of RhB on the BS-1 is comparative to those previously reported for BS and bismuth oxyhalides, exhibiting an improved photocatalytic performance because the data reported by earlier authors were obtained either at relatively strong light levels, high catalyst concentrations, low dye concentrations or long irradiation times (Table S2 (SI)).

To determine what are the main active species responsible for the degradation of RhB in the photocatalytic process, we carried out a series of trapping experiments to evaluate the effect of radical scavengers. The photodegradation of RhB on the BS-1 was repeated, but with addition of ascorbic acid (AC, $1 \text{ mmol} \cdot \text{L}^{-1}$), isopropyl alcohol (IPA, $1 \text{ mmol} \cdot \text{L}^{-1}$) and ammonium oxalate (AO, $10 \text{ mmol} \cdot \text{L}^{-1}$) to quench superoxide radical ions ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$) and holes (h^+), respectively^{44,45}. As shown in Fig.S16 (SI), the degradation of RhB was highly inhibited by AO (10.8%) and AC (20.5%), but no significant decrease was found in the presence of IPA (92.4%). This, of course, gives a strong argument in favor of the contribution of both $\cdot\text{O}_2^-$ and h^+ ,

as the main active ingredients, to the degradation of RhB in aqueous solution.

Fig.5 presents a possible explanation regarding the degradation mechanism of RhB. At first, under visible light irradiation, the BS-1 was excited to generate electrons (e^-) in the conduction band (CB) and h^+ in the valence band (VB, Eq.(9)). Meanwhile, the photosensitization of RhB under visible light may induce the generation of RhB radicals (RhB^* , Eq.(10))⁴⁶, and the RhB^* with the excited electrons was adsorbed onto the BS-1 surface. Subsequently, the photo-induced electrons interacted with the O_2 molecules adsorbed on the exposed active {001} facets of the BS-1 to produce $\cdot\text{O}_2^-$, a very reactive radical anion intermediate (Eq. (11)), while the photogenerated electrons in the RhB^* were injected into the conduction band of the BS-1, forming radical cations $\cdot\text{RhB}^+$ (Eq.(12)). At last, the $\cdot\text{RhB}^+$ was reacted with the active $\cdot\text{O}_2^-$ and h^+ , and finally degraded into inorganic compounds such as CO_2 and H_2O (Eq.(13)).

In order to understand the relation between the structure and properties of the BS materials, XPS, UV-Vis DRS, PL, EIS and photoelectric responses were performed to examine how the structure of the materials (BS-1–3) affects their photoelectric conversion.

The XPS analysis displays that there are no other elements in these samples besides C, O and Bi. The peak at 284.8 eV can be assigned to adventitious carbon species from the XPS measurement, while the peak at 288.9 eV can be ascribed to the carbonate ion in the BS materials¹¹ (Fig.S17 (SI)). The UV-Vis DRS analysis (Fig.6A) shows that all the three materials have a similar absorption profile in the range of UV and visible regions, with maximum absorptions at 300, 289 and 281 nm for the BS-1, -2 and -3, respectively. A clear blue shift was observed as shown by the green arrow in Fig.6A. It is interesting to note, however, that the BS-1 exhibits higher absorption intensity than the other two in the UV and especially visible region, probably indicating a higher visible light utilization efficiency. The optical bandgaps were determined to be 3.03 eV for the BS-1, 3.31 eV for the BS-2 and 3.13 eV for the BS-3 (Fig.6B), based on the Kubelka-Munk function⁴⁸, correlating well with the order found in the specific surface area analysis. Such a difference in bandgaps may not only be a reason to make the difference between the maximum absorption wavelengths⁴⁹. The narrower band gap of the BS-1 led to a wider absorption range, which may be a direct factor responsible for improving its photocatalytic activity due to its higher visible

Fig.5 Possible photocatalytic mechanism of RhB on the BS-1

Fig.6 UV-Vis diffuse reflectance spectra (A), the plots of $(ah\nu)^{1/2}$ vs $h\nu$ (B) and valence-band XPS spectra (C) of the BS-1, -2 and -3
 a is the optical absorption coefficient, h is the Plank's constant, and ν is photon frequency.

Fig.7 PL spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of the BS-1, -2 and -3 (A) and the EIS spectra of the BS-1, -2 and -3 under visible light irradiation (B)

light utilization efficiency. The VBs of BS-1, -2 and -3 were measured based on valence-band XPS spectra (Fig.6C), and the edges of the maximum energy were found at approximately 1.87, 1.87 and 1.71 eV, respectively. According to the optical bandgaps, the CB minima occur at approximately -1.16 , -1.44 and -1.42 eV, respectively. In view that the oxidation potentials of photo-generated h^+ in the BS photocatalysts were negative than the standard redox potential of $\cdot\text{OH}/\text{OH}^-$ (1.99 eV)⁵⁰, we suggest that the h^+ photogenerated on the surface of the BS materials could not react with $\text{OH}^-/\text{H}_2\text{O}$ to form $\cdot\text{OH}$. Therefore, it is reasonable that h^+ or $\cdot\text{O}_2^-$ are likely responsible for the oxidation of RhB over the BS catalysts, in agreement with above trapping experiments. The PL profiles (Fig.7A) show that the BS-1 has a significantly lower luminescent intensity, in comparison with the BS-2 and -3, strongly implying a lower recombination rate of e^- and h^+ under UV light irradiation (excitation wavelength, 280 nm). In particular, its luminescent band covers a considerably wider spectral range (380–620 nm, without large intensity gradients).

The time-dependent photocurrent responses (Fig.S18 (SI)) indicate that upon illumination the photocurrents of the BS electrodes were abruptly increased to maxima of 77.61 nA for the BS-1, 42.36 nA for the BS-2 and 53.23 nA for the BS-3, as well as having good reproducibility (three times). This means that the BS-1 electrode exhibited a higher efficiency of photoelectric conversion, i.e., photo-induced charge separation and transfer, compared to the BS-2 and BS-3 electrodes. The analysis of EIS (Fig.7B) reveals that the separation and transfer efficiency of

photogenerated electron-hole pairs of the BS-1 is higher than those of the BS-2 and BS-3 since the BS-1 electrode presented a smaller radius of impedance arc, thereby having a lower interfacial charge-transfer resistance⁵¹.

These results indicate that the BS-1 material exhibits a relatively narrow bandgap, a low recombination rate of e^- and h^+ , a high efficiency of photoelectric conversion and a small interfacial charge-transfer resistance, thus effectively promoting the separation and transfer of charge carriers, which may be why it has an enhanced photocatalytic performance.

4 Conclusions

In summary, we have developed a facile and green hydrothermal route for the controllable synthesis of BS materials with unique microstructures (large specific surface area, ultrafine grain size and high monodispersity). Importantly, the crystal growth directions ([001], [013] and [110]) of the BS family can be readily tuned by adjusting the concentration combination of citrate and urea. Urea was found to play multiple roles (e.g., carbon source, appropriate alkaline source, morphology control agent and crystal growth control agent) in the formation process of BS crystals. This is the first report that the formation mechanism of BS was related to the synergistic effect of the concentration combination of citrate and urea. In particular, when compared with those reported by other studies, the BS-1 material shows an improved photocatalytic activity to RhB under visible light irradiation probably due to an effective separation and transfer of charge carriers on the {001}

facets. Overall, this work represents an important contribution to current efforts in understanding the controllable green synthesis and application of inorganic micro- and nano-structures.

Supporting Information: available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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纳米片自组装的 $(\text{BiO})_2\text{CO}_3$ 单分散微米绒球的绿色可控合成 及其光催化性能

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Facile Green Synthesis of Highly Monodisperse Bismuth Subcarbonate Micropompons Self-assembled by Nanosheets: Improved Photocatalytic Performance

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Fig.S1 XRD patterns of the BS materials obtained at different TCD to BNP molar ratio of 0 (a), 1 : 1 (b), 2 : 1 (c), 3 : 1 (d) and 5 : 1 (e)

Fig.S2 FE-SEM images of the BS obtained at different TCD to BNP molar ratio of 0 (a), 1 : 1 (b), 2 : 1 (c), 3 : 1 (d) and 5 : 1 (e)

Fig.S3 XRD pattern and FE-SEM image of the BS-6

Fig.S4 TG curve of TCD

Fig.S5 XRD patterns and FE-SEM images of the BS materials obtained by replacing $\text{Na}_3\text{Cit} \cdot 2\text{H}_2\text{O}$ with citric acid (a) and sodium tartrate (b)

Fig.S6 XRD pattern of Bi_2O_3 obtained by replacing urea with NaOH

Fig.S7 FE-SEM images of the $(\text{BiO})_2\text{CO}_3$ obtained at 2 (a), 4 (b), 6 (c), 8 (d), 10 (e) and 12 h (f)

Fig.S8 XRD patterns of the $(\text{BiO})_2\text{CO}_3$ obtained at 2 (a), 4 (b), 6 (c), 8 (d), 10 (e) and 12 h (f)

Fig.S9 XRD patterns of the BS materials obtained at different temperatures: 393 K (a) and 433 K (b)

Fig.S10 FE-SEM images of the BS obtained at different temperatures: 393 K (a) and 433 K (b)

Table S1 Representative synthesis process of BS materials

Materials	Bi source	Organic solvents	Surfactant/polymer	Reaction temperature/time	Reference
BS-1	Bi(NO ₃) ₃ 5H ₂ O	—	—	413 K/10 h	The present work
(BiO) ₂ CO ₃ nanotubes	Bi(NO ₃) ₃ 5H ₂ O	ethylene glycol	—	423 K/12 h	1
(BiO) ₂ CO ₃ nanotubes	bismuth citrate	ethylene glycol	cetyltrimethylammonium bromide	473 K/1 h	2
Rose-like (BiO) ₂ CO ₃	ammonia bismuth citrate	—	—	453 K/12 h	3
Persimmon-like (BiO) ₂ CO ₃	Bi(NO ₃) ₃ 9H ₂ O	—	polyacrylamide	453 K/12 h	4
Sponge-like (BiO) ₂ CO ₃	Bi(NO ₃) ₃ H ₂ O	—	—	453 K/24 h	5
(BiO) ₂ CO ₃ nanostructures	bismuth citrate	mannitol solution	—	423 K/12 h	6
cube-like (BiO) ₂ CO ₃	Bi(NO ₃) ₃ 5H ₂ O	mannitol solution	—	423 K/12 h	7
(BiO) ₂ CO ₃ microspheres	ammonia bismuth citrate	—	polyvinylpyrrolidone	453 K/12 h	8

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Fig.S11 N₂ adsorption-desorption isotherm and pore size distribution (inset) of the BS-1

Fig.S12 N₂ adsorption-desorption isotherm and pore size distribution (inset) of the BS-2

Fig.S13 N_2 adsorption-desorption isotherm and pore size distribution (inset) of the BS-3

Fig.S14 Photodegradation degree of RhB in the first three cycles

Fig.S15 XRD pattern and FE-SEM image of the BS-1 after three cycles of photodegradation of RhB

Table S2 Superiority of the BS-1 in degradation of RhB compared to other Bi-based materials

Materials	catalyst/dye concentration/(g mol ⁻¹)	Photodegradation degree/time	Light intensity (W)	Reference
BS-1	2.39×10^4	99.6%/70 min	150	the present work
BS nanotubes	5.00×10^4	84.0%/150 min	500	1
Persimmon-like BS	1.00×10^5	—/120 min	500	4
BS microspheres	1.00×10^5	95.0%/90 min	350	8
BS nanosheets	1.00×10^5	94.0%/120 min	350	9
BS nanosheets	2.39×10^4	97.0%/100 min	300	10
BS microflowers	8.00×10^4	—/50 min	1000	11

BS microspheres	8.00×10^4	—/10 min	300	5
Flower-like BS	2.39×10^4	—/30 min	250	12
BiOCl Single Crystals	1.00×10^5	78%/120 min	400	13
BiOBr/BiOI heterojunctions	3.33×10^4	—/120 min	500	14

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Fig.S16 Degradation degree (ζ) of RhB on the BS-1 in the presence of different quenchers [ammonium oxalate (AO) to h^+ , ascorbic acid (AC) to O_2^- , and isopropyl alcohol (IPA) to $\cdot\text{OH}$]

Fig.S17 XPS survey spectra (A) and XPS spectra of C1s peaks of BS-1, -2 and -3 (B)

Fig.S18 A plot of current response *vs* time for the BS-1, -2 and -3 under visible light irradiation