SUPPORTING INFORMATION

Formamide-assisted one-step synthesis of BiOCOOH and Bi/BiOCOOH micro-/nanostructures with tunable morphologies, composition and their photocatalytic activities

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Sample No.		O_L	$O_{\rm V}$	O _C
	Binding energy (eV)	530.1	531.4	532.5
S2	Relative percentage (%)	44.4	40.0	15.6
S4	Relative percentage (%)	42.1	57.9	

Table S1. The relative percentages of the $\mathrm{O}_L, \mathrm{O}_V$ and O_C from S2 and S4.



Fig. S1. The digital photographs of samples obtained at different reaction times for S2, S4 and S5 systems.



Fig. S2. The XRD patterns of samples obtained at different reaction times for S2, S4 and S5 systems.



Fig. S3. The FESEM images of samples obtained at different reaction times: (a) 0 min, (b) 5 min, (c) 6 h and (d) 12 h for S2 system; (e) 5 min, (f) 10 min, (g) 6 h and (h) 12 h for S4 system; (i) 10 min, (j) 20 min, (k) 6 h and (l) 12 h for S5

system.

The temporal evolution experiments were carried out by only changing the hydrothermal reaction time through taking the formation process of S2, S4 and S5 as the examples. The time when the oven reaches the reaction temperature of 120 °C is defined as the reaction time of 0 min. For S2 system, white products can be obtained from 0 min to 12 h (Fig. S1). The corresponding XRD patterns show that the product obtained at 0 min shows poor crystallinity, while the product obtained at 6 h and 12 h show good crystallinity (Fig. S2), and they are all indexed to tetragonal BiOCOOH. As shown in Fig. S3, the product obtained at 0 min displays flower-like micro-/nanostructures with different sizes and poor dispersion. However, the morphologies of the samples do not change obviously at different reaction time from 5 min to 12 h, and they all show uniform flower-like microspheres. The results indicate that the BiOCOOH nanosheets are easy to self-assemble into flower-like microspheres. As for S4 system, at 0 min of reaction time, there is no product to form. At the reaction time between 5 min and 10 h, white product can be obtained.

The gray product is formed until the reaction time reaches 12 h (Fig. S1). The corresponding

XRD patterns illustrate that the BiOCOOH product obtained at 5 min shows poor crystallinity and

the crystallinity of the sample obtained at 6 h becomes better. With increasing the reaction time to

12 h, the metallic Bi is formed on BiOCOOH (Fig. S2). It can be seen from the SEM images that the product changes from small nanosheets to larger nanosheets, and then to circular nanosheets aggregate (Fig. S3). There are no products to form at 0 or 5 min of reaction time, and only white product can be obtained at 10 min and 6 h for S5 system. From 8 h to 12 h, the color of the product begins to turn gray and deepen gradually, indicating the formation of metallic Bi and the increasing content of Bi⁰ in S5 sample (Fig. S1). Their XRD patterns further confirm these results (Fig. S2). It can be found some nanoparticles and unformed microdisks in the product at 10 min. As the reaction proceeds, the nanoparticles become fewer and the skeletons of the microdisks become clearer, and finally these microdisks assemble into pancakes (Fig. S3).



Fig. S4. Plots of $(ahv)^2$ vs. hv curves for the five samples.

For a crystalline semiconductor, the optical absorption near the band edge follows the Tauc's equation: $ahv=A(hv-E_g)^{n/2}$, where *a*, *h*, *v*, *A* and E_g are the absorption coefficient, Planck constant, light frequency, proportional constant and band gap energy, respectively. Herein, n is 4 for BiOCOOH because of its characteristic of indirect band transition.¹ Fig. S4 displays the plots of $(ahv)^{1/2}$ versus photon energy (hv) for five samples.

References

¹ L. Yang, Q. Han, X. Wang and J. Zhu, Chem. Eng. J., 2015, 262, 169–178.