Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Synthesis, characterization and enhanced visible light photocatalytic activity of Bi_2MoO_6/Zn-Al layered double hydroxide hierarchical heterostructures

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Fig. S1 Image of photocatalytic reaction equipment (XPA-7, Xujiang Electromechanical Plant, China)

Details for the preparation of mechanically mixed Bi_2MO_6/Zn-Al LDH (5.5%) composite and N doped TiO2 photocatalysts

Mechanically mixed Bi_2MO_6/Zn-Al LDH (5.5%) composite was prepared by grinding finely the mixture containing 0.200 g Bi_2MO_6 and 0.011 g Zn-Al LDH for 10 min.

N doped TiO2 photocatalyst was prepared by means of solid-state reaction method using urea as a nitrogen source[1]. P25 TiO_2 (1.0 g) was finely milled with urea (2.0 g) and the mixture was heated at 400 ºC for 2 h. After cooling to the room temperature, the N doped TiO_2 photocatalyst was obtained.

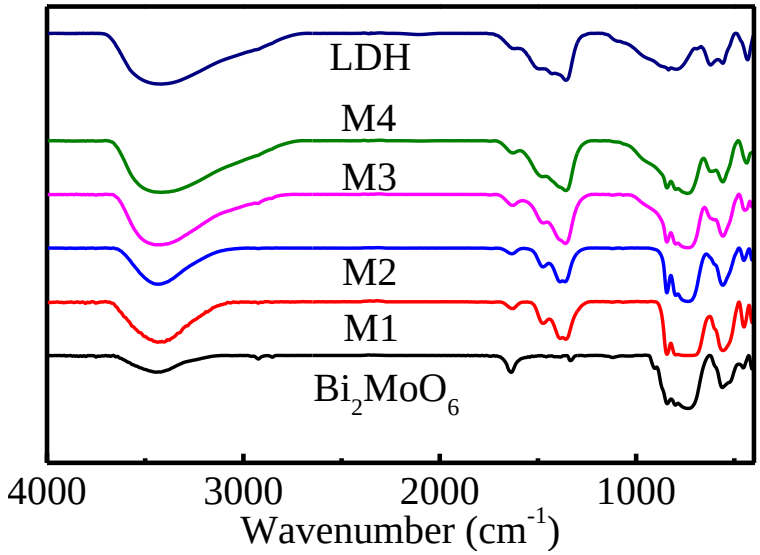

Fig. S2. FT-IR spectra of Bi_2MoO_6, Zn-Al LDH and their composites M1–M4.

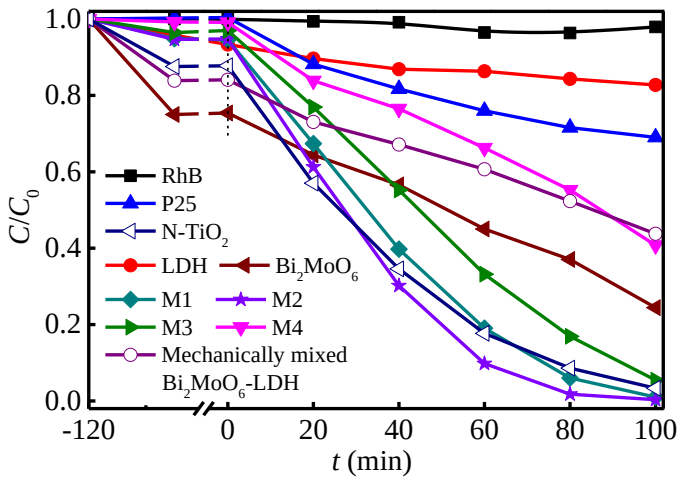

Fig. S3. Photocatalytic degradation of RhB, over various photocatalysts after different reaction time.

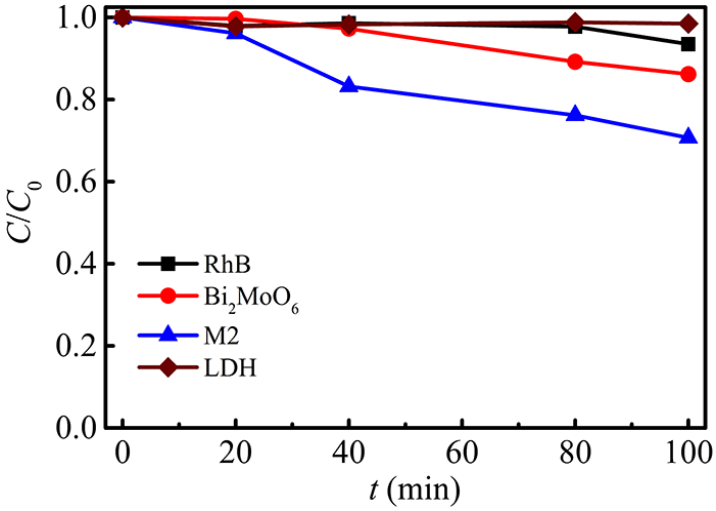

Fig. S4. TOC decrease of RhB solutions containing various photocatalysts.

Determination of E_g for as-prepared photocatalysts

E_g values were determined from the absorption spectra using the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α, ν and A are the absorption coefficient, light frequency, and proportionality constant, respectively. n was confirmed to be 1 by Parida's method [2]. Then the equation could be written as $(\alpha h\nu)^2 = A(h\nu - E_g)$. It could be noticed that the plot $(\alpha h\nu)^2 \sim h\nu$ is linear, as shown by the linear parts in the inset of Fig. 8. The

intersections of the extension lines of the linear parts and abscissa axis, where the $(\alpha hv)^2$ values are zero, are E_g values of photocatalysts, as shown by the dash lines in the inset of Fig. 8. From above equation, it can be seen that only when hv is equal to E_g, the value of $(\alpha hv)^2$ is 0, or the calculated E_g value for every photocatalyst is unique.

Potential determination of top of VB and bottom of CB for as-prepared Bi_2MoO_6 and Zn-Al LDH

The conduction band (E_{CB}) and valence band (E_{VB}) positions of the prepared samples are determined through the equations: $E_{VB} = X - E^e + 0.5E_g$ and $E_{CB} = E_{VB} - E_g$, where X is the Mulliken's electronegativity that is the geometric mean of the electronegativity of the constituent atoms (the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy), E^e is the energy of free electrons on the hydrogen scale (4.50 eV), and E_g is the band gap [3].

The X and E_g values of Bi_2MoO_6 are 5.55 eV [3] and 2.72 eV, respectively. Then E_{VB} and E_{CB} are calculated as follows:

E_{VB} = 5.55 eV - 4.50 eV + 0.5*2.72 eV = 2.41 eV

E_{CB} = 2.41 eV - 2.72 eV = -0.31 eV.

The E_g value of $[Zn_{0.66}Al_{0.34}(OH)_2](CO_3)_{0.17}\cdot 0.87H_2O$ is 3.07 eV. The electronegativity of Zn, Al, O, H, and C is 4.45 eV, 3.23 eV, 7.54 eV, 7.18 eV and 6.27 eV, respectively. Then the X, E_{VB} and E_{CB} values of $[Zn_{0.66}Al_{0.34}(OH)_2](CO_3)_{0.17}$ are calculated as follows:

$$X = \sqrt[5.68]{4.45^{0.66}3.23^{0.34}\cdot 7.54^{2.51}\cdot 7.18^{2}\cdot 6.27^{0.17}} = 6.59 \text{ eV}$$

E_{VB} = 6.59 eV - 4.50 eV + 0.5*3.07 eV = 3.62 eV

E_{CB} = 3.62 eV - 3.07 eV = 0.55 eV

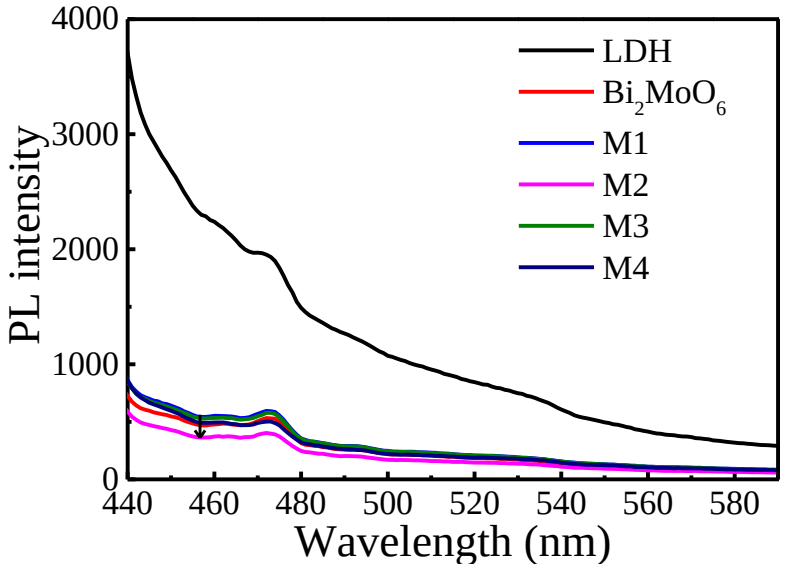

Fig. S5. PL spectra of Zn-Al LDH, Bi_2MoO_6 and their composites M1–M4.

Table S1

Samples	Content of Zn (%)	Content of Al (%)	Zn/Al ratio	LDH formula	LDH content (%)
Bi_2MoO_6	0	0			0
M1	2.39	0.50	1.98	$[Zn_{0.66}Al_{0.34}(OH)_2](CO_3^{2-})_{0.17}$	5.35
M2	4.53	0.95	1.97	$[Zn_{0.66}Al_{0.34}(OH)_2](CO_3^{2-})_{0.17}$	10.14
M3	11.15	2.30	2.00	$[Zn_{0.67}Al_{0.33}(OH)_2](CO_3^{2-})_{0.16}$	24.50
M4	18.73	3.92	1.97	$[Zn_{0.66}Al_{0.34}(OH)_2](CO_3^{2-})_{0.17}$	41.90
LDH	40.68	8.35	2.01	$[Zn_{0.67}Al_{0.33}(OH)_2](CO_3^{2-})_{0.16}$	89.41

1. D. Mitoraj and H. Kisch, *Angew Chem Int Edit*, 2008, **47**, 9975-9978.
2. L. Mohapatra, K. Parida and M. Satpathy, *J Phys Chem C*, 2012, **116**, 13063-13070.

3. Y.-S. Xu, Z.-J. Zhang and W.-D. Zhang, *Mater Res Bull*, 2013, **48**, 1420-1427.