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Photophysical and Photocatalytic Properties of Novel M_2BiNbO_7 (M = In and Ga)

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The structural formula of MB was shown in Figure S1. The structure of M_2BiNbO_7 (M = In and Ga) is shown in Figure S2. The structure of M_2BiNbO_7 (M = In and Ga) is composed of the three-dimensional network of MO_6 (M = Bi, Nb), stacked along [110] and separated by a unit cell translation (10.7146(5) or 10.4685(5) Å).

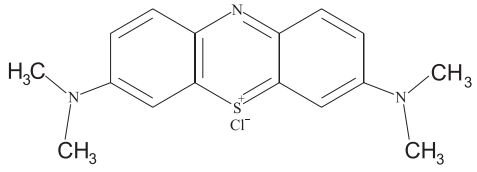

Figure S1. Structural formula of methylene blue.

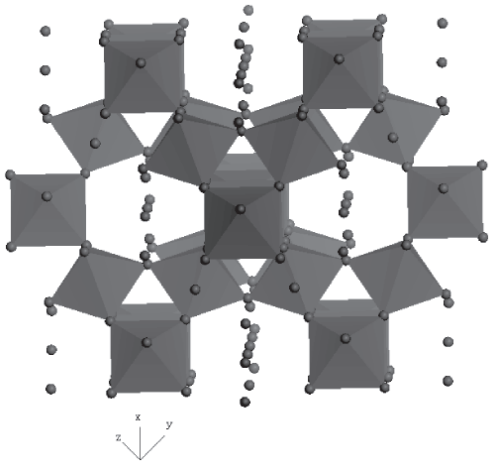

Figure S2. The schematic structural diagram of the cubic M_2BiNbO_7 (M = In and Ga) photocatalysts. Three-dimensional network of MO_6 stacked along [110] and separated by a unit cell translation.

For a crystalline semiconductor, it is commonly accepted that the optical absorption near the band edge follows the equation:[1,2] $\alpha h\nu = A(h\nu - E_g)^n$. A, α, E_g and ν are proportional constant, absorption coefficient, band gap, and light frequency, respectively. Within this equation, n determines the character of the transition in a semiconductor. E_g and n can be calculated by the following steps: plot $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ with an approximative value of E_g, then decide the value of n with the slope of the straightest line near the band edge, at last, plot $(\alpha h\nu)^{1/n}$ versus $h\nu$ and evaluate the band gap E_g by extrapolating the straightest line to the $h\nu$ axis intercept. Based on above method, the value of n for M_2BiNbO_7 (M = In and Ga) was calculated to be 0.5 from Figure 3 of the paper, indicating that the optical transitions for these oxides are directly allowed. Figure S3 shows the Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Ga_2BiNbO_7 and In_2BiNbO_7. Figure S2 showed that M_2BiNbO_7 (M = In and Ga) consisted of the network of MO_6, which is built by forming infinite corner-sharing MO_6 octahedra with the zigzag chains along [110]. This suggests that photogenerated electron-hole pairs in the M_2BiNbO_7 (M = In and Ga) photocatalysts can move easily in this direction, which may result in a high photocatalytic activities of M_2BiNbO_7 (M = In and Ga).

Figure S4 shows the effect of photocatalyst concentration on photocatalytic methylene blue degradation under visible light irradiation at room temperature in air for 90 min. It could be seen that MB concentration decreased with increasing photocatalyst concentration when the photocatalyst concentration was

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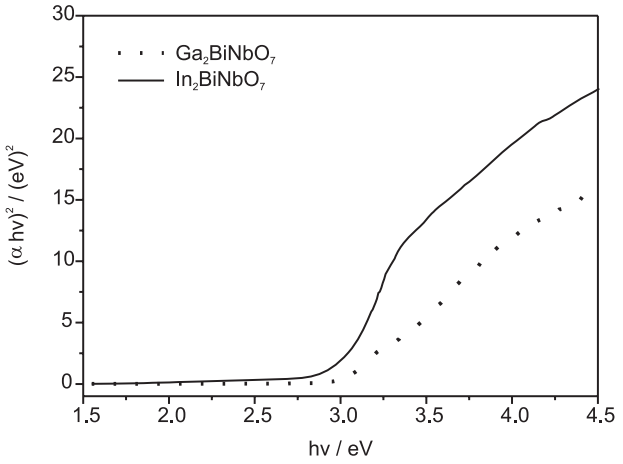

Figure S3. Plot of $(\alpha h\nu)^2$ *versus* hν for the M_2BiNbO_7 (M = In and Ga) photocatalysts.

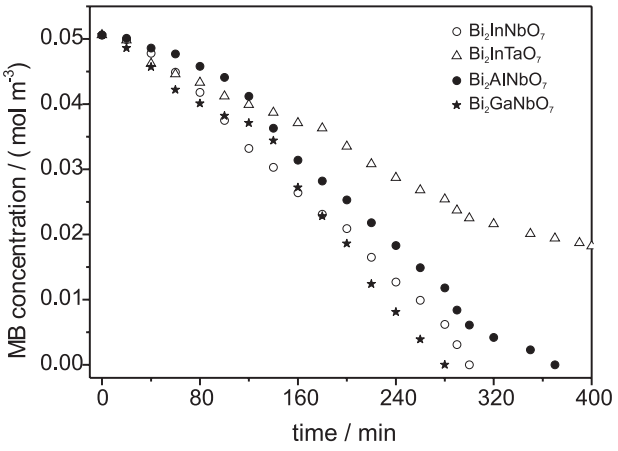

Figure S5. Photocatalytic methylene blue degradation under visible light irradiation (λ > 420 nm) at room temperature in the presence of Bi_2MNbO_7 (M = In, Al and Ga) and Bi_2InTaO_7.

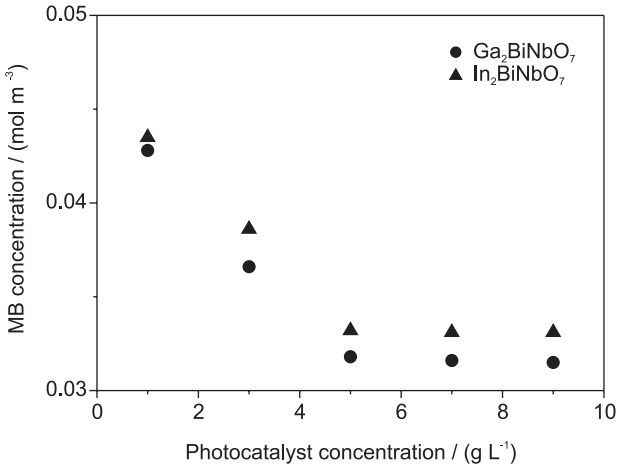

Figure S4. Effect of photocatalyst concentration on photocatalytic methylene blue degradation under visible light irradiation (λ > 420 nm) at room temperature in air for 90 min.

lower than 5 g L^{-1}. While MB concentration kept unchanging with increasing photocatalyst concentration when the photocatalyst concentration was higher than 5 g L^{-1}. The possible reason is the low capacity of visible light irradiation to penetrate in a media that contains a fine suspension of large amount of photocatalyst. Thus we chose 5 g L^{-1} as photocatalyst concentration.

Figure S5 shows photocatalytic methylene blue degradation under visible light irradiation (λ > 420 nm) in the presence of Bi_2MNbO_7 (M = In, Al and Ga) and Bi_2InTaO_7. The results showed that the solution color changed from deep blue to colorless and MB concentration in the solution was not detectable after visible light irradiation for 280, 300 and 370 min with Bi_2GaNbO_7, Bi_2InNbO_7 and Bi_2AlNbO_7 as the photocatalysts, respectively. However, MB concentration decreased only from 0.0506 to 0.0182 mol m^{-3} after visible light irradiation for 400 min with Bi_2InTaO_7 as the catalyst. The initial rates of MB degradation for Bi_2GaNbO_7, Bi_2InNbO_7, Bi_2AlNbO_7 and Bi_2InTaO_7 were about 3.012×10^{-6}, 2.811×10^{-6}, 2.279×10^{-6} and 1.350×10^{-6} mol s^{-1} m^{-3}, respectively. Table S1 shows the physical properties of Bi_2MNbO_7 (M = In, Al and Ga) and Bi_2InTaO_7. Table 3 of the paper shows the physical properties of M_2BiNbO_7(M=In and Ga). It could be seen that the surface areas of these compounds were nearly the same and their particle size were also very similar. Thus we can draw a conclusion that the photocatalytic activity of these compounds is as following order: $Ga_2BiNbO_7 > In_2BiNbO_7 > Bi_2GaNbO_7 > Bi_2InNbO_7 > Bi_2AlNbO_7 > Bi_2InTaO_7$.

Table S1. Physical properties of Bi_2MNbO_7 (M = In, Al and Ga) and Bi_2InTaO_7

Catalyst	Lattice[a] Parameter / (Å)	Average particle size / (μm)	Band gap / (eV)	Surface area / (m^2 g^{-1})	crystal structure
Bi_2InNbO_7	10.7793(2)[3]	1.4	2.7[3]	1.53	Pyrochlore type, cubic system with space group Fd-3m
Bi_2GaNbO_7	10.7342(2)[4]	1.5	2.75[4]	1.51	
Bi_2AlNbO_7	10.7171(2)[4]	1.4	2.9[4]	1.54	
Bi_2InTaO_7	10.7612(2)[5]	1.3	2.92[5]	1.57	

[a] The lattice parameter was obtained by the Rietveld structure refinement; [b] Measured by a 300 W Xe arc lamp (a cut-off filter λ > 420 nm; catalyst: 0.5 g; 100 mL methylene blue solution).

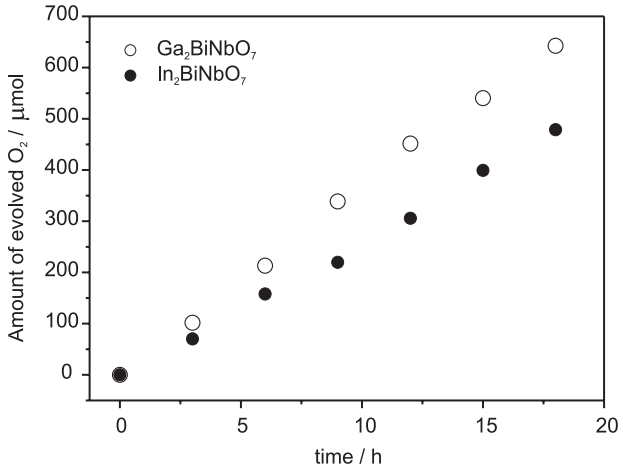

Figure S6. Photocatalytic O_2 evolution over M_2BiNbO_7 (M = In and Ga) from pure water under ultraviolet light irradiation. (Wavelength: $\lambda = 390$ nm, Catalyst: 1 g, H_2O: 300 mL, Light source: 400 W high-pressure Hg lamp.)

Figure S6 shows the photocatalytic O_2 evolution from pure water under UV light irradiation over the M_2BiNbO_7 (M = In and Ga) photocatalysts and the results are described in Table 3 of the paper. Similar to H_2 evolutions, the O_2 evolutions increased with illumination time and O_2 evolution rates also varied according to the following order: $Ga_2BiNbO_7 > In_2BiNbO_7$.

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