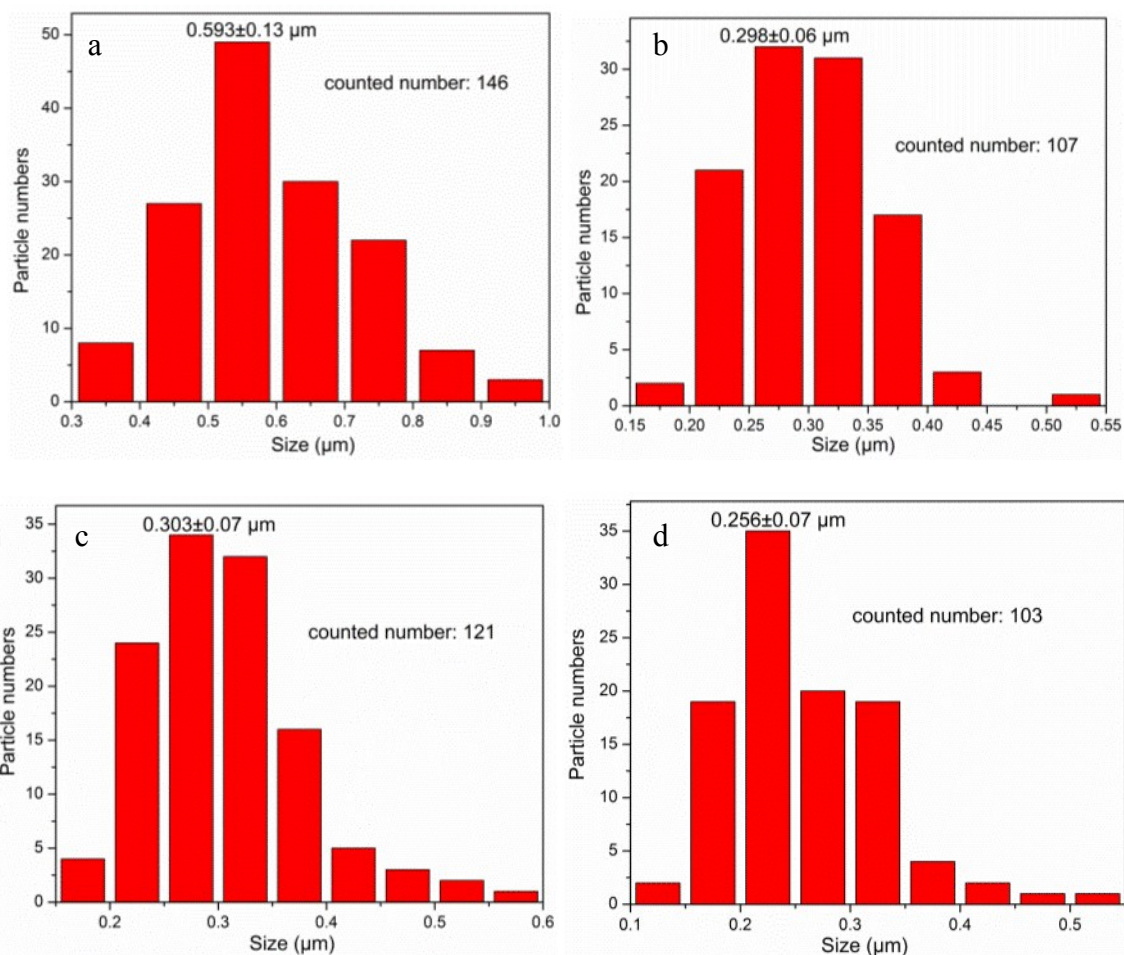


Key role of hydrochar in heterogeneous photocatalytic degradation of sulfamethoxazole using Ag_3PO_4 -based photocatalysts

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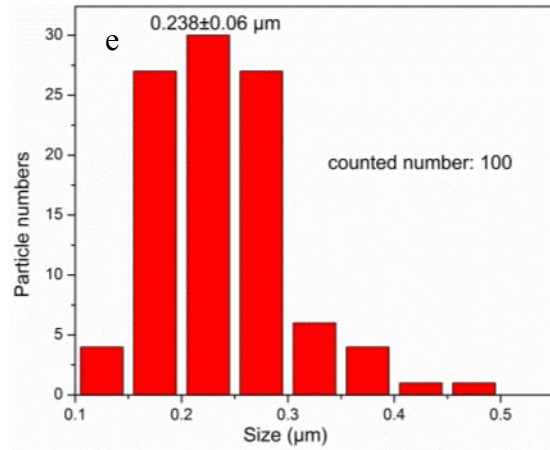


Fig. S1. Particle size distribution of (a) Ag_3PO_4 ; (b) $0.05\text{C}/\text{Ag}_3\text{PO}_4$; (c) $0.1\text{C}/\text{Ag}_3\text{PO}_4$; (d) $0.2\text{C}/\text{Ag}_3\text{PO}_4$; and (e) $0.3\text{C}/\text{Ag}_3\text{PO}_4$

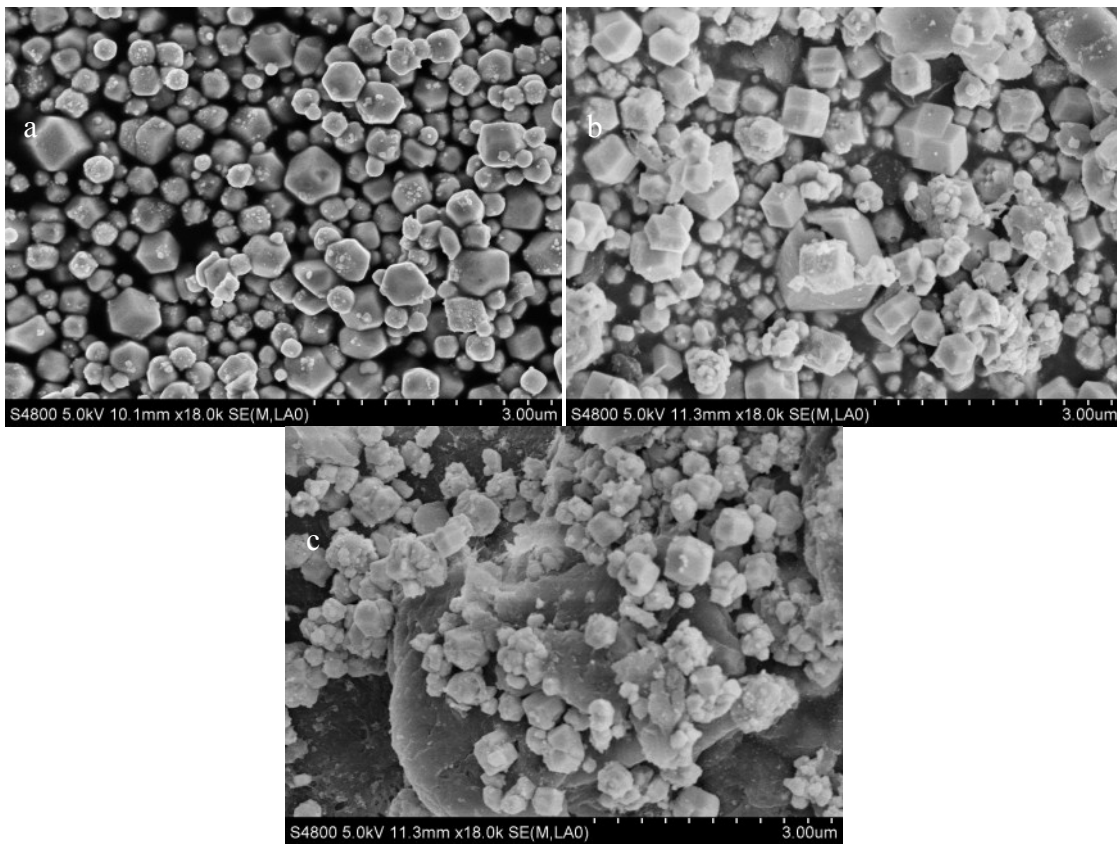


Fig. S2. (a) SEM pictures of (a) $0.05\text{C}/\text{Ag}_3\text{PO}_4$; (b) $0.2\text{C}/\text{Ag}_3\text{PO}_4$; and (c) $0.3\text{C}/\text{Ag}_3\text{PO}_4$

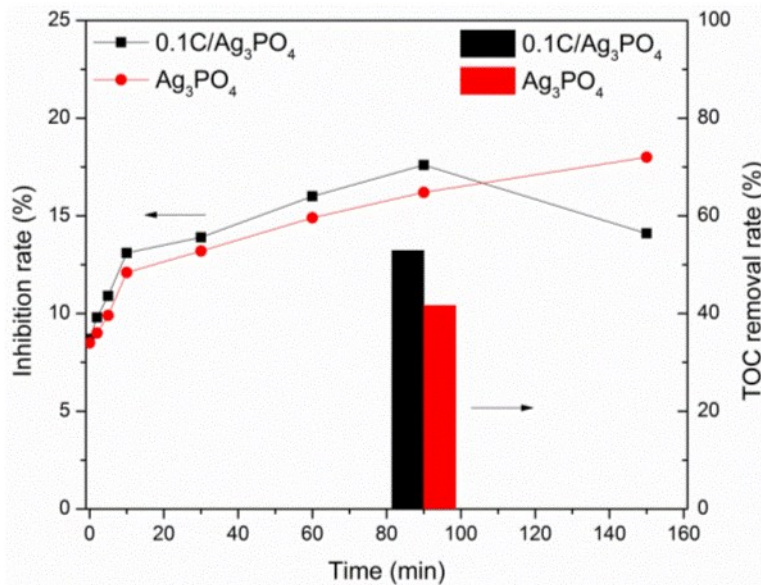


Fig. S3. The change of combined toxicity and TOC removal rate during SMX degradation by Ag₃PO₄ and 0.1C/Ag₃PO₄

It is expected that both the target compound and by-products are degraded completely during the SMX photocatalytic degradation process, so it is important to evaluate the combined toxicity change. As shown in Fig. S3, the inhibition rate on photoacteryium *V. qinghaiensis* sp.-Q67 (Q67) bioluminescence increased gradually from 8.5% to more than 14% for both photocatalysts during the whole photocatalytic process. For 0.1C/Ag₃PO₄, while most of the SMX was degraded after 90 min of irradiation, the inhibition rate of the bacteria bioluminescence decreased from 17.6% to 14.1%, indicating that the intermediate products transformed from the SMX were also degraded with the extended illumination time. Meanwhile, although Ag₃PO₄ was in the process of mainly degrading SMX, the inhibition rate of the bacteria bioluminescence still increased from 16.2% to 18.0%. Our group also observed a similar photocatalytic-degradation phenomenon of the SMX solution by other Ag₃PO₄-based composites under visible light illumination^{1, 2}. Thus, The intermediate products are more difficult to degrade and have higher toxicity than the target SMX. After 90 min of irradiation, the TOC removal rate is 52.91% for 0.1C/Ag₃PO₄ and 41.66% for pure Ag₃PO₄. The higher TOC removal rate contributed to the enhancement of the photocatalytic activity of 0.1C/Ag₃PO₄ due to the incorporation of hydrochar.

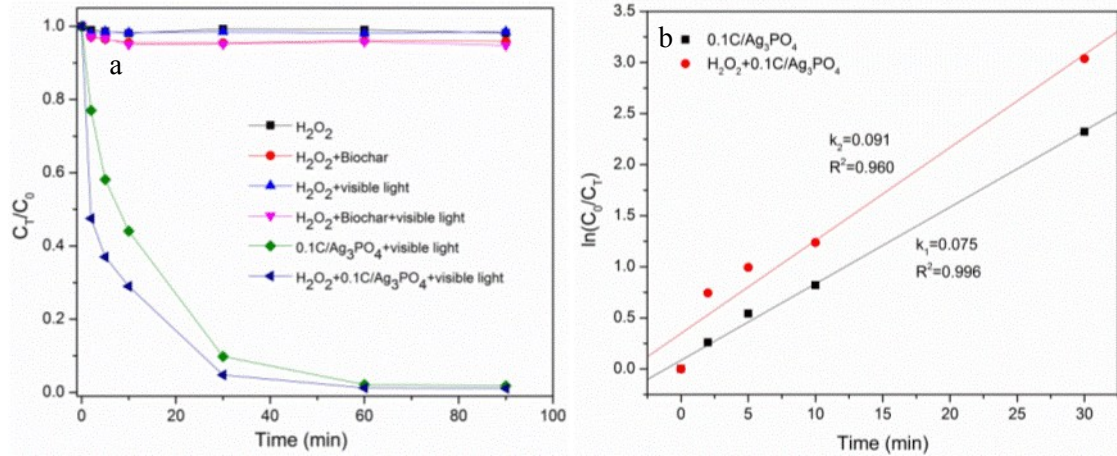
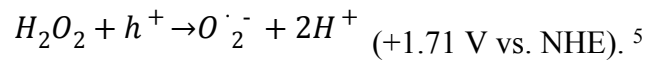
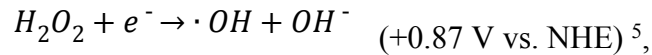


Fig. S4. Removal of SMX under various reaction conditions (a); and photocatalytic rate of $0.1C/Ag_3PO_4$ and $H_2O_2+0.1C/Ag_3PO_4$ under visible light irradiation (b).

As shown in Fig. S4(a) and (b), with the photocatalyst $0.1C/Ag_3PO_4$ under visible light, the addition of 10-mM H_2O_2 can enhance the photocatalytic activity of SMX degradation. The removal rate was 0.091 min^{-1} , which is 1.2 times of the only photocatalyst under visible light. A similar result was obtained from other Ag_3PO_4 -based composite photocatalysts. For example, the RhB removal rate of 15 wt% Ag_3PO_4 - Bi_2MoO_6 - H_2O_2 system ($k=0.03585 \text{ min}^{-1}$) is 7.2 times of only 15 wt% Ag_3PO_4 - Bi_2MoO_6 ($k=0.005 \text{ min}^{-1}$) under visible light³. The addition of H_2O_2 could affect the photocatalytic process in two aspects. Firstly, the H_2O_2 is prone to adsorb on the catalyst surface, and the adsorbed H_2O_2 would react with holes on the catalyst surface, as shown in Eq⁴:



Consumption of holes by adsorbed H_2O_2 could result in a retarded SMX photocatalytic degradation. On the other hand, as electron scavengers, H_2O_2 could react with electrons as shown in Eq.⁶



which would increase the separation efficiency of photogenerated electrons and holes and thus facilitate the activity by synergetic effects.

In this case, the reasons of enhanced performance of the $0.1C/Ag_3PO_4$ - H_2O_2 system may be assigned to two aspects. The first reason is that it is easier for holes produced in the photocatalyst valence band to contact with SMX than with adsorbed H_2O_2 ⁷, because the

potential difference between the valence band (VB) of Ag_3PO_4 and $\text{O}_2^-/\text{H}_2\text{O}_2$ (+1.71 V/NHE) ⁵ ($\Delta E=1.19$ V) is small compared to the difference between the potential of the VB of Ag_3PO_4 and the oxidation potential of SMX (0.9 V) ⁸ ($\Delta E=2.0$ V). The other reason is that the biochar facilitates the transfer of electrons produced in the conduction band (CB) of the photocatalyst, and the transferred electrons could be trapped preferentially by H_2O_2 to form $\cdot\text{OH}$. This is because of the larger potential difference between the CB reduction potential of Ag_3PO_4 and $\cdot\text{OH}/\text{H}_2\text{O}_2$ ($\Delta E = 0.42$ V) compared to the CB reduction potential of Ag_3PO_4 and $\text{O}_2/\text{H}_2\text{O}_2$ ($\Delta E = 0.245$ V), which benefits the electron-trapping process of H_2O_2 . According to the above analysis, the enhanced photocatalytic activity of the 0.1C/ Ag_3PO_4 - H_2O_2 system is complementary evidence that holes are the crucial radicals to oxidize SMX in this case.

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