Supplementary information for

$Cu_2(OH)PO_4$/*g*-C_3N_4 composite as an efficient visible light-activated photo-Fenton photocatalyst

Changhong Chen, Yan Zhou, Ningning Wang, Linyu Cheng, Hanming Ding*

School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China

* Corresponding author. Email: hmding@chem.ecnu.edu.cn

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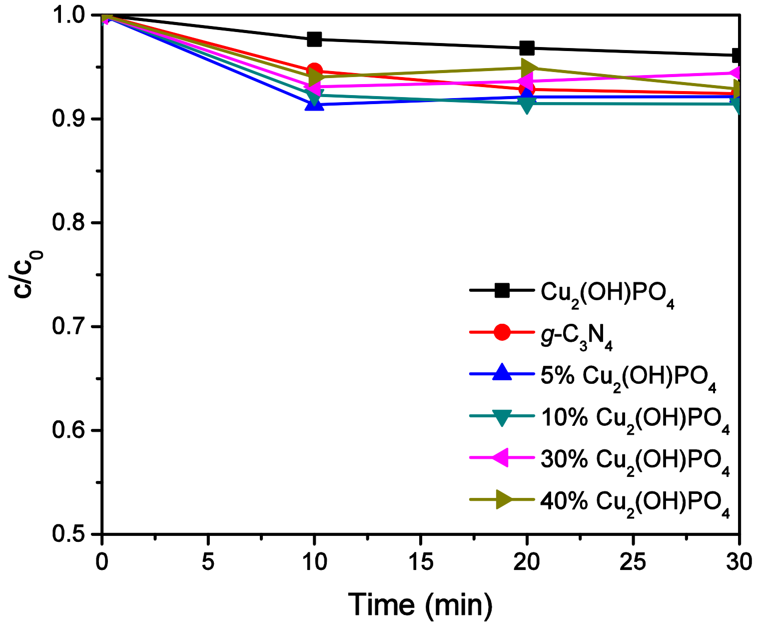
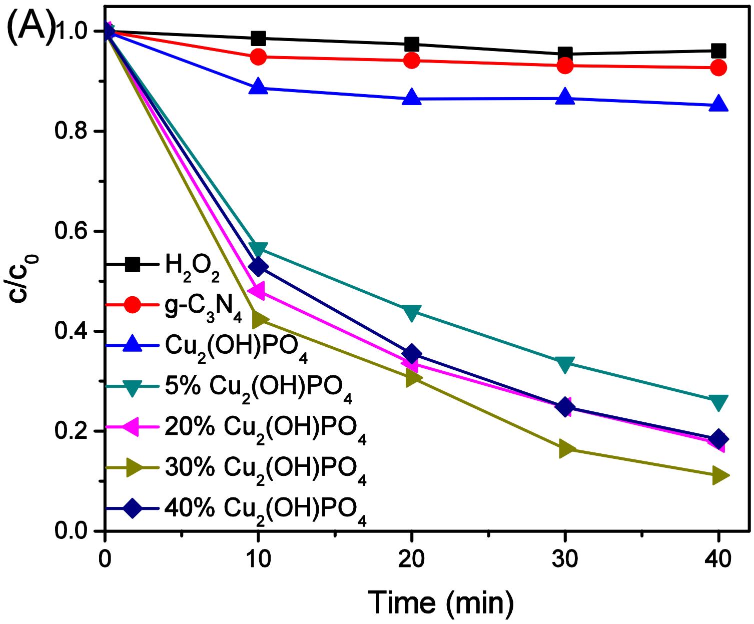


Figure S1. The adsorption curves of RhB over the different catalysts in the dark under stirring. Experimental conditions: 50 mL of 10 mg/L RhB solution, 0.02 g of catalyst, pH = 5.0.



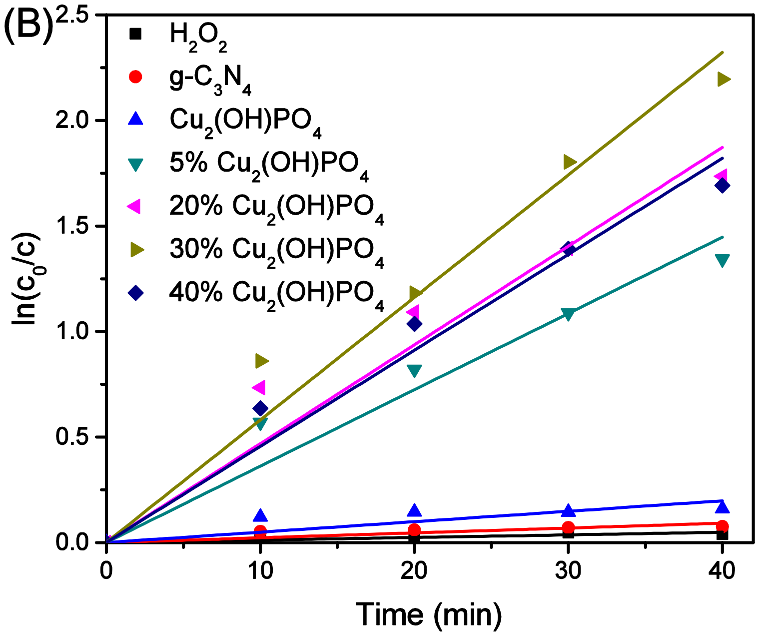
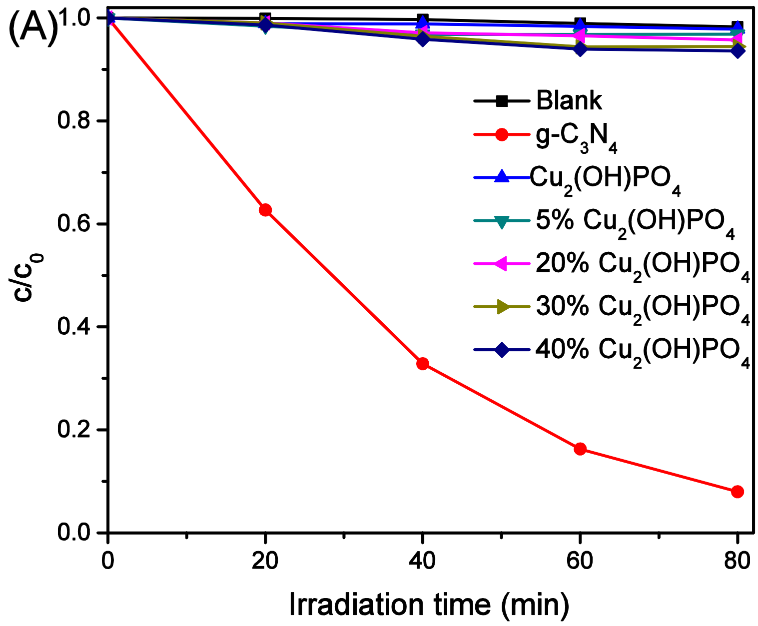


Figure S2. (A) The Fenton effect of RhB degradation over the different catalysts in the presence of H_2O_2 (without light irradiation). (B) Kinetics of RhB degradation over the different catalysts in the presence of H_2O_2 (without light irradiation). (H_2O_2 in the figures means only with H_2O_2 without the catalyst)

Table S1. The reaction rate contants (*k*) of Fenton reaction without visible light.

Sample	*g*-C_3N_4	$Cu_2(OH)PO_4$	5% $Cu_2(OH)PO_4$	20% $Cu_2(OH)PO_4$	30% $Cu_2(OH)PO_4$	40% $Cu_2(OH)PO_4$
k (min^{-1})	0.0023	0.0050	0.036	0.047	0.058	0.046



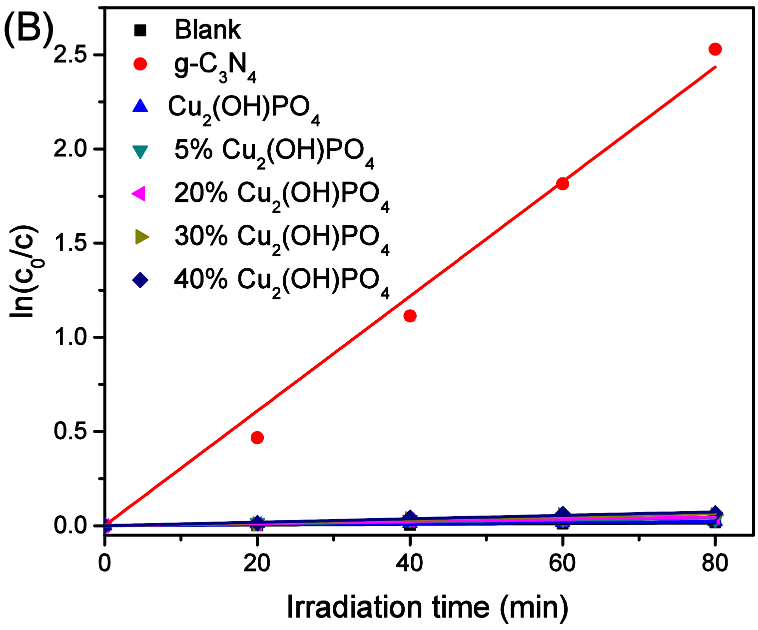


Figure S3. (A) The photocatalytic effect of RhB degradation over the different catalysts under visible light irradiation without H_2O_2. (B) Kinetics of RhB degradation over the different catalysts under visible light irradiation without H_2O_2.

Table S2. The reaction rate contants (*k*) of the photocatalytic reactions in the absence of H_2O_2.

Sample	*g*-C_3N_4	$Cu_2(OH)PO_4$	5% $Cu_2(OH)PO_4$	20% $Cu_2(OH)PO_4$	30% $Cu_2(OH)PO_4$	40% $Cu_2(OH)PO_4$
k (min^{-1})	0.030	2.8×10^{-4}	5.1×10^{-4}	5.8×10^{-4}	8.0×10^{-4}	9.2×10^{-4}

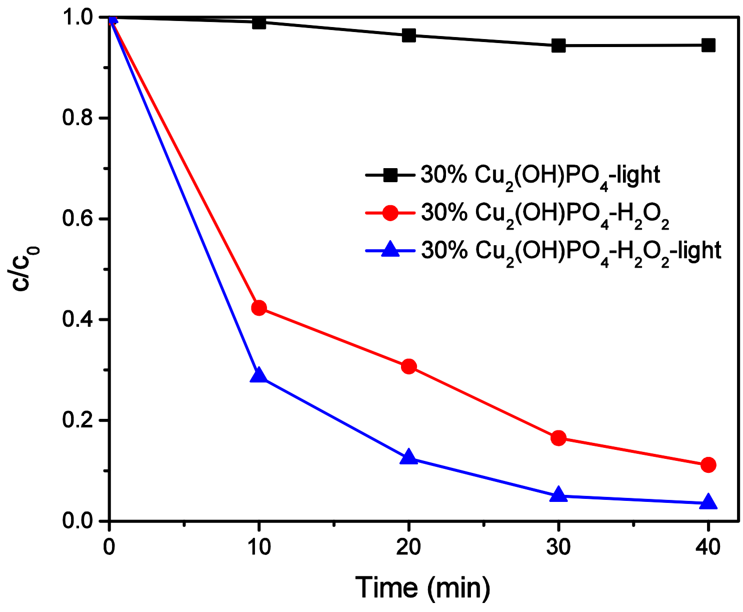
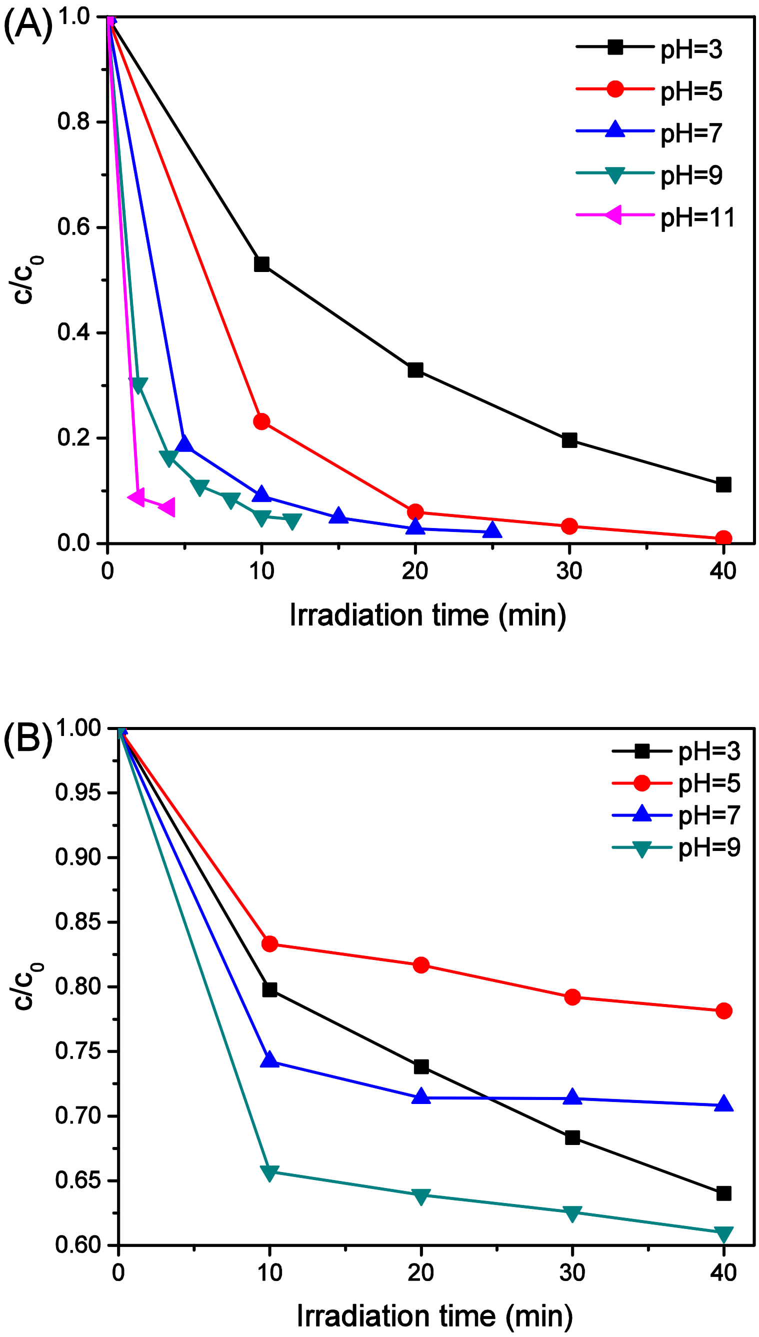


Figure S4. RhB degradation over 30% $Cu_2(OH)PO_4$ solely under visible light irradiation, solely in the presence of H_2O_2, and in the presence of H_2O_2 under visible light irradiation.



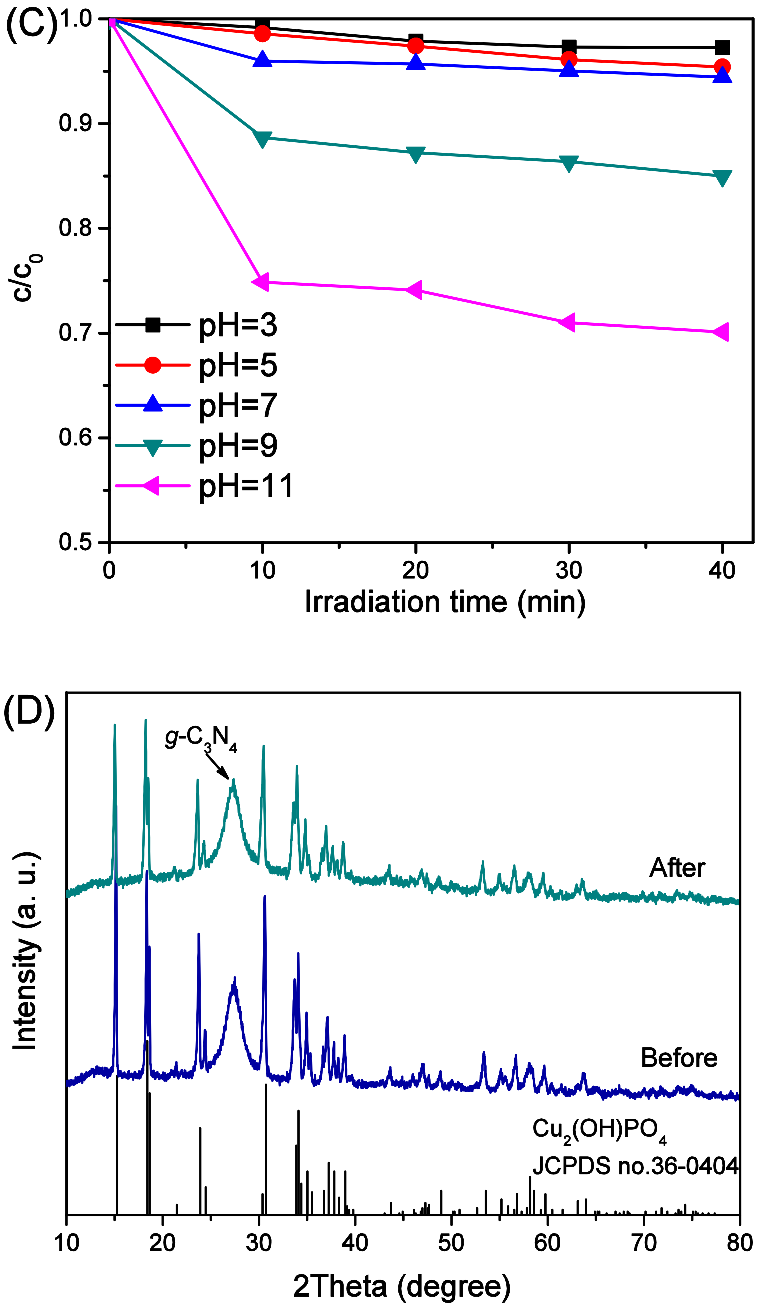


Figure S5. Effects of the initial pH value on the degradation of RhB by (A) 30% $Cu_2(OH)PO_4$ and (B) pure $Cu_2(OH)PO_4$ in the presence of H_2O_2 under visible light irradiation. (C) Effects of the initial pH value on the degradation of RhB only in the presence of H_2O_2 under visible light irradiation (without the catalysts). (D) XRD diffraction patterns of 30% $Cu_2(OH)PO_4$ before and after the photo-Fenton photocatalytic reaction **at pH 11**.

Effects of the initial pH values on the RhB degradation efficiency

It is generally accepted that the pH value is one of the decisive factors in the Fenton process. One major drawback of homogeneous Fenton reaction is the narrow range of pH values. In our work, the initial pH value of the reaction mixture under native conditions was about 5 (10 mg/L RhB solution with the catalyst, without any pH adjustment). All the works have been carried out at this pH value if not specifically stated.

The effects of pH on the RhB degradation over the $Cu_2(OH)PO_4$/*g*-C_3N_4 catalyst (30% $Cu_2(OH)PO_4$) have been investigated by adjusting the initial pH values by adding 1.0 M H_2SO_4 or 1.0 M NaOH in the range of 3-11 (measured prior to the addition of H_2O_2). As shown in Figure S5A, the RhB degradation efficiency was obviously affected by the initial pH in the range of 3-11. The RhB degradation efficiency increases with increasing the initial pH. In the catalytic system, $Cu_2(OH)PO_4$, *g*-C_3N_4, and H_2O_2 could have contribution to the improved degradation efficiency. According to the work reported by Wang et al., the RhB degradation rate over *g*-C_3N_4 in the presence of H_2O_2 under neutral conditions is lower than that under acidic conditions.[1] That means *g*-C_3N_4 has a negative effect on the degradation efficiency when the initial pH increases.

As indicated in Figure S5B, the catalytic activity of $Cu_2(OH)PO_4$ changes with increasing the initial pH. At pH 3, the RhB degradation activity is abnormally high. This may be associated with the partial dissolution of catalyst,[2] as the homogeneous Fenton reaction usually has a faster rate than the heterogeneous Fenton reaction at acidic media. At the pH range of 5-9, $Cu_2(OH)PO_4$ is stable. The RhB degradation efficiency was slightly increased with increasing the initial pH, which is consistent with the previous report.[3] However, further increasing pH leads to the decomposition of $Cu_2(OH)PO_4$. Thus, the optimal pH range for the degradation is 5-9. In addition, RhB could be decolorized with H_2O_2 rapidly under basic conditions even without using the catalyst (Figure S5C), which suggests that H_2O_2 and $Cu_2(OH)PO_4$ at alkaline pH should play important roles in the improved degradation efficiency in our catalytic system.

It is proposed that the reactive species is not H_2O_2 at alkaline medium, but rather the HO_2^- anion (pK_a for H_2O_2 is 11.6).[4] An increase in pH would lead to an increased concentration of HO_2^-. HO_2^- anion can be further converted to $\bullet O_2^-$ radicals and other reactive species by holes generated during the photo-Fenton photocatalytic processes. At the same time, high level of hydroxide ions (OH^-) in alkaline medium induced the generation of hydroxyl free radicals ($HO\bullet$), which came from the photooxidation of OH^- by holes forming on the 30% $Cu_2(OH)PO_4$ ($OH^- + h^+ \rightarrow HO\bullet$). Since hydroxyl free radical is the dominant oxidizing species in the photo-Fenton photocatalytic process, the photodegradation of RhB is therefore accelerated at higher pH. This observation has been justified by the previous works.[5, 6]

It should be mentioned that the composite catalyst is stable in the pH range of 3-11. XRD diffraction patterns of 30% $Cu_2(OH)PO_4$ before and after the photo-Fenton photocatalytic reaction at the initial pH of 11 are given in Figure S5D. As shown in Figure S5D, the structure of the composite catalyst keeps unchanged after the photo-Fenton photocatalytic reaction at pH 11. This result suggests that the $Cu_2(OH)PO_4$/g-C_3N_4 composites are stable even in alkaline solutions.

References:

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