

Supporting Information

Synthesis and Characterization of Near-Infrared Persistent Luminescent Cr-doped Zinc Gallate-Calcium Phosphate Composite

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Synthesis of CZGO-ACP composite using PAA-free ACP

In this method, a PAA-free ACP was first synthesized. 0.1 mmol of PAA and 0.81 mmol $\text{Ca}(\text{OH})_2$ were dissolved in 50 mL deionized water and was stirred for 30 minutes at RT. Next, 100 mL isopropyl alcohol was added dropwise to the solution and the mixture was continuously stirred for another 30 min. Next, 0.54 mmol $(\text{NH}_4)_2\text{HPO}_4$ was added and was stirred for 12 hours at RT to allow the reaction to go to completion. The white precipitate was collected by centrifugation, followed by two rounds of washing with deionized water. The sample was dried at 60 °C for 10 hours, and then annealed at 800 °C for 5 hours to remove the PAA. To make the composite, 0.023 mmol of ACP and 0.046 mmol of CZGO were dissolved in 1.7 mL deionized water and 3.4 mL isopropyl alcohol. The solution was stirred for 30 minutes at room temperature. Next, the solution was transferred to a 25 mL Teflon lined autoclave to undergo hydrothermal treatment at 120 °C for 30 minutes. After cooling to RT, the precipitate was parted using the centrifuge and was washed twice using deionized water. Finally, the sample was dried in the oven at 60 °C for 10 hours.

Synthesis of PAA-ACP and PAA-ACP+Zn

0.054 mmol of PAA and 0.4 mmol of $\text{Ca}(\text{OH})_2$ were dissolved in 24.7 mL of deionized water, and the solution was stirred for 30 minutes at room temperature to form a Ca-PAA complex. 49.3 mL of isopropyl alcohol was added dropwise to the solution with magnetic stirring. After finishing adding the isopropyl alcohol, the solution was stirred for an additional 30 minutes. Next, 0.268 mmol of $(\text{NH}_4)_2\text{HPO}_4$ was added and the solution was stirred for 24 hours. The final product, PAA-ACP, was collected by centrifuge, followed by two washes with deionized water and dried at 60 °C for 10 hours.

For Zn introduction, all procedures were kept the same except 0.044 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added after mixing PAA and $\text{Ca}(\text{OH})_2$ in the first step. The final product was denoted PAA-ACP+Zn.

Synthesis of CZGO-ACP with additional Zn (CZGO-ACP+Zn)

In a 250 mL beaker, 0.4 mmol of $\text{Ca}(\text{OH})_2$ and 0.054 mmol of PAA were dissolved in 24.7 mL of deionized water and the solution was stirred for 30 minutes under room temperature. After, 0.044 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 mmol of CZGO were added to the solution. This was followed by adding 49.3 mL of isopropyl alcohol to the solution dropwise. As isopropyl alcohol was added to the solution, the solution turned cloudy. The solution was then stirred for an additional 30 minutes. Next, 0.268 mmol of $(\text{NH}_4)_2\text{HPO}_4$ was added and stirred for 24 hours. The CZGO-ACP+Zn powder was separated with centrifugation, washed twice with deionized water, and dried in the oven at 60 °C for 10 hours.

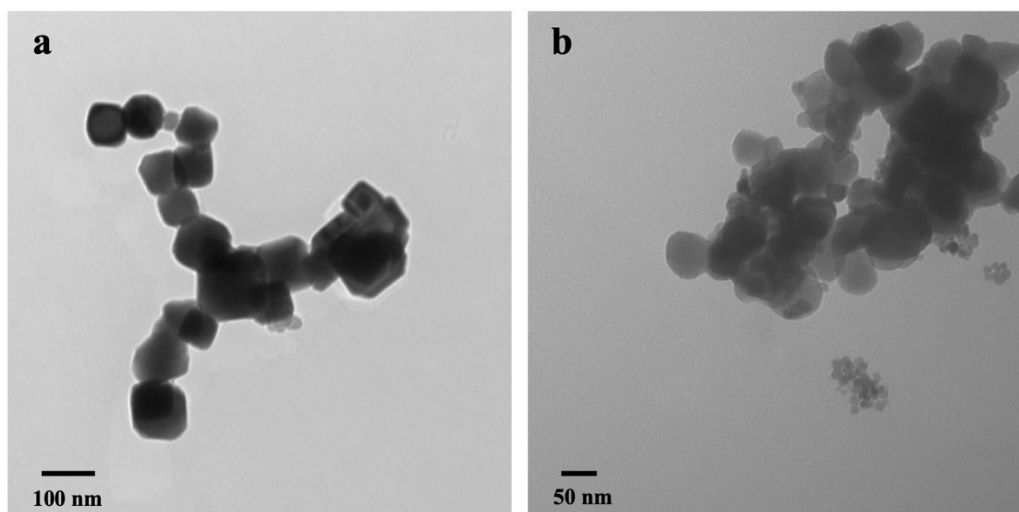


Figure S1. TEM images of (a) PAA-free ACP, and (b) CZGO-ACP prepared by mixing PAA-free ACP with CZGO.

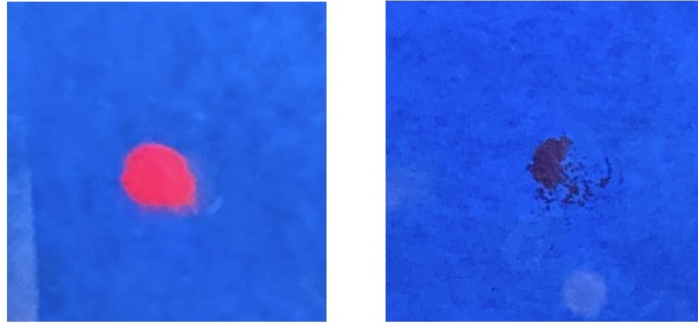


Figure S2. UV-excited luminescence images of CZGO (left) and CZGO mixed with PAA-free ACP (right). The excitation wavelength is 254 nm.

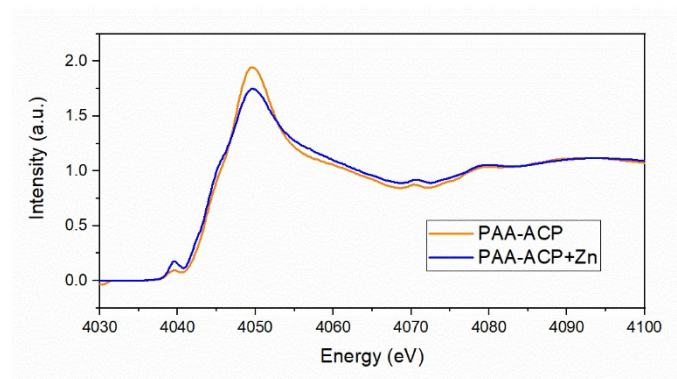


Figure S3. The Ca K-edge XANES of PAA-ACP and PAA-ACP with added Zn as precursor (PAA-ACP+Zn).

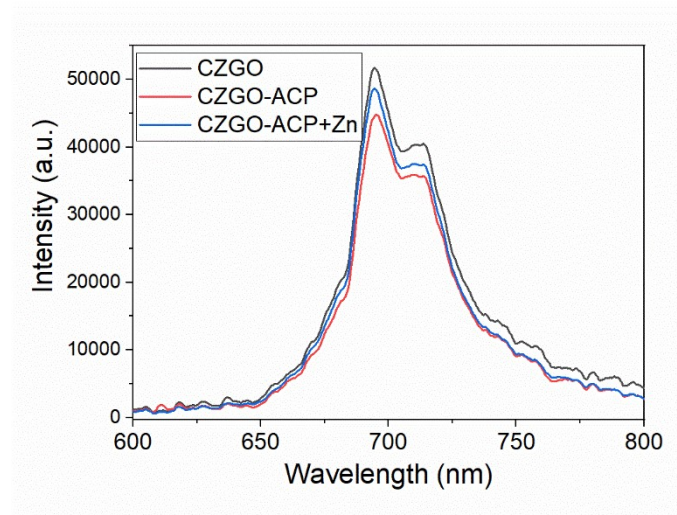


Figure S4: Emission photoluminescence spectra of CZGO-ACP+Zn in comparison with CZGO and CZGO-ACP

