Dear Editors:

We would like to submit the enclosed manuscript entitled “Au@AgPt Core/Cage Nanoframes as Photothermal Catalyst for Enhanced NIR-Induced 4-Nitrophenol Reduction”, which we wish to be considered for publication in “Chinese Journal of Catalysis”.

The selection and optimization of catalysts have been a subject of considerable research interest in recent decades. The continuous pursuit of achieving more effective reaction rates is always an unwavering endeavor for scientists. Nowadays, bimetallic and multimetallic nanocatalysts, comprised of plasmonic and catalytic components, have recently emerged as a promising approach to achieving high catalytic performance due to synergistic effects. Plasmonic nanomaterials exploiting the LSPR effect efficiently induce both photothermal conversion and the generation of nonthermalized (hot) charge carriers. These two phenomena can both contribute to the enhancement of the catalytic activities under light conditions. In addition, frame/skeleton-like nanostructures and rough surface are particularly valuable in catalysis. Although numerous nanoparticles have been designed in recent years to enhance the catalytic efficiency, nanoparticles that simultaneously possess multiple catalytic advantages are still scarce. Therefore, how to rational design and manufacture advanced photothermal catalysts with both high activity and stability is still an urgent problem to be addressed.

Herein, we design and synthesize a trimetallic nanostructure of Au@AgPt core/cage nanoframe based on capability-oriented principles, which consists of a controllable hollow silver-platinum (AgPt) alloy nanoframe and in-built plasmonic gold nanorod (Au NR). Additionally, in our study, through systematic investigation of the catalytic efficiency of a series of Au@AgPt core/cage nanoframe composites with varying silver/platinum content ratios for the reduction of 4-NP under non-light conditions, we observed that as the Pt content increases, there is an initial enhancement in catalytic performance, reaching its peak with Au@AgPt-8. However, further increases in Pt content lead to a slight decrease in performance. The apparent rate constant of the catalytic reduction of 4-NP by Au@AgPt-8 reaches 0.72 min⁻¹, which is about 10.9 times that of the bimetallic Au@Ag. And under 785 nm laser irradiation, the photothermal performance of the samples also shows an initial increase followed by a gradual decrease with increasing Pt content. Among them, Au@AgPt-2 exhibits
the most favorable photothermal heating performance. Notable, under 785 nm laser irradiation, the Au@AgPt-4 nanocatalysts featuring an optimal Pt content and robust photothermal performance (the photothermal heat conversion efficiency was measured to be 26.96%) can even surpass the catalytic efficiency of Au@AgPt-8. This optimized nanocatalyst of Au@AgPt-4 required approximately one minute to complete the reduction reaction. Furthermore, the Au@AgPt-4 nanocatalyst maintains high catalytic performance after five cycles of photothermal catalytic testing, exhibiting no significant changes in morphology. These results highlight that this trimetallic core/cage nanoframe nanostructure can serve as an efficient and stable photothermal catalyst for the degradation of organic pollutants.

The superior properties of such a sophisticated architecture can be attributed to several synergistic effects and structural advantages:

(1) The nanoframe structure and the rough surface provide a large surface area, optimizing the availability of surface atoms for reactant molecules adsorption and interaction. This maximization of reactive sites enhances the efficacy of catalytic processes, thereby significantly improving the overall catalytic performance.

(2) The Au NRs and Ag in the alloy nanoframe can support strong LSPR, which is capable of efficiently harvesting and concentrating laser energy, thereby enhancing the local electromagnetic field and catalytic reactions on the nanoframe surface. In addition, hollow structure and rough surface tend to form stronger local electromagnetic fields.

(3) The LSPR-excited photothermal effect and high-energy hot electrons both contribute to the enhancement of the catalytic activities under light conditions.

(4) The nanoframe structure allows the laser to enter the core to irradiate the surface of the Au NRs and induce multiple reflections and scattering, enhancing the utilization of incident laser energy.

(5) The nanoframe structure with large voids can facilitate the diffusion of reactants and products, enhancing the mass transfer and allowing for a more efficient reaction process.

(6) The external AgPt alloy nanoframe bestows a greater stability than metallic monomers. In addition, this robust nanoframe can provide physical stability to the Au NRs and protect them from complicated reaction conditions, maintaining the integrity and longevity of the plasmonic properties.

This study provides a rational design for nanoscale materials with plasma-
enhanced properties, offering valuable guidelines for the design and construction of high-performance plasmon-based catalysts in the future.

This paper is original and has been written by the stated authors who are all aware of its content and approve its submission. No conflict of interest exists. I hope that the reviewers find our work valuable and suitable for publication in your journal.

Thank you for consideration!

With best wishes.

Sincerely Yours

Jian Zhu