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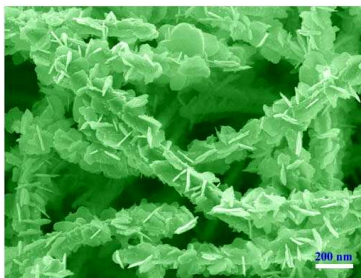
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Enhanced Photocatalytic Properties of Biomimetic Ag/AgCl Heterostructures

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Enhanced Photocatalytic Properties of Biomimetic Ag/AgCl Heterostructures

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Hierarchical Ag/AgCl hetero-structures have been fabricated in high-yield by copying the natural architecture of branch with green leaves, which exhibit higher photocatalytic activities than Ag/AgCl nanowires, AgCl nanoparticles, Ag nanowires, and N-doped TiO₂ for the degradation of organic contaminants under visible light irradiation.

Silver halides, especially silver chloride (AgCl), have recently attracted considerable attention owing to their unique photocatalytic properties.¹ The most interesting feature of these photocatalysts is self-sensitization process as a result of the photogenerated Ag nanoclusters during the photocatalytic process.² More specifically, the surface plasmon resonance (SPR) effect of metallic Ag nanoclusters could effectively enhance the photocatalytic properties and stabilities of silver halides in visible-light region.³ Additionally, these Ag nanoclusters could also serve as good electron acceptors for facilitating photoexcited electron quick transfer from their contact interface and decreasing the probability of electron-hole recombination.⁴ For instance, Huang et al. reported that the Ag/AgCl powders with micrometer scale have been proved to be stable and efficient visible light photocatalysts.⁵ However, note that the morphology and structure of photocatalysts play an crucial role in determining their photocatalytic properties. Thereby, much effort has been recently devoted to the fabrication of Ag/AgCl photocatalysts with different dimensions as well as heterostructures for further optimizing their catalytic performances.⁶

Meanwhile, the rationally controlled assembly of biomimetic photocatalysts has been gradually attracted extensive interests inspired by the photochemical process in nature.⁷ It is well known that the natural hierarchical structures of branch with green leaves could achieve highly efficient conversion of sunlight to chemical energy by photosynthetic process. Thereby, it has been speculated that in photocatalytic fields, the similar well-controlled hierarchical structures could provide high specific surface area and shorten the diffusion paths to active surface sites, which may provide a means of improving photoenergy conversion efficiency.^{6a,8} However, in the case of Ag/AgCl photocatalysts, the related artificial synthesis of biomimetic heterostructures as well as their photocatalytic performances have been rarely reported until now.

Herein, we present a facile and general growth route for

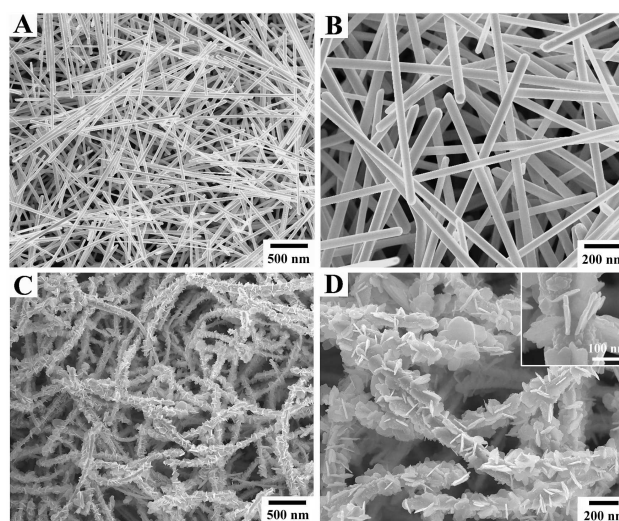


Fig. 1 (A, B) SEM images of Ag nanowire prepared by 1,2 BG reduction; (C,D) SEM images of AgCl nanoplate-Ag/AgCl nanowire hierarchical structures by reacting Ag nanowires with CuCl₂ at room temperature.

single-step synthesis of AgCl nanoplate-Ag/AgCl nanowire hierarchical heterostructures by copying the natural architecture of branch with green leaves. Moreover, the structure and composition of Ag and AgCl can be further tailored by rationally adjusting the synthetic parameters. Their photocatalytic studies for the degradation of organic contaminants under visible light irradiation indicate that this novel Ag/AgCl hierarchical nanostructure exhibits higher activities than Ag/AgCl nanowires, AgCl nanoparticles, and Ag nanowires. This work will probably pave a new pathway for learning from nature and for utilization of solar energy with artificial biomimetic photocatalysts.

Fig. 1A and 1B show the Ag nanowires fabricated by a modified polyol process, which would serve as the starting templates and silver ion source for the subsequent oxidation fabrication of Ag/AgCl nanoproducts. It can be clearly seen that the as-synthesized Ag nanowires possess an average diameter of ~100 nm and with the length of about several micrometers. Interestingly, when these Ag nanowires were reacted with CuCl₂ in PVP aqueous solutions at room temperature, a novel Ag/AgCl hierarchical structure confirmed by XRD characterizations (shown in Fig. 2A) has been fabricated by this simple oxidation process. More specifically, the surfaces of Ag/AgCl nanocables were

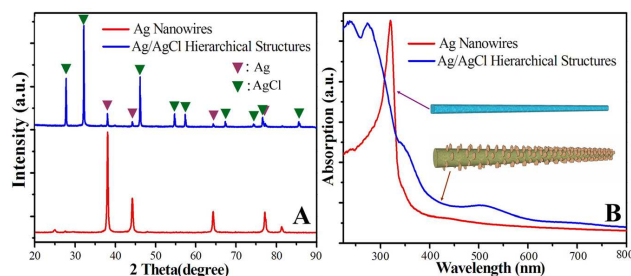


Fig. 2 (A) XRD patterns, (B) ultraviolet-visible diffusive reflectance spectrums of Ag nanowire and Ag/AgCl nanoplate-nanowire hierarchical structures.

completely covered by AgCl nanoplates to construct the nanoplate/nanowires junction hierarchical nanostructure. The enlarged SEM image (inset Fig. 1D) clearly reveals that AgCl nanoplates with an average diameter of 500 nm and thickness of 30 nm have been formed on the Ag/AgCl nanocables, no individual and isolated AgCl nanoparticles has been obviously observed. In order to further confirm the metallic Ag core-nanowires in the presence of final samples, both the outward AgCl nanoshells and nanoplates have been completely dissolved with NH_4OH . As shown in Fig. S1, the preserved Ag core-products also exhibit a nanowire-like structure, but their diameters have been decreased markedly and the surfaces have been partially corrupted as a result of the oxidation growth of AgCl nanoshells and nanoplates. Furthermore, the X-ray Diffraction (XRD) pattern shown in Fig. 2A reveals that the main diffraction peaks of this hierarchical structure could be primarily indexed to the body-centered cubic structure of AgCl (JCPDS.No.06-0505), and only a small diffraction peak of metallic Ag has been observed, which is generally in agreement with the EDS results (shown in Fig. S2). Moreover, the ultraviolet-visible diffuse reflectance spectrums (shown in Fig. 2B) reveal that the pure Ag nanowires could absorb the light with a wavelength shorter than 320 nm, which should be due to the electrons directly bonded to the silver atom that act as bulk silver.⁹ However, AgCl nanoplate-Ag/AgCl nanowire possesses an absorption edge and wavelength shorter than 400

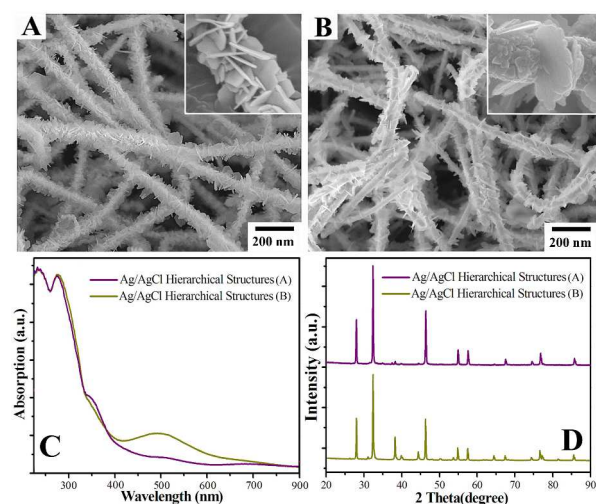
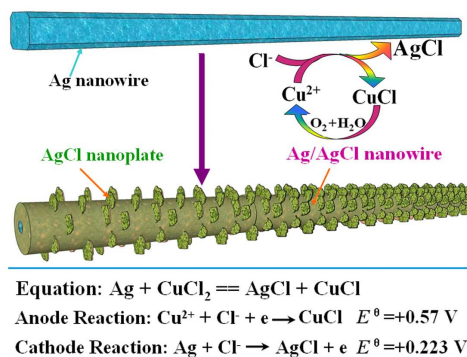


Fig. 3 SEM image of Ag/AgCl nanoplate-nanowire hierarchical structures with increasing the amount of CuCl_2 to 0.1 M (A) and with decreasing the amount of CuCl_2 to 0.025 M (B); their ultraviolet-visible diffusive reflectance spectrums (C) and XRD patterns (D).

nm, a broad absorbance peak at 500 nm has been observed, which should be ascribed to the residual metal Ag nanowires.¹⁰ These demonstrations clearly confirm that the as-prepared hierarchical heterostructures fabricated by this modified oxidation process are only constructed by Ag/AgCl nanocable and AgCl nanoplates, and no absorption and diffraction peaks corresponding to other impurities are involved.

Furthermore, note that the structures and compositions of Ag/AgCl nanocables-nanoplate hierarchical products could be further rationally tailored by adjusting the CuCl_2 concentrations. As shown in Fig. 3A, with increasing of CuCl_2 up to 0.1 M, the number of AgCl nanoplates has been obviously increased and Ag/AgCl nanocables have been completely covered by the AgCl nanoplates. The UV-vis absorption spectrum shown in Fig. 3C clearly reveals that the absorption peak of metallic Ag has completely disappeared. Furthermore, the XRD pattern shown in Fig. 3D further confirms that the diffraction peaks could be indexed to AgCl, and no evident diffraction peaks corresponding metallic Ag has been detected, which is in agreement with the SEM and UV-vis observations. In contrast, when the concentration of CuCl_2 has been reduced down to 0.025 M, only a few AgCl nanoplates have been observed on the surface of Ag/AgCl nanocables. Moreover, the UV-vis absorption spectrum and XRD pattern (Fig. 3C,D) reveals that both the absorption and diffraction peaks of metallic Ag have been slightly increased.



Scheme 1 Schematic illustrations for the growth process of Ag/AgCl nanoplate-nanowire hierarchical structures by reacting Ag nanowires and CuCl_2 at room temperature.

Based on the above experimental results, we identified a possible reaction mechanism for explaining the growth process of AgCl nanoplate-Ag/AgCl nanowire hierarchical structures by reacting Ag nanowires and CuCl_2 at room temperature, and the schematic illustration has been shown in Scheme 1. In the presence of PVP, when CuCl_2 has been introduced into Ag nanowire aqueous solution, the oxidation of Ag nanowires by Cu^{2+} ions ($E^0_{\text{Cu}^{2+}/\text{CuCl}} = +0.57 \text{ v}$) has been started immediately because of Cl^- ions could effectively reduce the redox potential of Ag species from +0.80 v (Ag^+/Ag vs Standard Hydrogen Electrode (SHE)) to +0.223 v (AgCl/Ag). Furthermore, the formed AgCl nanocrystals in-situ grows on surfaces of Ag nanowires to form Ag/AgCl core-shell nanowires. On the other hand, because of the higher redox potential of $\text{Cu}^{2+}/\text{CuCl}$ than that of AgCl/Ag , the Cu^{2+} ions have been reduced into Cu^+ ions, which reacted with Cl^-

ions to form CuCl. It is well known that the stability of CuCl is relatively poor, which could be rapidly oxidized into Cu²⁺ ions by the O₂ in the atmosphere in the reaction system. For comparison, when the same synthesis process was performed in the pure N₂ atmosphere, the CuCl has been detected in the final hierarchical products (Fig. S5). However, note that the exact reasons for the formation of nanoplate/nanowire hierarchical structures can not be completely understood and a more detailed study is still underway.

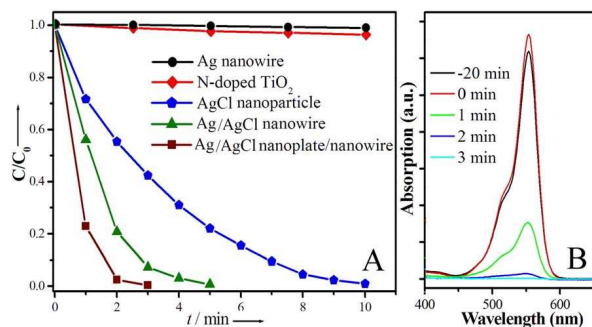


Fig. 5 (A) Photocatalytic activities of Ag/AgCl nanoplate-nanowire hierarchical structures for RhB degradation under visible-light irradiation ($\lambda > 420$ nm); (B) UV-Vis absorption spectrum of RhB at different reaction time.

Their photocatalytic behaviors were explored for the degradation of Rhodamine B (RhB) dyes under visible-light irradiation (shown in Fig. S6).¹¹ To the best of our knowledge, this novel Ag/AgCl biomimetic heterostructures was used, for the first time, as the catalyst for this photocatalytic reaction. For comparison, the photocatalytic performances of Ag/AgCl nanowires, AgCl nanoparticles, commercial N-doped TiO₂, and Ag nanowires have also been studied and compared in Figure 4. As shown in Fig. 5A, it can be clearly seen that except for single-crystalline Ag nanowires and N-doped TiO₂, all these AgCl based photocatalysts exhibit excellent photocatalytic activities for the RhB degradation. Among them, the Ag/AgCl biomimetic (shown in Fig. 1) heterostructure exhibits the highest photocatalytic activity, which can completely degrade RhB dye in only 3 min. Furthermore, the complete degradation of RhB dye over Ag/AgCl core-shell coaxial hetero-nanowires (shown in Fig. S3A) takes about 5 min, while the pure AgCl nanoparticles need about 8 min. Thereby, these demonstrations indicate that the construction of AgCl nanoplate-Ag/AgCl nanowire hierarchical structures has been proved to be an available and successful route for improving the photocatalytic properties of Ag/AgCl crystals. Furthermore, it has been considered that the plasmon effect of Ag core-nanowires effectively enhances the light absorption and facilitates photoexcited electron transfer to AgCl semiconductor. Moreover, the unique biomimetic structure of AgCl nanoshells and nanoplates could greatly improve both absorption and degradation performances for organic dyes. However, the photocatalytic mechanism over this Ag/AgCl hierarchical structure cannot be completely understood and a more detailed study is still underway.

Furthermore, the photocatalytic stability of as-prepared AgCl nanoplate-Ag/AgCl nanowire hierarchical structures has

been studied. These AgCl nanoplate-Ag/AgCl nanowire were recycled and reused for five cycles, and their photocatalytic performances have been shown in Fig. S7. It can be found that the as-prepared hierarchical structures still maintain a high photocatalytic activity for the degradation of RhB dyes during all these five cycles. More specifically, the degradation time of RhB dye is usually in the range of 3 min. Furthermore, these demonstrations clearly reveal that the biomimetic heterostructure could serve as a stable and efficient visible-light photocatalyst.

In summary, we have demonstrated a facile and efficient one-step oxidation procedure for fabrication of Ag/AgCl hierarchically biomimetic heterostructure at room temperature. Moreover, their photocatalytic performance studies indicate that this novel biomimetic photocatalyst exhibited much higher catalytic activities than both Ag/AgCl nanowires and AgCl nanoparticles for the degradation of organic contaminations under visible-light irradiation. This study may provide some inspiration for the rational design and the facile synthesis of hetero-photocatalysts with a high and tunable catalytic property through a biomimetic strategy.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure, and additional figures. See DOI: 10.1039/b000000x/

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