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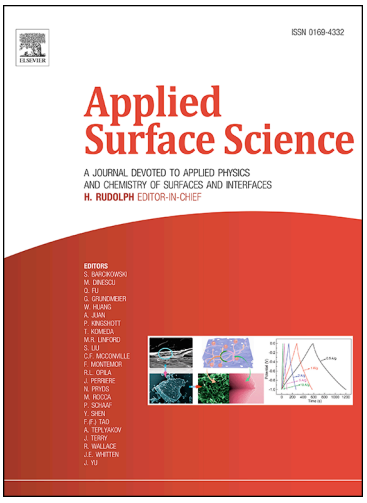

Full Length Article

Facile tuning of Ag@AgCl cubical hollow nanoframes with efficient sunlight-driven photocatalytic activity

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Full Length Article

Facile tuning of Ag@AgCl cubical hollow nanoframes with efficient sunlight-driven photocatalytic activity

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Abstract: In this work, a facile controlled synthesis of plasmonic photocatalyst, Ag@AgCl hollow cubic cage with the tuning of nanoframe structures was reported. AgCl cubical hollow nanoframes were primarily prepared using sacrificial NaCl template protocol. Ion exchange reaction between Ag^+ in the solution and NaCl, in presence of poly(vinylpyrrolidone) (PVP) led to continuous nucleation followed by growth of AgCl on the surface of sacrificial NaCl template. The tuning of AgCl nanoframe structures was obtained by changing the $AgNO_3$ concentration in the reactions. Afterwards, ethylene glycol assisted reduction of AgCl, produced Ag@AgCl, the metal@semiconductor composite with the homogeneous distribution of Ag nanoparticles on the surface of the AgCl hollow nanoframes. Efficient sunlight-driven photocatalytic activity to degrade Methylene blue (MB) (50 mL; 10mg/L) with these Ag@AgCl hollow frames was also demonstrated. The plasmonic photocatalysts were exhibited photodegradation rates about 0.098-0.184 min^{-1} with high catalytic activity and recyclability for five cycles. Additionally, active species entrapping experiments were performed and a possible mechanism for the enhanced photocatalytic performance of the synthesized plasmonic photocatalyst was also proposed.

Keywords: Ag@AgCl, cubical nanoframes, poly(vinylpyrrolidone) (PVP), sacrificial template, photocatalyst, sunlight irradiation

1. Introduction

Considering the combined effect of localised surface plasmon resonance (LSPR) of the metal nanoparticles and the facile separation of charge carriers created under light irradiation at metal-semiconductor interface, several silver based metal@semiconductor systems e.g. Ag@AgCl, Ag@AgCl/TiO_2, Ag@AgBr, Ag@AgI, AgI/Bi_2SiO_5, Ag@Ag_3PO_4, Ag_3PO_4/Ag/Ag_2MoO_4, Ag@Ag_2MoO_4 and as well as multi-heterostructured photocatalysts e.g. Ag@AgCl/TiO_2/rGO_N(nitrogen-doped reduced graphite oxide), g-C3N4/Ag2CO3/AgBr, Ag@$AgCO_3$/N-doped graphene, AgCl/Ag/$CaTiO_3$ Ag@AgCl/g-C_3N_4, AgCl/Ag/$AgFeO_2$, Ag@AgCl/$Bi_4Ti_3O_{12}$, Ag@AgCl/$SrTiO_3$ have been explored to design and develop efficient visible light plasmonic photocatalysts [1-36]. Recently hole co-catalyst modification to enhanced the photocatalytic activity of the Ag-based photocatalyst was also reported [37, 38]. Among them, Ag nanoparticles on AgCl nano/microstructures as Ag@AgCl or the reverse as AgCl@Ag were extensively studied as an efficient plasmonic photocatalyst [1-2, 4, 9-14, 18-27, 29-36]. The precise control of size, shape, structure and assembly of photocatalyst has received enormous importance owing to the fact that the photocatalytic performances of the materials are strongly governed by these aspects. Ag@AgCl plasmonic photocatalysts with a range of different morphologies including nanowires, microsphere, hollow microsphere, triangular pyramids, cube, hollow cubic cage and frame structure are known [1, 4, 18-21, 25-27, 29-30, 32]. Even though there is a report of site-selected synthesis of Ag@AgCl nanoframes [21], a route to tune the cubic cage hollow nanoframe structure of Ag@AgCl is conspicuously absent. In general, many studies indicated that the Ag@AgCl posses excellent photocatalytic activity in presence of visible-light [1, 4, 9, 11-13, 18-25, 27, 29-36] but only a few studies demonstrated the similar activity in presence of direct sunlight [4, 18, 19, 25, 29, 35]. The cubical morphology Ag@AgCl was mostly used for the latter case [18, 19, 25, 35].

However, in terms of energy conservation as well as utilization, sunlight is the extremely important and prospective renewable energy source for the function of the photocatalysts, due to the availability, economic, efficiency, accessibility, and capacity compared to other renewable energy sources, also known as 'alternative energy' to fossil fuel energy sources [5, 39-41]. Therefore, the development of high-efficient and recyclable sunlight-driven photocatalysts for the photocatalytic degradation of organic pollutants is of general concern and utmost importance in today's scenario [5, 18, 19, 25, 29, 39- 44].

An *et al* reported the synthesis of cubical Ag@AgCl photocatalysts in ethylene glycol with poly(vinylpyrrolidone) (PVP) which exhibit photodegradation of methylene blue (MB) under sunlight irradiation [19]. The template-free synthesis of Ag@AgCl cubical nanostructures and sunlight-driven photocatalysis for the photodegradation of organic pollutants (e.g. methyl orange and 4-chlorophenol) was reported by Zhu *et al* [25]. Recently Ag@AgCl cubic cage photocatalysts were synthesized by Tang *et. al.* using a novel sacrificial saltcrystal (NaCl)-template process, and LSPR induced charge carrier transfer from metal (Ag) nanoparticles to semiconductor (AgCl) surface was observed within 150 fs [20]. The site-selected monodispersed Ag@AgCl nanoframe with 1.0-1.3 μm of edge length and defined edges was further synthesized via modified Tang method by Han *et. al.*[21].

Herein, we present the controlled synthesis of Ag@AgCl hollow cubic cage with tuning of nanoframe structures via modified Tang method [20]. A general strategy has been developed to synthesize uniform AgCl hollow cubic cage structures by using sacrificial NaCl template, and Ag@AgCl composite hollow cubic cage was further obtained by ethylene glycol-assisted reduction of AgCl. The formation mechanism was also explored by spectroscopic and microscopic studies. It was shown that the development of the hollow AgCl cubes involves the dissolution of sacrificial NaCl cubical template via ion exchange diffusion reaction between Ag^+ in the solution and NaCl template in presence of poly(vinylpyrrolidone) (PVP), which led to continuous nucleation followed by the controlled growth of AgCl on the surface of sacrificial NaCl template. It was revealed that the concentration of Ag^+