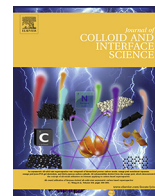




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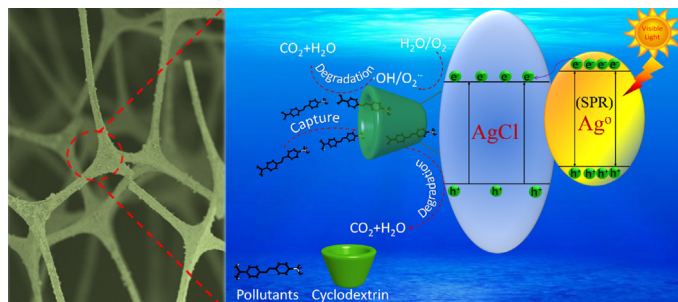
Cyclodextrin-functionalized Ag/AgCl foam with enhanced photocatalytic performance for water purification

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GRAPHICAL ABSTRACT

Per-6-thio- β -cyclodextrin (SH- β -CD) coated Ag/AgCl (Ag/AgCl@ β -CD) foam was purposeful design and prepared for enhancing Ag/AgCl photocatalytic performance in organic pollutants decomposition. Considering that the SH- β -CD is capable of capturing organic contaminants via host-guest interaction, resulting in the aggregation of those organic contaminants around the Ag/AgCl particles. And then the photogenerated reactive oxide species by Ag/AgCl particles under visible light could attack directly those captured organic pollutants. As a result, the photodegradation rate of organic pollutants by Ag/AgCl@ β -CD foam is obviously improved (2.6 times) compared with the pure Ag/AgCl foam.



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ABSTRACT

The application of visible light-induced photocatalysts for photocatalytic pollution mitigation has become a promising strategy due to the inexhaustible solar energy. And how to improve pollutants degradation rate is still a meaningful work. Many researchers dealt with this issue by enhancing visible light absorption of photocatalysts. However, few studies focus on this issue by improving semiconductor's absorption property of organic pollutants. Hence, in this work, we prepared the Ag/AgCl foam coated per-6-thio- β -cyclodextrin (SH- β -CD) to improve the photocatalytic activity of Ag/AgCl foam. Here, we chose SH- β -CD because it has a special cavity that can effectively absorb and capture proper organic pollutants via host-guest interaction, which makes it an ideal pollutants surface adsorber when coated on the surface of Ag/AgCl particles. Hence, those trapped pollutants in the cavities can be attacked directly by those reactive oxidation species (ROS) that produced by Ag/AgCl particles under visible light irradiation, resulting in the significant promotion of pollution mitigation rate. The experimental results demonstrated the photodegradation rate constant of methyl orange (MO) by Ag/AgCl@ β -CD foam ($k = 0.120 \text{ min}^{-1}$) increased approximately 2.6 times compared with pure Ag/AgCl from ($k = 0.048 \text{ min}^{-1}$).

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We anticipate our SH- β -CD modified Ag/AgCl foam would be a promising candidate for photodegradation of organic pollutants in wastewater remediation.

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1. Introduction

In the last few decades, water pollution has becoming a serious issue with the rapid development of industrialization and geometric growth of population [1]. And the polluted water has brought the serious threat and damage to plants and organisms living in or around it [2–3]. And even worse circumstances may happen if effective and proper measures are not taken in a timely manner [4–5]. Hence, researching for an effective strategy to remove organic pollutants from water has become a crucial topic. In recent years, photocatalytic technology has shown great potential in wastewater remediation as the light is the pollution-free and inexhaustible energy [6–8]. As the photosensitive semiconductors, some photocatalytic nanoparticles, such as titanium dioxide (TiO_2) [9–11], zinc oxide (ZnO) [12–13], silver halides AgX ($X = \text{Cl}, \text{Br}, \text{I}$) [6,14–16], have drawn increasing attention in the fields of photodegradation of organic contaminants under light irradiation. Among those semiconductors, although TiO_2 has received widely studied in wastewater treatment due to its low-cost, high stability and nontoxicity, the large band gap of TiO_2 (3.2 eV) requires the irradiated light in the UV range, resulted in the low utilization efficiency of solar energy [8,17–18]. Hence, in order to full utilization of solar energy, many researchers have focused on AgX semiconductors. As AgX are unstable under visible light and can decompose into metal silver particles (Ag^0) [19], which are able to absorb strongly visible light because of their strong surface plasmon resonance (SPR) effect [20–22]. As a result, the photocatalytic activity of AgX can be obviously improved. However, how to further improve the photocatalytic activity of semiconductors in the decomposition of organic pollutants is still a serious problem. To address this issue, the photocatalytic activity of semiconductors, understanding the process of photodegradation of organic pollutants by semiconductor is necessary. The process can be described that photocatalysts can firstly absorb the organic pollutants, resulting in the aggregation of organic pollutants around photocatalysts. Simultaneously, when photocatalysts

absorb light energy, the electrons (e^-) will be excited from valence band (VB) conduct band (CB) and leave the positive hole (h^+) on the VB. Those photoexcited e^- , h^+ further react with H_2O or O_2 in the water to produce the reactive oxide species (ROS), such as superoxide ($\text{O}_2^{\cdot-}$) and hydroxyl radical ($\cdot\text{OH}$), which can oxidize and decompose those organic pollutants around photocatalysts [8–9]. Base on this, it is reasonable to improve the photocatalytic activity of semiconductors by enhancing their absorption capacity of organic pollutants and their efficient light harvesting. Many researchers have focused on efficient light harvesting of semiconductors via various methods. For example, previous reports showed the photocatalytic activity of semiconductors can enhance obviously by deposited metal nanoparticles (Au, Ag) on their the surface because those metal nanoparticles are able to absorb strongly visible light due to their strong SPR effect [23–25]. However, few studies have designed a strategy to improve photocatalytic decomposition of organic pollutants via enhance semiconductor's absorption capacity of organic pollutants.

Hence, we designed one per-6-thio- β -cyclodextrins (SH- β -CD) coated Ag/AgCl foam to enhance the photocatalytic activity of Ag/AgCl for organic pollutants decomposition. We chose SH- β -CD for the following reasons, firstly, the SH- β -CD can easily coat on the surface of Ag/AgCl particles [26]. Secondly, as a derivative of β -cyclodextrin (β -CD), which consists of α -1,4-linked glucose units, SH- β -CD has a toroidal structure with a special hydrophobic cavity, which makes it capable of capturing and absorbing organic targets via host-guest interaction [27–29]. It is anticipated that coating SH- β -CD on the surface of Ag/AgCl particles is able to increase organic pollutants elimination rate because those organic pollutants trapped in the cavity of SH- β -CD can be attacked directly by the ROS that generated by Ag/AgCl particles under visible light irradiation. The overall preparation of Ag/AgCl@ β -CD foam was shown in the Fig. 1a. Here, melamine foam (MF) was chosen as the substrate because of its chemical stability and low cost. More importantly, its interconnected backbone is an ideal platform for immobilization of metal nanoparticles. The MF was firstly coated

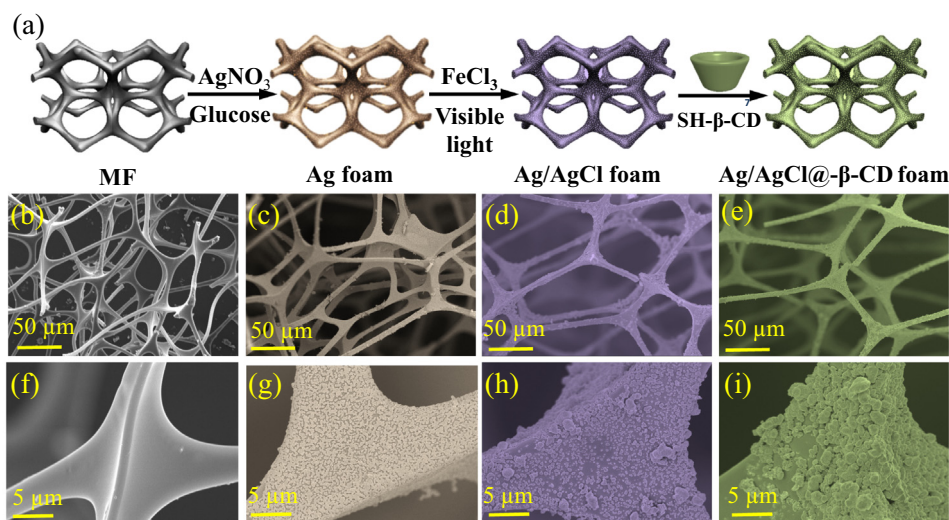


Fig. 1. (a) Schematic illustration of synthesis of Ag/AgCl@ β -CD foam. (b–e) SEM pictures of MF (b), Ag foam (c) Ag/AgCl foam (d) and Ag/AgCl@ β -CD foam (e). (f–i) The enlarged pictures of MF (f), Ag foam (g), Ag/AgCl foam (h) and Ag/AgCl@ β -CD foam (i).

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