



# Plasmon-assisted degradation of methylene blue with Ag/AgCl/montmorillonite nanocomposite under visible light



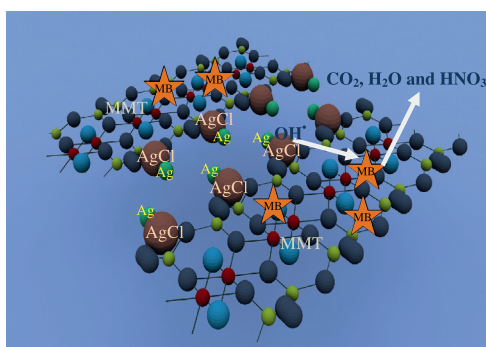
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## HIGHLIGHTS

- Ag/AgCl–MMT nanocomposite was synthesis by dispersion method and light irradiation.
- Montmorillonite play important role in stability of nanocomposite for photocatalysis.
- The optimal amount of photocatalyst is very low about 0.09 g/L.
- The band gap for AgCl in nanocomposite is 3.7 eV, but it is active under visible light.
- The surface plasmon resonance of Ag nanoparticles on AgCl makes it active in visible region.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Metal–semiconductor compounds, such as Ag/AgX (X = Cl, Br, I), enable visible light absorption and separation of photogenerated electron–hole through surface plasmon resonance (SPR) effect. However, the electron–hole generated and separated by light are vulnerable in Ag/AgX phase because of the occurrence of secondary recombined. In order to more effectively utilize the SPR photocatalytic effect, nanoparticles are located in a matrix. In this article, Ag/AgCl nanoparticles were synthesized in montmorillonite (MMT) matrix using dispersion method and light irradiation. The structure, composition and optical properties of such material were investigated by transmission electron microscopy (TEM), UV–visible diffuse reflectance spectroscopy (UV–Vis DRS), X-ray diffraction (XRD) and FTIR. Powder X-ray diffraction showed intercalation of Ag/AgCl nanoparticles into the clay layers. The as-prepared plasmonic photocatalyst exhibited an enhanced and stable photoactivity for the degradation of methylene blue (MB) under visible light. The high activity was attributed to the surface plasmon resonance (SPR) exhibited by Ag nanoparticles on the surface of AgCl. The detection of reactive species by radical scavengers displays that  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}^-$  are the main reactive species for the degradation of MB under visible light irradiation. The studies showed that 20 min illumination under visible light can complete degradation of methylene blue (MB), and indicate a high stability of photocatalytic degradation. The mechanism of separation of the photo-generated electrons and holes at the Ag/AgCl–MMT nanocomposite was discussed.

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## Introduction

Silver halides (AgXs) are well known photosensitive materials extensively applied as source materials in photography films, i.e., they are photoactive to both UV and visible light irradiation, in

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spite of their large band gap, e.g., a direct band gap of 5.6 eV (221 nm) and an indirect band gap of 3.25 eV (382 nm) for AgCl. However, unwanted and uncontrolled photographic process of AgXs caused by photo generated electrons (reduction process:  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$ ) under light irradiation inhabits pure AgXs to be directly used as stable photocatalysts. Therefore, a great number of attempts have been made to improve the photo-stability of silver halides by efficiently trapping photogenerated electrons and transferring them to oxidizing species. (i) Using some inert support including silica and zeolite had proved that it could stabilize the silver halides by preventing  $\text{Ag}^+$  of silver halides from reducing to  $\text{Ag}^0$  [1–3]. (ii) Using AgXs as co-photocatalyst with other semiconductors (SCs) [4–8]. (iii) Using Ag/AgX by reducing  $\text{Ag}^+$  to  $\text{Ag}^0$  on the surface of AgX particles during the synthesis process [9,10]. Stable photocatalysts including AgX/support composites, AgX/SC or Ag/AgX have been well used in the photodegradation of organic pollutants. The noble metal nanoparticles (NPs) have attracted considerable interest due to their surface plasmon resonance (SPR), which accelerates the separation process of the photo-generated electrons and holes in the semiconductor catalyst [11]. Many researchers have demonstrated that the Ag NPs deposited on semiconductor show efficient plasmon resonance in the visible region [12,13]. On the other hand, silver halide has high band gap and absorption of light above 380 nm is not possible by AgX alone. But it has shown that Ag nanoparticles deposit on AgX or other semiconductors show the plasmonic absorption of visible light [14,15]. Ag/silver halide composites as an excellent charge-separation promoter and built in acceptor have been widely investigated in recent years.

Recent studies showed that doping a semiconductor onto a suitable support has several advantages in photocatalysis processes: (1) increases the activity of the semiconductor, (2) decreases the high turbidity, (3) increases the adsorption of pollutants, (4) minimize electron/hole recombination, (5) prevent uncontrollable growth of particles, (6) prevent particle aggregation, and (7) controls particle size [16,17]. It is well known that clay minerals possess many unique properties such as an ability to “swell” in aqueous environments, high surface area, and high cationic exchange capacity which lead them ideal adsorbents for multiple applications [18–21]. Among the many kinds of clay minerals, montmorillonite (MMT) has been recognized as an effective adsorbent due to its large specific surface area (SSA) and high cationic exchange capacity (CEC) [22]. Montmorillonite are a subset of aluminosilicate clays having a 2:1 layer structure [23]. Within the layers of these clays, substitution of other metal ions for silicon or aluminum can occur resulting in a net negative charge on the surface of the clay platelet. This negative charge is offset by hydrated cations, such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . The surface chemistry of montmorillonite clays can be altered by exchanging the predominant inter-laminar cations with organic materials and inorganic cations that are positively charged.

In our previous work, we reported incorporation of AgXs in mesoporous (MCM-41) and microporous (mordenite) materials [1,2]. The results showed that mordenite zeolite is a good candidate for degradation of methylene blue dye with respect to MCM-41 material. It can be attributed strong surface plasmon resonance band due to Ag nanoparticles in mordenite zeolite. But high amount of Ag/AgBr/mordenite nanocomposite needs for degradation of methylene blue (MB). In the present report, we explore a simple synthetic route for silver chloride/silver nanoparticles (AgCl/Ag-NPs) in MMT and poly(vinyl alcohol) (PVA) using dispersion system and light irradiation. Methylene blue was chosen as the model compound to evaluate the photoactivity and stability of the synthesized catalysts, and tungsten filament Philips lamp was used as the visible light source. In addition, the detailed formations of silver chloride/silver nanoparticles in montmorillonite

were scrutinized using diffraction pattern, transmission electron microscopy, and diffuse reflectance spectroscopy.

## Experimental

### Materials

The commercial sodium montmorillonite clay (NaMMT), <25  $\mu\text{m}$  montmorillonite, cation exchange capacity (CEC) = 92.6 meq/100 g) was purchased from Southern Clay Products (Gonzales, TX). It was used as matrix. The silver nitrate (Merk), poly(vinyl alcohol) (PVA, molecular weight: 13,000, Aldrich, USA) and hydrochloric acid were served as dispersing agent in the experiment. All chemicals and reagents were used as received without further purification. The dye of methylene blue (C.I. name: Basic Blue 9,  $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$ ) (Scheme 1) was purchased from Fluka company.

### Synthesis of Ag/AgCl/montmorillonite nanocomposite

The 1.00 g of MMT was dissolved in 50 mL of silver nitrate aqueous solution (0.02 M) and 20 mL of hydrochloric acid 0.05 M was added to the MMT/silver nitrate solution. The reaction between silver and chloride ions was conducted for 3 h at 25 °C. The light irradiation for 20 min provided the silver chloride/silver nanoparticles (AgCl/Ag-NPs) in MMT. The resulting samples were thoroughly washed with distilled water to remove  $\text{NO}_3^-$  ions and hydrochloric acid. The final products were obtained by centrifugation (2000 rpm, 30 min) and dried in an oven at 50 °C. The prepared samples are termed as Ag/AgCl–MMT. The resulting product was gray in color.

### Synthesis of Ag/AgCl/PVA nanocomposite

The 0.01 g of PVA was dissolved in 10 mL of silver nitrate aqueous solution (0.02 M) and 2 mL of hydrochloric acid 0.05 M was added to the PVA/silver nitrate solution. The reaction between silver and chloride ions was conducted for 3 h at 25 °C. The light irradiation for 20 min provided the silver chloride/silver nanoparticles (AgCl/Ag-NPs). The resulting samples were thoroughly washed with distilled water to remove PVA and hydrochloric acid. The final products were obtained by centrifugation (2000 rpm, 30 min) and dried in an oven at 50 °C. The prepared samples are termed as Ag/AgCl NP. The resulting product was dark violet in color.

### Synthesis of AgCl bulk

A 40 mL silver nitrate aqueous solution (0.02 M) was dissolved in 40 mL of hydrochloric acid 0.05 M. The reaction between silver and chloride ions was conducted for 3 h at 25 °C. The resulting samples were thoroughly washed with distilled water to remove hydrochloric acid. The final products were obtained by centrifugation (2000 rpm, 30 min) and dried in an oven at 50 °C. The prepared samples are termed AgCl bulk.

### Characterization

Powder X-ray diffraction of all samples was recorded on a Siemens D5000 with Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). XRD was used to identify the crystal phase of the powders were analyzed from 2° to 70° (2 $\theta$ ) with a step size of 0.01  $\text{^\circ}$  to assess the crystalline of the samples under study. The UV–Vis diffused reflectance spectra (UV–Vis DRS) obtained from UV–Vis Scinco 4100 spectrometer with an integrating sphere reflectance accessory.  $\text{BaSO}_4$  was used as a reference material, and UV–Vis absorption spectra were

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