



Degradation of Blue Ink Solution by Silver Chloride Photocatalyst การสลายของสารละลายน้ำหมึกสีน้ำเงินโดยใช้ปฏิกิริยาโฟโตคะตะไลซิส ของซิลเวอร์คลอไรด์

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Abstract

AgCl was synthesized by the ion-exchange reaction with some metallic Ag nanoparticles on its surface. Its size was in the range 1-2 μm . The XRD diffraction patterns matched with the cubic phase of AgCl crystal with some weak diffraction peaks of metallic Ag. Ag nanoparticles were also detected by scanning electron microscope (SEM). The product showed high photocatalytic degradation efficiency for orange G dye and blue ink solution under UV light irradiation. AgCl crystals prepared with different conditions had no metallic Ag nanoparticles on the surface and showed lower photocatalytic activity.

Keywords: Metallic Ag, Silver chloride, Photocatalyst, Blue inks

บทคัดย่อ

ซิลเวอร์คลอไรด์ (AgCl) ถูกสังเคราะห์ขึ้นโดยปฏิกิริยาการแลกเปลี่ยนไอออนบนพื้นผิวกับอนุภาคนาโนของแร่เงิน โดยมีขนาดอยู่ในช่วง 1-2 ไมโครเมตร รูปแบบการเลี้ยวเบน XRD สัมพันธ์กับเฟสลูกบาศก์ของผลึก AgCl โดยมีค่าการเลี้ยวเบนสูงสุดของแร่เงินบางส่วน อนุภาคนาโนของแร่เงินยังตรวจพบได้โดยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) ผลการศึกษาแสดงให้เห็นว่า ปฏิกิริยาโฟโตคะตะไลซิสมีประสิทธิภาพสูงในการสลายสีย้อมสีส้ม G และสารละลายน้ำหมึกสีน้ำเงินภายใต้การฉายรังสียูวี ผลึก AgCl ที่เตรียมขึ้นภายใต้สภาวะอื่นๆ ไม่ปรากฏอนุภาคนาโนของแร่เงินบนพื้นผิว รวมถึงมีปฏิกิริยาโฟโตคะตะไลซิสในระดับที่ต่ำกว่า

คำสำคัญ : แร่เงิน ซิลเวอร์คลอไรด์ ปฏิกิริยาสังเคราะห์แสง หมึกสีน้ำเงิน

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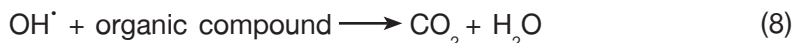
Introduction

Silver chloride (AgCl) is photosensitive materials extensively used in photographic films and optical devices. On absorbing a photon, AgCl particle generates an electron and a hole, and subsequently the photogenerated electron combines with an Ag ion to form an Ag metal atom. Ultimately, a cluster of Ag atoms is formed within AgCl particle upon repeated absorption of photons. Due to this instability under sunlight, AgCl is provided the very basis for chemical photography. Recently, the application in photocatalysis with plasmonic photocatalysts (Ag/AgCl) having stronger absorption and activity under visible light has attracted scientists' attention all over the world and becomes a hotspot in the field of photocatalysis (Lou et al., 2011). A variety of morphologies of AgCl have been reported, for example, Ag/AgCl core-shell nanowires were synthesized from oxidation reaction of Ag nanowires and FeCl_3 at room temperature. The oxidation reaction was explained based on the lower redox potential of Fe^{3+} ions than that of Ag species resulting in the migration of electrons from Ag nanowires to Fe^{3+} ions to form the AgCl nanowires. This oxidation process was also attempted with other metal chlorides such as CuCl_2 solution to fabricate a novel nanoplate/nanowire Ag/AgCl (Bi & Ye, 2009). Uniform heart-like AgCl was fabricated in the presence of ethylene glycol (EG) and polyvinyl pyrrolidone (PVP) under heating at 140 °C for 7 h. Heart-like morphology arose from the merge of four cubes by oriented-attachment (Liao et al., 2012). Ion-exchange reaction between NaCl with Ag_2WO_4 microrods (as the template) produced rod-like morphology of Ag/AgCl with rough surfaces. Cubic Ag/AgCl and spherical Ag/AgCl are generally synthesized for decomposition of organic pollutants.

The hypothesized pathways for the photocatalytic degradation of organic pollutants by Ag/AgCl under UV light irradiation were schematically illustrated in Figure 1. AgCl absorbs photons from UV light with energy equal or greater than its band gap (3.25 eV), electrons in the valence band can be excited and jump up into the conduction band and leaving behind a hole in the valence band (Eq. (1)). The electron-hole pairs may recombine (Eq. (2)), or electron and hole may separate and finally be trapped as reduced Ag atom (Ag^0) (Eq. (3)), or Cl^0 atom (Eq. (5)). In



general, the photogenerated electrons may also be trapped by O_2 in the solution to form superoxide ions (O_2^-) (Eq. (4)) which further transform to other reactive oxygen species. These active species also would degrade the dye molecules (Jiang & Zhang 2011). Despite this competing electron trapping reaction, however, the presence of metallic Ag atoms seem to indicate that the trapping of free electron by Ag^+ ions (Eq. (3)) located within the matrix may be the more favorable route. While the left over holes diffuse into the AgCl matrix to oxidize Cl^- ions to Cl atoms (Eq. (5)) which are very reactive for oxidizing species in the surrounding solution (Eq. (6)) (Dong et al., 2012). The hole may also oxidize the adsorbed OH^- at the interface to the powerful $\cdot OH$ radical (Eq. (6)) which subsequently would undergo the dye degradation as well.



Objectives

The aims of this study are as follows:

1.1.1 To characterize the physical properties of the as-prepared AgCl powders using XRD, SEM, and DRS techniques.

1.1.2 To evaluate the photocatalytic activity for blue ink solution of the as-prepared AgCl

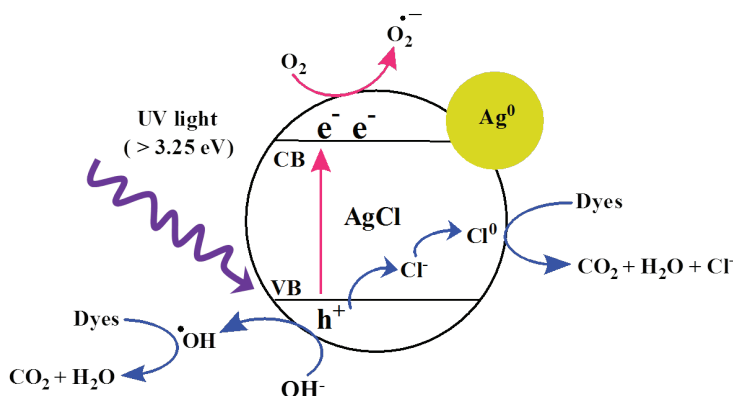


Figure 1 Schematic illustration of the AgCl photocatalytic degradation of organic pollutants under UV light irradiation

Materials and methods

In this work, AgCl was synthesized by ion-exchange method. At first, 0.2 M of AgNO_3 was prepared in acetic acid solution and refluxed for 1 hour. Concurrently, AlCl_3 solution was prepared 2.5 M of AlCl_3 solution with deionized water and was slowly poured into the AgNO_3 solution with stirring continuously. The white powder of AgCl was obtained, washed with deionization water, and dried at 40 °C. Finally, AgCl powder was obtained and assigned as AgCl-S.

To compare the condition of synthesis method, we have prepared the second type of AgCl without refluxing which is assigned as AgCl-NR.

The third type of AgCl was prepared in the absence of acetic acid solution. The obtained AgCl is referred to as AgCl-NA.

The fourth type of AgCl was prepared in the absence of vinyl acetate. The obtained AgCl is referred to as AgCl-NV.

The synthesized AgCl catalysts were characterized by a powder X-ray diffractometer (XRD) using $\text{CuK}\alpha$ radiation. The textural structures were studied by scanning electron microscope (SEM).

For the photocatalytic measurement, 0.1 g of catalyst powder was added into 100 mL of 0.25 v/v of blue ink solution and stirred in the dark for 1 hour. After that, the suspension was exposed to UV light irradiation. Every 1 hour, the solution was taken out and collected by centrifugation to determine the concentration by UV-visible spectrophotometer.



Results

SEM images clearly indicated that AgCl-S, AgCl-NA, AgCl-NR, AgCl-NV synthesized by these methods exist in irregular morphology with size in the range 1-2 μm as shown in Figure 2. XRD patterns showed the diffraction pattern with 2θ at 27.82, 32.24, 46.25, 54.82, 57.45, 67.42, 74.44, 76.72 and 85.67° corresponding to (111), (200), (220), (311), (222), (400), (331), (420) planes that can be indexed to the face center cubic of AgCl as shown in Figure 3. In addition, a weak diffraction peak at 38.1° was also observed which is assigned to the (111) plane of metallic Ag (or Ag⁰) coexisting with AgCl in this sample (Dong et al., 2013). The sample of synthesized AgCl possessed two broad absorption peaks about 460 and 580 nm while the commercial AgCl have no SPR absorption band, which was attributed to SPR effect of Ag nanoparticles generated on the AgCl particle surfaces (Choi et al., 2010; Wang et al., 2009). Metallic Ag nanoparticles on the AgCl surface are able to absorb light in the visible range due to the absorption properties of surface plasmon resonance (SPR) as shown in Figure 4. AgCl commonly exists in the cubic morphology which is inert towards dye degradation. When the morphology was transformed to near spherical particle of about 1 μm , the photocatalytic property was observed in discoloring the 0.1 v/v of Orange G dyes with efficiency more than 90% within 120 minutes under UV light irradiation as shown in Figure 5. Figure 6 showed the spectral changes of blue ink solution at the maximum absorption of 600 nm together with the blue color decreased within 7 hours when it was degraded by AgCl under UV light irradiation. Indicating that, the degradation efficiency was found that AgCl degraded blue ink solution completely in 7 hours. In addition, no degradation was observed in the dark condition for this AgCl samples.

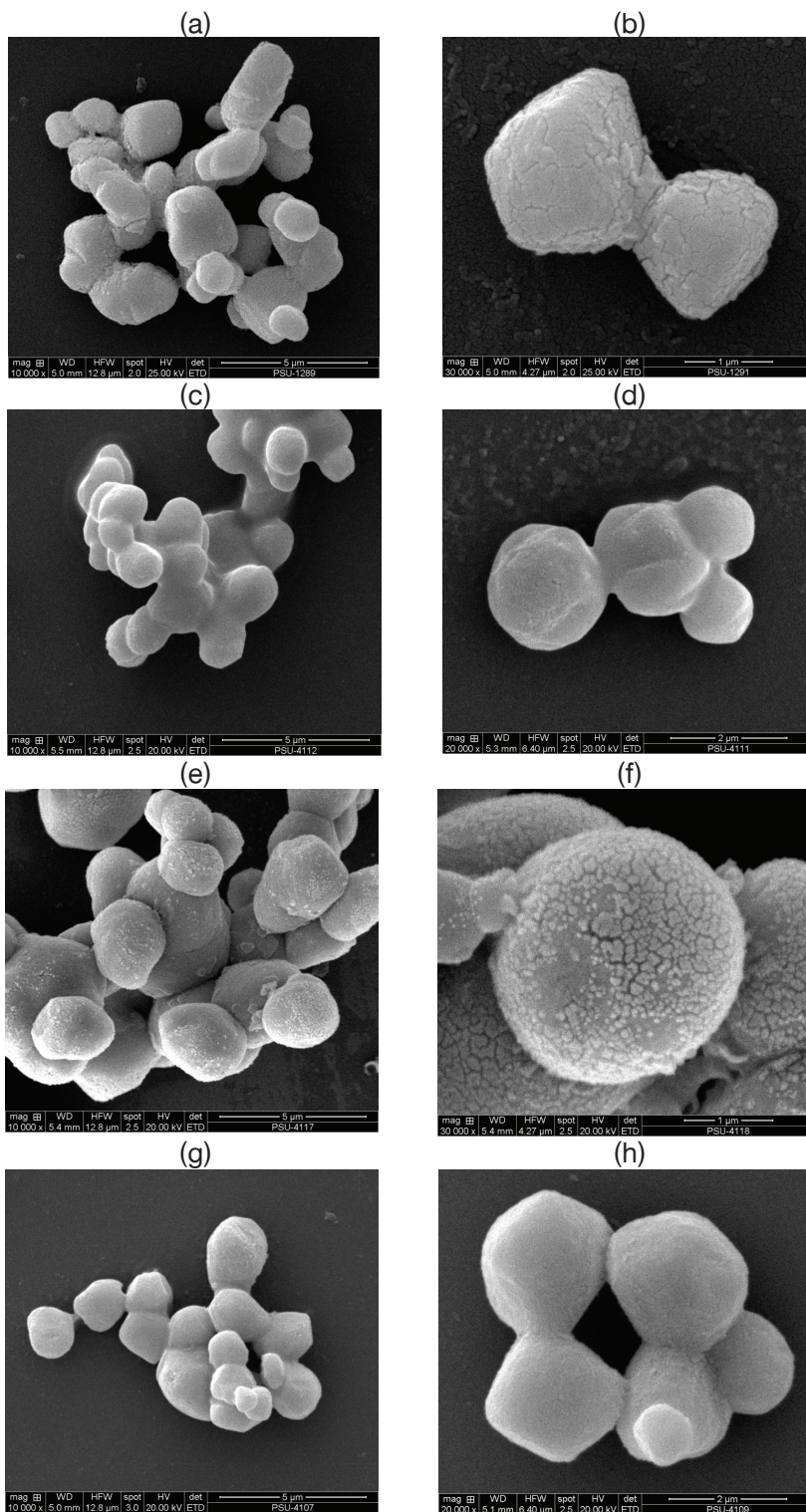


Figure 2 SEM image of (a)-(b) AgCl-S, (c)-(d) AgCl-NA (e)-(f) AgCl-NR and (g)-(h) AgCl-NV

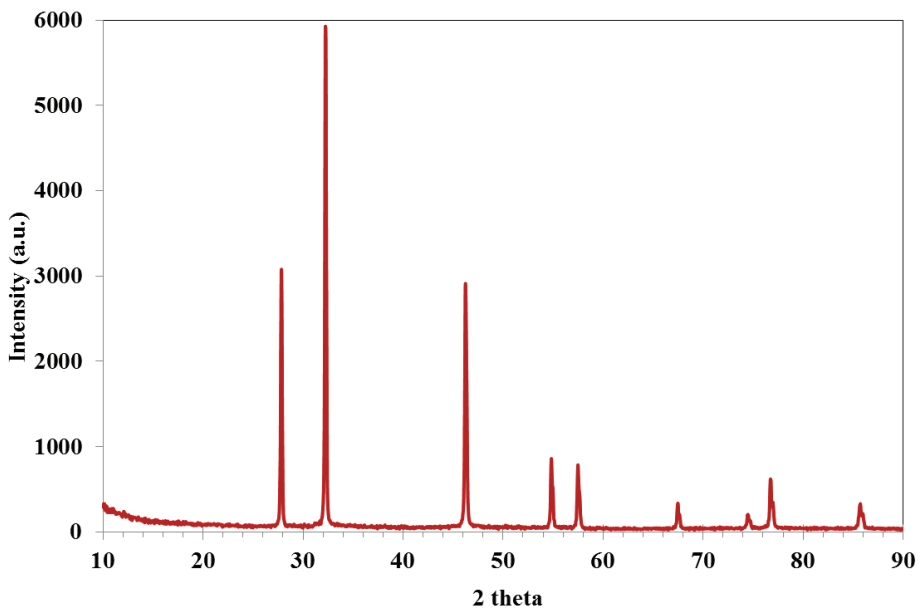


Figure 3 XRD pattern of synthesized AgCl

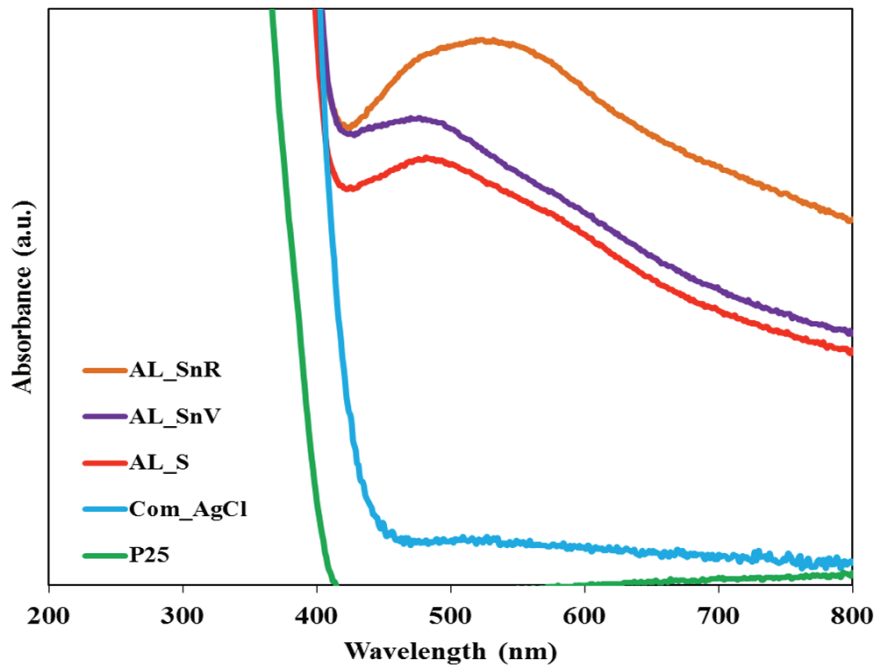


Figure 4 DRS spectra of different AgCl samples

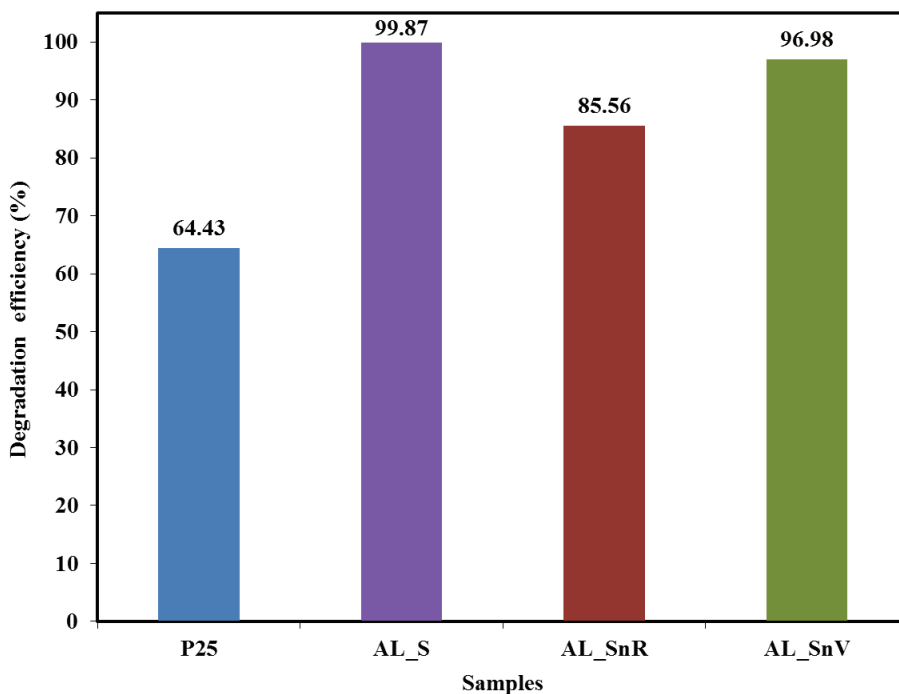


Figure 5 photodegradation efficiency of orange G dye with different AgCl

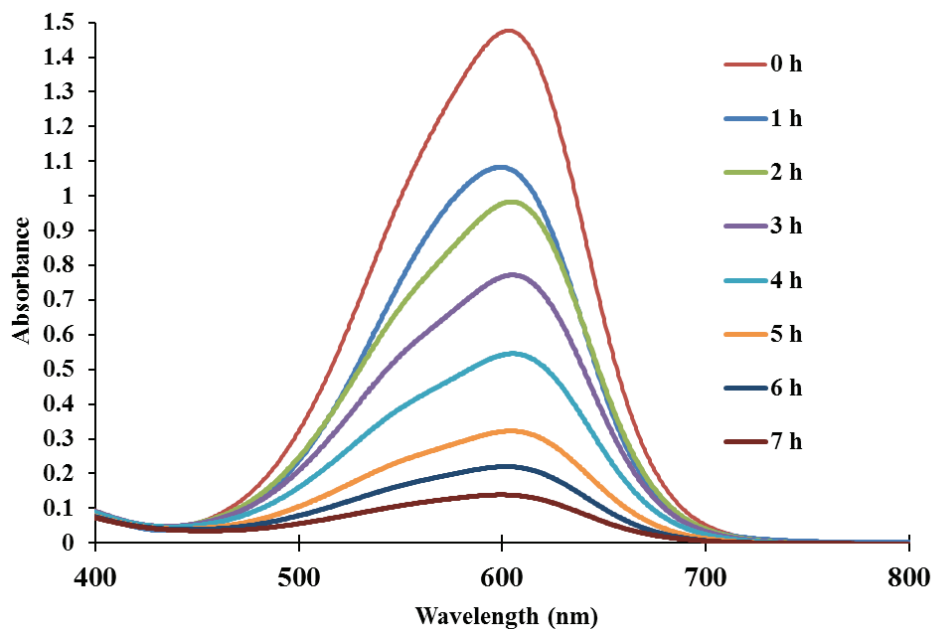


Figure 6 Spectral change of blue ink solution



Discussion

In the diffractometer, the angle and intensities of the high-angle reflected beams serve as a ‘fingerprint’ for the crystal structure. Therefore, the unknown crystalline materials can be identified by comparing the XRD pattern with a database of Joint Committee on Powder Diffraction Standards (JCPDS), which lists an invaluable reference source (Kelsall et al., 2005). The intensity of diffraction peaks of synthesized AgCl was higher than the commercial AgCl implying high crystallinity of synthesized AgCl. The photocatalytic activity of AgCl was attributed to the presence of metallic Ag nanoparticle deposited on AgCl surface which was observed by SEM images. These metallic particles may be reduced from some parts of Ag ions during the synthesis process. This absorption behavior of metallic Ag corresponded with the observation reported by other researchers that it was originated from the characteristic absorption of surface plasmon resonance (SPR) of metallic Ag on the AgCl surface (Zhang et al., 2009; Han et al., 2011). Therefore, the absorption spectra in the visible range can be used to confirm the existence of metallic Ag (or Ag⁰) in AgCl. The SPR band intensity and wavelength depend on the factors such as the metal type, shape, particle size, orientation, and contact area with the substrate (Rycenga et al., 2011). The photodegradation of near spherical AgCl was higher than that of commercial AgCl and Degussa P25 TiO₂ indicating that the near spherical morphology was more active in the new morphology. Moreover, the near spherical AgCl exhibits two UV-visible absorption peaks from the DRS measurement attributable to the presence of metallic Ag particles on the surface of AgCl crystal that can absorb UV-visible light.

Conclusion

In this work, AgCl powder was successfully synthesized by ion-exchange method. The better photocatalytic activity of orange G dye and blue ink solution by using synthesized AgCl as catalysts was explained based on the presence of metallic Ag particle settled on AgCl surface confirmed by SEM images which not only can absorb the UV-visible light but also exhibits strongly electrostatic interaction that is favorable for the photocatalytic degradation. Metallic Ag nanoparticles act



as electron acceptor and reduce the recombination rate of electron-hole pairs, resulting in the high photocatalytic activity. The high crystallinity also influences to the high photocatalytic activity.

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