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Short Communication

# Preparation of tabular silver bromide and its photocatalytic performance

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ABSTRACT

Silver bromide is widely used in photographic film which is prepared by the emulsion method using gelatin, and it is also known that the gelation assists the formation of AgBr with various shapes and sizes. In order to investigate the photocatalytic activity as one of the applications of AgBr, the preparation of shape-controlled AgBr was carried out. It is found that the emulsion method controlled by varying the concentration of gelatin and Br/Ag molar ratios was effective to improve AgBr photocatalytic activity.

## 1. Introduction

Silver halide, especially silver bromide, is well known as photographic materials [1,2]. Nowadays, the production of photographic film has been reducing since film cameras are being replaced by digital cameras [3]. In our previous study, catalytic activity of AgBr in hydrogen evolution reaction from methanol/water solution still remained after 200 h under UV irradiation [4]. Furthermore, AgBr in $AgNO_3$ aqueous solution was found to be active for oxygen evolution under UV irradiation.

So far, the achievement of the one step photo water splitting has been reported by using materials covering the water redox potentials, for example AgBr [5–8]. Although it has high potential for application as water spitting photocatalyst, there are just a few publications related to AgBr as catalysts for water photo splitting [9–12]. However, Ag cluster formation on AgBr is induced by the photo-decomposition under exposure to light. In addition, the electron-hole pair recombination and Ag formation in AgBr competitively proceed at the same time from our previous reports [4].

Recently, shape and size control have been introduced as the other approach for AgBr preparation by the emulsion synthesis gelatin, dimethyl sulfoxide (DMSO), dyes, and organic substances [1,13–15]. In view point of the environmental and financial aspects, the emulsion method is appropriate because of its low AgBr consumption. This method has been widely used in photographic chemistry but not photocatalyst study. In this study, we attempted the preparation of AgBr as a photocatalyst using the emulsion method. Though large amount of gelatin has been generally used for the shape control, we employed lower gelatin compositions from 0.05 to 0.5 wt.% for the preparation. Furthermore, effects of aging temperature and Br/Ag molar ratio on AgBr shape and size were also investigated. As mentioned in experimental section, the photoactivity was also examined. And alcohol–water solution was employed to confirm that AgBr C.B. is more negative than reduction potential of water, and to evaluate photocatalytic activity from amounts of evolved hydrogen gases.

In photographic field, the usage of higher than 10 wt.% of gelatin led to the formation of amorphous AgBr with tabular shape. In our study, tabular AgBr was successfully obtained with compositions as low as 0.5–0.05 wt.%. The addition of 0.5 wt.% of gelatin was the optimum value for the formation of tabular shape and the high photocatalytic performance was observed.

## 2. Experimental

AgBr having tabular shapes was prepared by emulsion method. $AgNO_3$ aq.sol.(33 mL) and KBr aq.sol.(33 mL) were dropped at the same time into dissolved gelatin aqueous solution (30 mL) at 40 °C while stirring, then the emulsion (gelatin concentration 0.5 wt.%) was aged at various temperatures with different Br/Ag molar ratios for appropriate time in the dark room. After the ripening process, tabular AgBr was obtained by dryness at room temperature after wash and decantation using an ethanol/water solution for many times. The Br/Ag molar ratio was varied from 1, 2, and 4 and the emulsion was ripened at 20 °C for 120 h. Then, Br/Ag molar ratio was fixed at 4 and emulsion was ripened at various temperatures (20, 40, 60, 80 °C) for 24 h.

UV–Visible light (UV–Vis) diffuse reflectance spectra were recorded on a SHIMADZU UV–Vis spectrophotometer UV-2400PC. The structure and the phase of the sample were determined by X-ray diffraction (XRD) with a Rigaku RINT2000 diffractometer using Cu-Kα radiation, with an operation voltage of 30 kV and an operating current of 20 mA. The scan rate of 2°/min was applied to record the patterns in the range

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of 10–70° at a step of 0.02°. The morphology was observed by scanning electron microscopy (SEM; S-4800, HITACHI).

The photocatalytic hydrogen evolution reactions were carried out using an inner irradiation type Pyrex vessel in an open-circulation system. AgBr powder (0.1 g) was dispersed in a 10 vol.% ethanol aqueous solution (140 mL). The reactant suspension was irradiated under a 100 W high-pressure Hg lamp via a quartz tube filled with a flow cooling water to maintain temperature of the reactant suspension at room temperature during the reaction and for removing IR irradiation. The suspension was followed by thorough deaeration through bubbling with Ar gas for 1 h. Then, the suspension was stirred continuously under Ar flow with 20 mL min$^{-1}$ and irradiated through a water filter. The evolved hydrogen was analyzed by gas chromatograph (Shimadzu GC-8A) using column (length 2 m) packed with Molecular Sieves 5A(mesh 60/80) and column temperature at 60 °C as with previously reported in Ref. [4].

## 3. Result and discussion

Table 1 showed summary of AgBr samples prepared by each emulsion conditions. Prepared AgBr samples are defined as RxCyTz where R is the Br/Ag molar ratio, C is the aging temperature and T is the aging time; for example, R1C20T120 is the sample that had Br/Ag ratio of 1, and was aged at 20 °C for 120 h. Fig. 1 showed the XRD patterns of prepared AgBr. In each preparation method and conditions, only AgBr crystal pattern was detected. UV–Vis spectra of each prepared AgBr are shown in Fig. 2. AgBr has absorption edge at ca.480 nm but, AgBr obtained by lower Br/Ag molar ratio shows a blue shift compared to higher Br/Ag molar ratio. This blue shift observation may have originated from smaller and better dispersed AgBr particle in the emulsion method.

Fig. 3 shows SEM images of AgBr prepared at different conditions in which images from a to h are AgBr prepared via the emulsion method. From images a to c, AgBr(RxC20T120) was prepared at 20 °C for 120 h with ratio varying from 1, 2 and 4 for 24 h, respectively. It is pointed out that the Br/Ag molar ratio gives the great effect on the formed particles size as it becomes bigger when the ratio increases. Moreover, as the ratio increases, particle size distribution seems to be broaden as the precipitation/crystallization rate was accelerated. From images d to h, samples (R4CyT24) were prepared with the Br/Ag molar ratio of 4 while the aging temperatures were 5, 20, 40, 60 and 80 °C, respectively.

Fig. 4 shows particle size distribution analysis in different aging conditions. When the aging was carried out at 5 °C, the particle sizes of R4C5T120 were from 1 to 2 μm. At 20 °C, the formation of particle with ~1 μm in size was observed in R4C20T120. However, temperatures higher than 20 °C acted negatively to the formation of controlled-AgBr particles, resulting in the broaden particle distribution curves with peak at about 1.5 μm at 40 °C in R4C40T120 and 2.5 μm at 80 °C in R4C80T24, respectively. It seems that formation of bigger particles up to 3–4 μm is favored at high temperatures due to Ostwald ripening process. Generally, AgBr crystal growth process is explained by the diffusion of Ag$^{+}$ ions to AgBr surface to react with absorbed Br$^{-}$ ions. Therefore, the particles prepared with higher Br/Ag molar ratios are formed bigger than others prepared in lower Br/Ag molar ratios. Moreover, the high temperatures also seem to promote the dissolution of small AgBr particles for the growth of AgBr particles. SEM observations shown in Fig. 3 are in consistent with this explanation. It can be pointed out that most of AgBr particles in SEM images showed the same

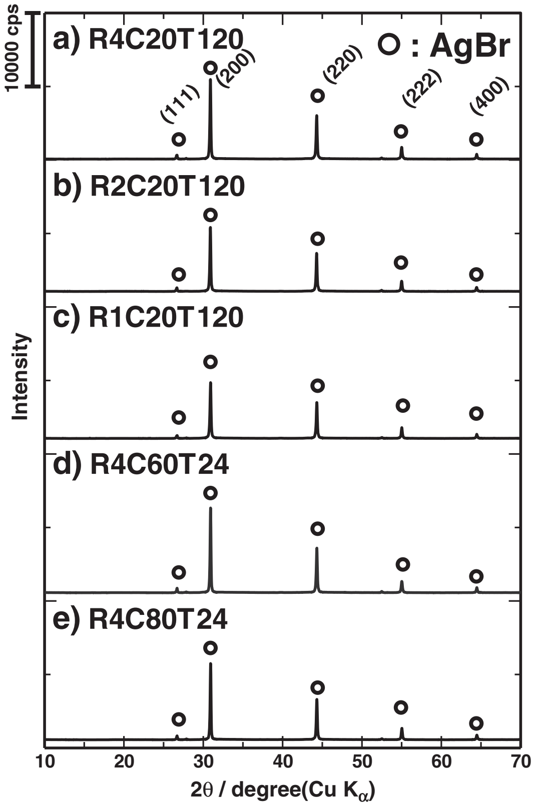

**Fig. 1.** XRD patterns of AgBr powder with different Br/Ag ratios (a–c) and different aging temperatures (d–e): a) R4C20T120, b) R2C20T120, c) R1C20T120, d) R4C60T24, e) R4C80T24.

**Table 1**
Summary of preparation conditions of silver bromide.

| Prepared sample name | Aging temp. [°C] | Br/Ag molar ration[-] | Aging temp. [h] | Concentration of gelatin in emulsion [wt.%] |
|---|---|---|---|---|
| R1C20T120 | 20 | 1 | 120 | 0.5 |
| R2C20T120 | 20 | 2 | 120 | 0.5 |
| R4C20T120 (T24)[a] | 20 | 4 | 120 2(4)[a] | 0.5 |
| R1C40T120 | 40 | 1 | 120 | 0.5 |
| R2C40T120 | 40 | 2 | 120 | 0.5 |
| R4C40T120 | 40 | 4 | 120 | 0.5 |
| R4C5T120 (T24)[a] | 5 | 4 | 120 2(4)[a] | 0.5 |
| R4C40T120 (T24)[a] | 40 | 4 | 120 2(4)[a] | 0.5 |
| R4C60T24 | 40 | 4 | 24 | 0.5 |
| R4C80T24 | 60 | 4 | 24 | 0.5 |

[a] T24 was aged time for 24 h, and was prepared for to observe surface of samples.

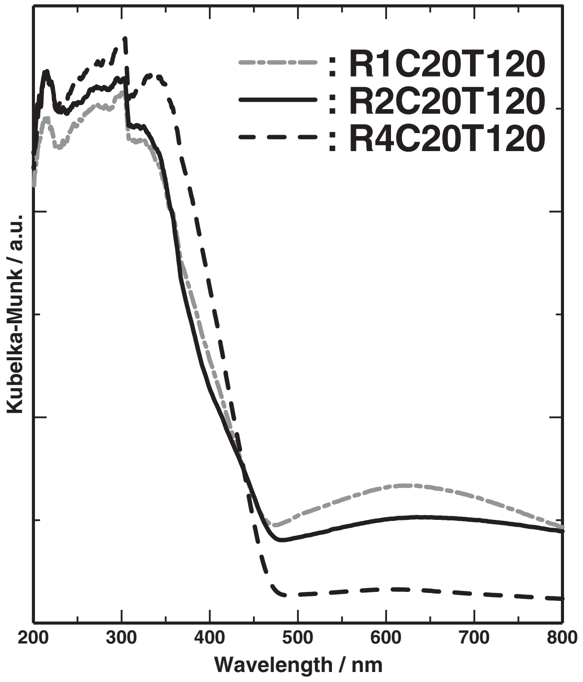

**Fig. 2.** UV–Vis spectra of AgBr powder with different Br/Ag ratios.