



A study on the preparation and application of Ag/TiO₂ complex sol-part 1: Preparation and properties of Ag/TiO₂ complex sol

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ABSTRACT

The primary aim of this study is to explore the property of Ag/TiO₂ complex sol. Ag/TiO₂ complex sols are prepared at different pH values. The results show that the reaction of Ag and Ti(OH)₄ is not suitable for the generation of Ti-O-Ag under alkaline conditions. Dried complex sols formed under acid conditions have a smaller particle size, whereas dried gels formed under alkaline conditions present a laminated structure. With increasing concentration of AgNO₃, specific surface area and pore volume of the dried gel are larger, but the orifices become smaller. In the case of excess AgNO₃, for example 4-10 dried gel, there is a reverse effect on particle size.

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KEYWORDS

Complex sol;
Particle size;
Specific surface;
Pore volume.

INTRODUCTION

The gel method is a chemical method in which a metal or semi-metal alkoxysilane is subjected to hydrolysis and polycondensation. In this technology, an inorganic precursor is used with acid-base catalysts to generate reticular compounds. This technology makes it possible for processing at low temperatures, and organic materials can be incorporated into the inorganic phase without decomposition. This method allows the preparation of many products, such as powder, gel, dried gel, fiber and coatings^[1,2]. The gel method allows the metal oxide of functional groups to be coated onto various materials, serving the purpose of surface modification^[3-10]; for example: glass^[11], metal^[12] or organic high polymers^[13-16].

Once made use of a sol-gel method to make compound photo-catalyst in the past research paper, by

with amplification TiO₂ it stirred up a wave-length^[17-20], but for applied compound sol in fabrics of the dyeing and finishing of research not much, so this research will synthesize various compound sol and make into dry gel and discuss a making the condition is to the related property of the sol or the dry gel, with is used as the reference that the follow-up appliance processes.

EXPERIMENTAL

Materials

Titanium *n*-butoxide (99%, TTB); ethyl alcohol, acetic acid, nitric acid, sodium hydroxide, hydrochloric acid, were purchased from Shimadhisashi Pharmaceutical; ethyl acetoacetate (EAc) was purchased from NIHON SHIYAKU INDUSTRIES; silver nitrate was purchased from Wako Pure Chemical Inc. Ltd..

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METHODS

Preparation of complex sol

With vigorous stirring 10ml of butyl titanate (TTB) was added to 30ml of absolute ethyl alcohol, and then 2ml of acetic acid and 0.2ml of acetylacetone were added. After stirring for 30 minutes, a uniform and transparent solution was obtained (solution A). Distilled water (1ml) was slowly added to 15ml of ethyl alcohol, and 0.1ml of 1M nitric acid was added slowly, then the mixture was stirred for 30 minutes to obtain solution B. By adding solution B slowly into solution A, it was possible to obtain a uniform and transparent yellowish sol. After stirring for 1 hour, 40ml of distilled water was added to produce a white sol. At different pH values (2~10), the TiO₂ sol at the concentration specified above was added to a solution of AgNO₃, thus forming a reaction system. Stirring was continued for 3 hours to obtain the Ag/TiO₂ complex sol. Next, an Ag/TiO₂ dried complex sol was prepared by drying the sol for 2 hours at 80°C, then the dry gel were wash with distilled water until to neutralize.

Analysis and measurement

Fourier transform infrared spectroscopy in the attenuated total reflection mode (FT-IR/ATR) spectra of the dried gels was recorded with a Bio-Rad Digilab FTS-200 spectrometer using an MCT detector. A diamond crystal was used as the internal reflectance element. Single-beam spectra were the result of 64 scans. The spectral resolution was 4 cm⁻¹. The surface mor-

phologies of the films were observed with a JEOL model JSM 6400 scanning electron microscope. A gold coating was deposited onto the samples to avoid charging the surface. The distributions of all atoms of the Ag/TiO₂ dried gels were analyzed by energy-dispersive X-ray spectroscopy (EDS; model EDSEM, JEOL, Tokyo, Japan). A Bruker-AXS D8 was used for X-ray powder diffraction (parallel beam optics, Cu-target, scintillation counter, sampler changer with rotation). The samples were run with 40 kV, 100mA, 5-60°/2θ, 0.01° stepsize and 5 sec counting time. The surface area and pore volume of the dried samples were determined through nitrogen physisorption analysis, using a Quantachrome Autosorb-1 system. The five-point BET calculation was used to determine the surface area.

RESULTS AND DISCUSSION

FT-IR

To analyze the property of various sols, Ag/TiO₂ dried complex sol was prepared by drying the sol for 2 hours at 80°C. Figure 1 depicts FT-IR spectra of Ag/TiO₂ dried complex sols prepared at different pH values. Among dried gels of 1380cm⁻¹ and 1625 cm⁻¹, absorption peaks of Ti-O-Ti and >C = O groups are clear, of which >C = O is represented by the >C = O absorption peak of a compound of Ag and ethyl acetylacetone. In figure 1a-D, there is obviously a C = C absorption peak at 1540cm⁻¹. It can thus be proved that, although AgNO₃ is likely to form AgOH under

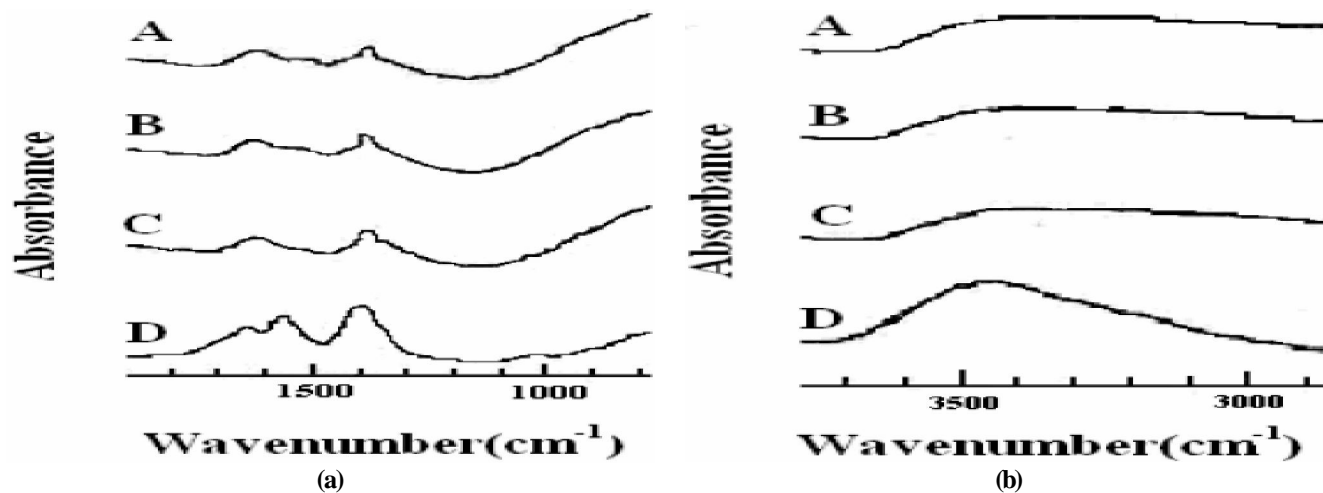


Figure 1 : FT-IR of Ag/TiO₂ dry gel. (A): 4-1 (B): 4-6 (C): 4-10 (D): 10-10

alkaline conditions, it is unlikely to react with $\text{Ti}(\text{OH})_4$ to generate Ti-O-Ag after polycondensation. This can be deduced from an obvious O-H absorption peak at 3442cm^{-1} . But, no obvious difference exists in figure 1b-A to 1b-C.

SEM and EDS

As illustrated in figure 2, the particle sizes of dried complex sols increase with increasing pH, and TiO_2 is made available at the white section. The particles are slightly bigger, since silver nitrate readily forms silver hydroxide under alkaline conditions, which is easily adhered to the surface of TiO_2 . Secondly, the appearance of the dried gel differs a little, due to different con-

centrations of silver nitrate. As illustrated in figure 2, when the concentration of silver nitrate becomes higher, the silver component in the dried gel increases (the black part) with a decreasing amount of TiO_2 (the white spot). By comparing the acid-base of 2-c and 2-d, acid $\text{Ti}(\text{OH})_4$ is easily bonded with Ag in the compound, thus forming Ti-O-Ag of smaller particles. Conversely, alkali AgOH presents a laminated structure due to larger

TABLE 1 : Various signs of complex sols are defined below

Sign	Definition	Concentration of AgNO_3 (g/ml)
4-1	Complex sol prepared with 1ml of AgNO_3 at pH 4	5.7×10^{-5}
4-3	Complex sol prepared with 3ml of AgNO_3 at pH 4	1.71×10^{-4}
4-6	Complex sol prepared with 6ml of AgNO_3 at pH 4	3.42×10^{-4}
4-10	Complex sol prepared with 10ml of AgNO_3 at pH 4	5.7×10^{-4}
6-10	Complex sol prepared with 10ml of AgNO_3 at pH 6	5.7×10^{-4}
8-10	Complex sol prepared with 10ml of AgNO_3 at pH 8	5.7×10^{-4}
10-10	Complex sol prepared with 10ml of AgNO_3 at pH 10	5.7×10^{-4}

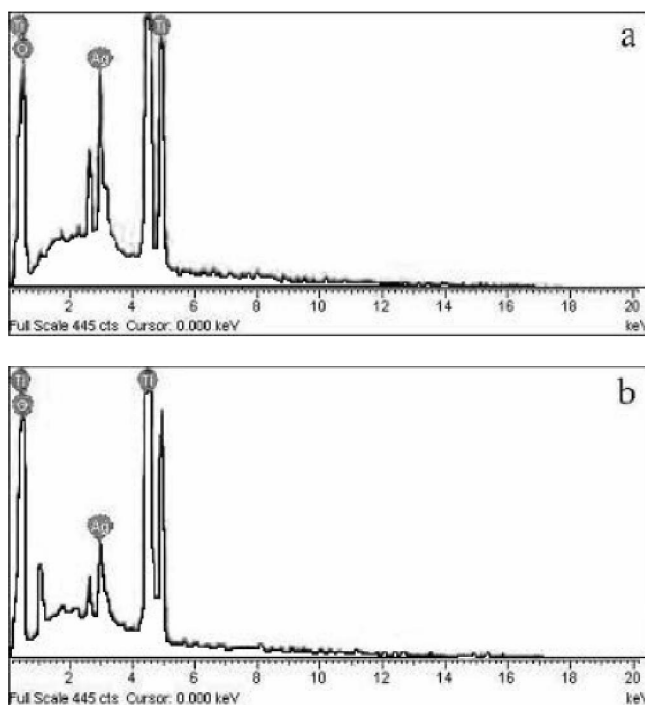


Figure 3 : EDS of Ag/TiO_2 dry gel. (a): 4-10, (b): 6-10

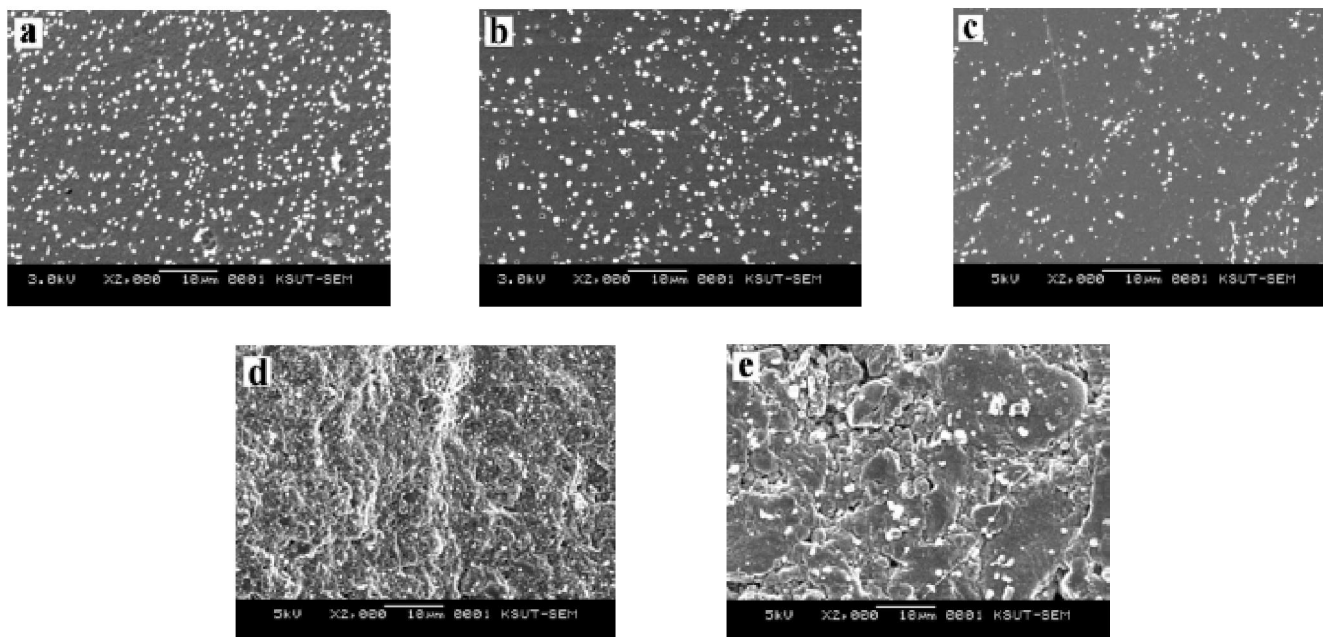


Figure 2 : SEM of vary Ag/TiO_2 complex dry gel. a): 4-1, b): 4-6, c): 4-10, d): 6-10, e): 10-10

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TABLE 2 : EDS of Ag/TiO₂ dry gel

Elements	Property							
	Weight (%)				Atomic (%)			
	a ¹	b	c	d	a	b	c	d
O	78.04	81.75	84.01	87.30	92.07	93.37	94.18	95.42
Ti	18.65	16.71	15.20	12.43	7.35	6.37	5.69	4.54
Ag	3.31	1.54	0.79	0.27	0.58	0.26	0.13	0.04
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

¹a: 4-10, b: 6-10, c: 8-10, d:10-10

TABLE 3 : Specific surface area, pore size and pore volume of Ag/TiO₂ dry gel

Samples	Specific surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
4-3	234.8926	3.4591	0.148446
4-6	263.5813	3.2292	0.188117
4-10	186.9373	2.7699	0.081909
10-10	79.1247	8.7123	0.079545

particles and the difficulty of bonding with Ti(OH)₄. In addition, EDS analytical data for the Ag/TiO₂ dried complex sol are shown in figure 3 and TABLE 1. It can be seen that relative content (% , w/w) of Ag in the dried gel will decline with the increasing pH value.

X-ray analysis

Figure 4 depicts the X-ray analysis of the dried gels. There is an obvious Ag atom absorption peak in the case of 2θ at 28°, 32° and 42°. When AgNO₃ is added with a tenfold difference, the absorption peak differs significantly, as shown in figure 4-a, and 4-c. It can be seen that the concentration of silver nitrate will affect the content in the dried complex sol, but not the crystal structure. The acid-base conditions have no influence on the crystal structure of the dried gel.

B.E.T.

As given in TABLE 3, any change of silver nitrate content will have an influence on the particle size of the dried gel. With increasing concentrations of AgNO₃, the surface area and the pore volume of the dried gel become larger, along with smaller particles. In the case of excessive amount of AgNO₃, for example, 4-10 dried gel, there is a reverse effect on particle size. This is because many Ti-O-Ag molecules are mixed together, and the aperture of dried Ti-O-Ag is likely depressed into a flat structure. In an alkaline state, the deposits of AgOH likely yield more opportunities for condensation, or even

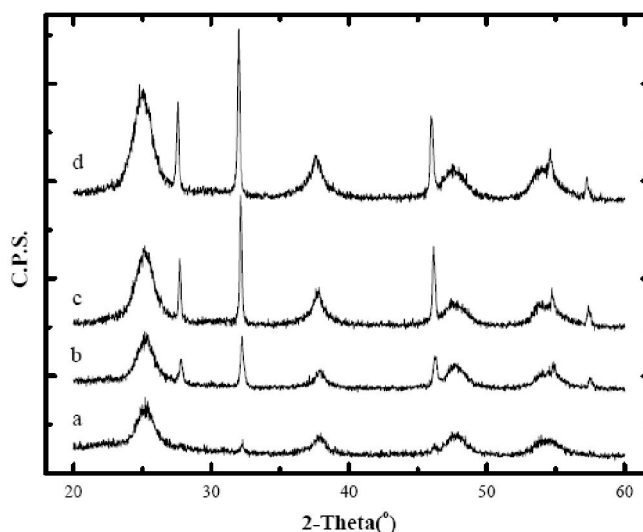


Figure 4 : X-ray of Ag/TiO₂ complex dry gel. a): 4-1, b): 4-6, c): 4-10, d): 10-10

crack upon drying; thus, it presents the largest aperture but the smallest specific surface area and orifice volume.

CONCLUSIONS

This study has prepared Ag/TiO₂ complex sol at different pH values. The objective was to explore the property of dried complex sol. The following conclusions are drawn from the test results. (1) Dried complex sols prepared under acid conditions have smaller particles, whereas those prepared under alkaline conditions present a laminated structure. The relative weight percentage of Ag in the dried gel decreases with increase of pH value. (2) The concentration of AgNO₃ has an influence upon the weight percentage of dried complex sols but not on the crystal structure. Meanwhile, acid-base conditions have no influence upon the crystal structure of the dried gel. (3) In the case of increasing concentration of AgNO₃, specific surface area and the pore volume of the dried gel was increased, but the orifice size becomes smaller. In the case of an excessive amount of AgNO₃, there is a reverse effect on particle size. Under alkaline conditions, the dried gel presents the largest aperture but the smallest specific surface area and orifice volume.

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