



Fabrication and Characterization of Nanometer-sized AgCl/PMMA Hybrid Materials

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Abstract

Nanometer-sized AgCl/PMMA hybrid materials were synthesized by in situ polymerization. XRD analyses indicated that the prepared samples were amorphous in structure. SEM and EDS analyses indicated that the elements of Ag, Cl in the materials were homogeneous distribution. HSEM images showed that the AgCl nanoparticles in the hybrid materials were spherical in shape, the size was ca. 50nm, particle size distribution was in narrow range, and no agglomerates were clearly observed. The transmissivity and the solubility of the hybrid materials decreased with the increase of AgCl contents in hybrid materials. The TG-DTA analyses indicated that the weight of the hybrid material kept constant above 400°C, the weight loss was 96.98%, and organic compounds were completely decomposed at 385.60°C. The nanometer-sized AgCl/PMMA hybrid materials had some photochromic effect.

Keywords: AgCl, Nanoparticles, Hybrid materials, Nanomaterials, Photochromism

1. Introduction

Inorganic/organic nanometer hybrid materials are the nanomaterials which organic materials hybridize with inorganic materials in nanoscale, including inorganic nanoparticles dispersed in organic matrix and nanoscaled organic compounds in inorganic materials. Inorganic/organic nanometer hybrid materials have attracted increasing interests due to their unique optical, electronic properties and many other specialities[1-7]. AgCl has good photochromism, and it has been well documented. There are also some papers on the preparation and properties of AgX nanoparticles[8-12], but the hybridization of nanometer-sized AgCl with polymer was rarely reported. In the paper, inorganic/organic nanometer hybrid photochromic plexiglass was prepared by hybridization of AgCl nanoparticles with polymethyl methacrylate (PMMA), and some preliminary results were obtained.

2. Experimental Section

2.1 Preparation of nanometer-sized AgCl (coated with oleic acid)/PMMA hybrid material

AgCl nanoparticles, AgCl and Cu²⁺ coexistence nanoparticles in hydrosol were modified with oleic acid which has unsaturated double bond, and AgCl nanoparticles, AgCl and Cu²⁺ coexistence nanoparticles organosols were obtained, as indicated in references[10-11]. These nanoparticles were mixed with methyl methacrylate (MMA) at a certain ratio. Prepolymerization was performed after an amount of initiator was added into the above mixture. When the viscosity of the mixture increased to a certain value, the mixture was poured into a mould. Then the mould was placed into an oven, polymerization was carried out at 110°C for 2h. After the mould was naturally cooled down to room temperature,

nanometer-sized AgCl/PMMA hybrid materials were obtained.

2.2 Characterization methods

XRD analysis was performed with a Japanese Rigaku D/MAX-IIB X-ray diffractometer using Cu $K\alpha_1$ radiation and a curved graphite crystal filter, the working current and voltage were 20mA and 40kV, respectively. The scanning speed was 4°/min, and step was 0.02°. The transmissivity was measured by 754 UV-Visible spectrophotometer made by Shanghai electric optical instruments limited company. The morphology of the hybrid materials was observed with a JXA-840 scanning electron microscope made by Japanese JEOL company. EDS analysis was performed using OXFORD ISIS-300 energy dispersion x-ray spectrometer. High resolution SEM observation of the fracture plane of the hybrid materials was conducted by a S-4200 scanning electron microscope made by Japanese Hitachi company. TG-DTA analysis was carried out with a SDT-2960 thermal analyzer made by American PERKIN-ELMER company in atmosphere, measuring temperature range was 100°C-600°C, and the temperature-rising rate was 10 °C /min.

3. Results and Discussion

3.1 XRD analysis of nanometer-sized AgCl/PMMA hybrid materials

Sample 1 (Volume content of AgCl was 1%), sample 2 (AgCl and Cu²⁺ volume content 1.5%), sample 3 (Volume content of AgCl 2%) were characterized by XRD, as shown in Figure 1. It is seen from Figure 1 that a wide peak appeared at diffraction angle $2\theta=14^\circ$, the peak is the characteristic peak of the typical amorphous organic compound. Therefore, the hybrid material was amorphous in structure. There are no obvious diffraction peaks of AgCl. This is probably due to little AgCl content, or AgCl nanoparticles without crystallization.

3.2 SEM and EDS analysis

In order to investigate the influence of AgCl content on the structure of the hybrid materials, the samples 1, 2 and 3 were fractured at room temperature, and the fracture planes were studied by SEM, as shown in Figure 2. It can be seen that the fracture planes were tenacity fractures. The convex-concave extent decreased with the increase of AgCl content. The samples were further observed by high resolution SEM in order to understand the existence and distribution of AgCl nanoparticle in the matrix, as shown in Figure 3. It is seen from Figure 3 that AgCl nanoparticles were spherical in shape, size distribution was in narrow range, and no obvious aggregates were observed. AgCl nanoparticles size was ca. 50nm. Samples were also investigated with EDX in order to understand the elements distribution in the matrix, as indicated in Figure 4. It is seen that elements of C, O, Ag, Cl uniformly dispersed in the matrix, and Ag and Cl distribution density increased with the increasing in AgCl content.

3.3 Optical property of nanometer-sized AgCl/PMMA hybrid materials

The transmissivity of samples 1, 2 and 3 was measured using pure PMMA as a reference, as indicated in Figure 5. It is seen that transmissivity of the hybrid materials decreased with the decrease of wavelength at high wavelength range (800-600nm) and with the increase of AgCl content. This is owing to the absorbance and reflection of AgCl. The transmissivity of sample 2 was lower than that of sample 3 at middle wavelength range (550-360nm), and this is due to the absorbance of Cu. The transmissivity of samples increased gradually with the decrease of wavelength at low wavelength range (450-360nm), and this is attributed to the decrease in absorbance of the materials.

3.4 Solubility of hybrid materials analysis

100mg of samples 1, 2 and 3 were added into 6ml of chloroform, toluene and ethanol, respectively, for 2h. The results were summarized in Table 1. It is seen that sample 1 and 2 dissolved in chloroform, not in toluene and ethanol, sample 3 dissolved partly in chloroform, also not in toluene and ethanol. This is due to AgCl served as cross-linking dots in the matrix. For one thing, the polymer chains twisted to form physical cross-linking on the surfaces of AgCl nanoparticles; for another, polymerization of surface modifier on the surface of AgCl nanoparticles with matrix formed chemical cross-linking. With the increase of AgCl content, the cross-linking networks centered at AgCl nanoparticles increased, the structure of the samples was transformed from soluble linear structure to insoluble cross-linking structure. The dissolution behavior also indicated the hybrid materials were surely formed [1,6]. Figure 6 is the relationship between transmissivity and wavelength for samples dissolved in chloroform. It is seen that transmissivity decreased with the increase of AgCl content.

3.5 TG-DTA analysis

TG-DTA curves of sample 3 were shown in Figure 7. From TG curve, it can be seen that the weight loss of hybrid material was 96.98%, and the weight kept constant when temperature was above 400°C. It is seen from DTA curve that an obvious exothermic peak appeared at 385.60°C, this is owing to decomposition of the organic compounds.

3.6 Photochromism analysis

Samples 1, 2 and 3 were placed under sunlight, change of color of hybrid material was observed, as shown in Table 2. It is indicated that color of samples became darker with the increase of AgCl content and prolongation of lighting-time.

Consequently, AgCl content should be high in order to obtain an ideal photochromic materials.

4. Conclusions

4.1 Nanometer-sized AgCl/PMMA hybrid materials were synthesized by in situ polymerization. The transmissivity and dissolution of the hybrid materials decreased with the increase of AgCl content.

4.2 XRD analyses indicated that the prepared samples were amorphous in structure.

4.3 The TG-DTA analyses indicated that the weight of the hybrid material kept constant above 400 °C, the weight loss was 96.98%, organic compounds were entirely decomposed at 385.60 °C.

4.4 SEM analysis revealed that the fracture plane of the hybrid material was tenacity fracture at room temperature. EDS analyses indicated that the elements of Ag, Cl in the materials were homogeneous distribution. HRSEM images showed that the AgCl nanoparticles in the hybrid materials were spherical in shape, the size was ca. 50nm, particle size distribution was in narrow range, and no agglomerates were observed.

4.5 The nanometer-sized AgCl/PMMA hybrid materials had some photochromic effect.

References

- Golden J.H., Deng H.B., Disalvo F.J., et al. (1995). Monodisperse 10 Å diameter metal clusters in a polymeric host: the monomer as solvent approach. *Science*, 268, 1463-1466
- Wang J., Tang M., Zhang F., et al. (2007). Modification of optical waveguide material PMMA with nano-silicon by sol-gel approach. *Key Eng. Mater.*, 336-338, 549-551
- Zhuang W., Zhang J. H., Liu J., et al. (2008). Preparation and characterization of nano-TiO₂/polylactide composites. *Acta Materiae Compositae Sinica*, 25(3), 8-11
- Liao J. G., Li Y. B., Wang X. J., et al. (2008). Nano-hydroxyapatite/polycarbonate composite I: Preparation and characterization. *Acta Materiae Compositae Sinica*, 25(3), 63-67
- Dong X.T., Zhang L., Zhang W., et al. (2001). Preparation and characterization of nanometer-sized CeO₂ polystyrene hybrid material. *Acta Phys.-Chim. Sin.*, 17(8), 739-742
- Zhang Y., Zhou G. E., Li L. et al. (1998). Preparation and structure of monodispersed nano-TiO₂/PMMA materials. *Chin. J. Mater. Res.*, 12(3), 291-294
- Dong X.T., Sun J., Liu G. X., et al. (2003). Preparation and characterization of nanometer-sized CeO₂/PMMA hybrid material. *Acta Chim. Sin.*, 61(1), 122-125
- Fu S.L., Yue J., Liu S.W. (1997). Study of preparation and properties of AgBr/I nanoparticles latex. *Light Sensitive Materials*, 15(3), 14-20
- Dong X. T., He Y., Yan J.H., et al. (2003). Preparation and characterization of nanosized AgBr/PMMA photochromic hybrid material. *Acta Phys.-Chim. Sin.*, 19(12), 1159-1162
- Feng X. L., Dong X. T., Li X. Q., et al. (2004). Preparation and characterization of AgCl and Cu²⁺ coexistent nanoparticles sol. *Rare Metal Mater. Eng.*, 33(9), 1003-1005
- Dong X. T., Feng X. L., Wang J. X., et al. (2005). Preparation and characterization of nanosized AgCl hydrosol. *Mater. Sci. Technol.*, 13(1), 45-48
- Dong X. T., Feng X. L., Wang J. X., et al. (2005). Preparation and characterization of AgI nanoparticles hydrosol. *Rare Metal Mater. Eng.*, 34(5), 761-763

Table 1. Solubility of different AgCl contents in hybrid materials

Solvents	Sample 1	Sample 2	Sample 3
Chloroform	Soluble	Soluble	Partly soluble
Toluene	Insoluble	Insoluble	Insoluble
Ethanol	Insoluble	Insoluble	Insoluble

Table 2. Photosensitivity of nanometer-sized AgCl/PMMA hybrid materials

Lighting-time	Sample 1	Sample 2	Sample 3
2h	No obvious change	No obvious change	Slightly dark
4h	No obvious change	Slightly dark	Darker

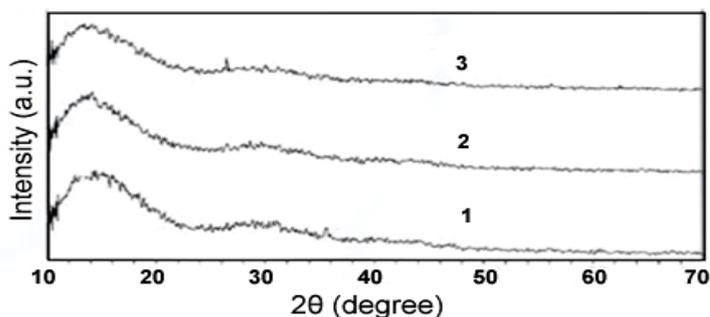
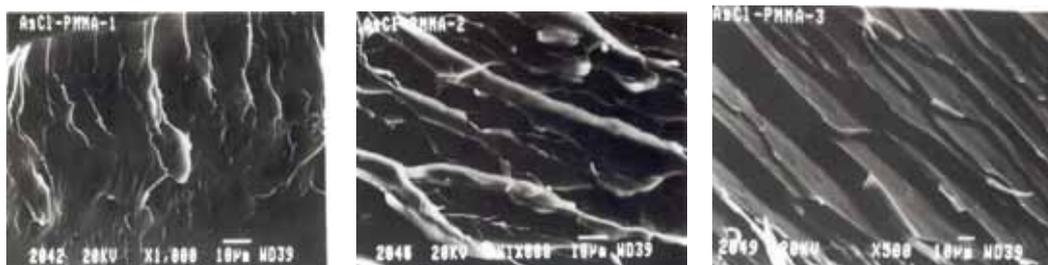


Figure 1. XRD patterns of nanometer-sized AgCl/PMMA hybrid materials

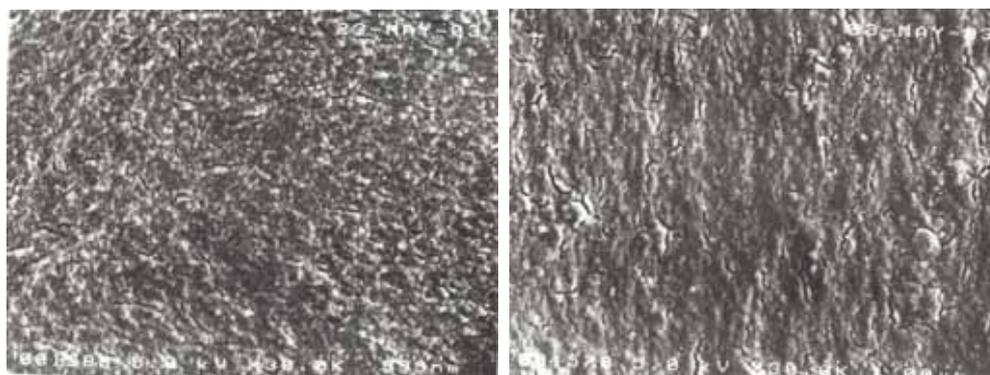


Sample 1 (×1K)

Sample 2(×1K)

Sample 3(×500)

Figure 2. SEM images of the fracture planes of nanometer-sized AgCl/PMMA hybrid materials



Sample 2(×30K)

Sample 3(×30K)

Figure 3. HRSEM images of the fracture planes of nanometer-sized AgCl/PMMA hybrid materials

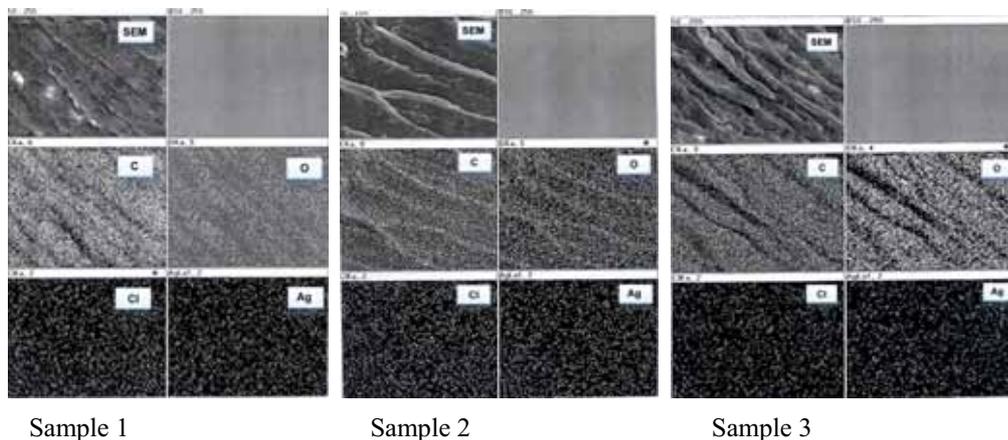


Figure 4. SEM and EDS surface analysis of fracture planes of nanometer-sized AgCl/PMMA hybrid materials

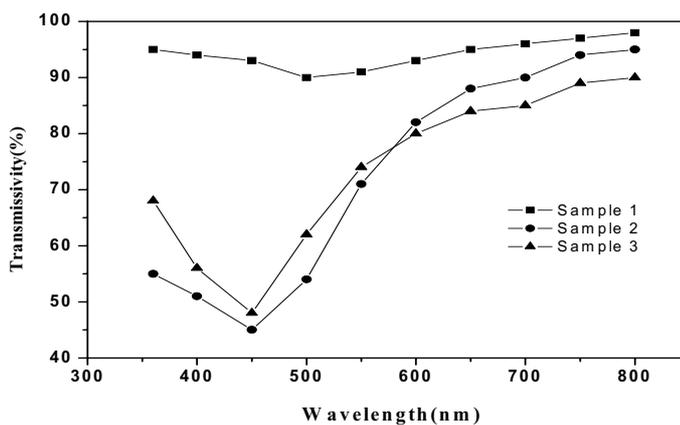


Figure 5. Relationship between transmissivity of different AgCl contents in hybrid materials and wavelength

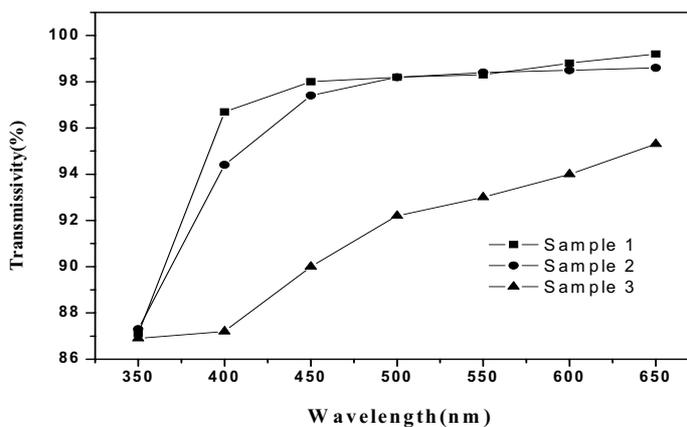


Figure 6. Relationship between transmissivity of the mixtures of hybrid materials dissolved in chloroform and wavelength

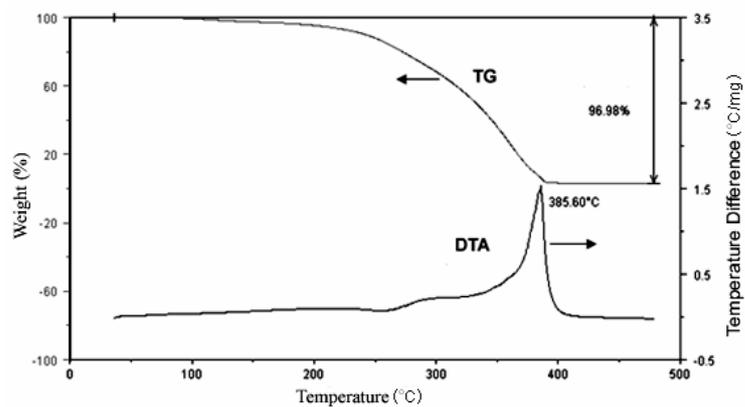


Figure 7. TG-DTA curves of nanometer-sized AgCl/PMMA hybrid material