Preparation of New Composite Films Composed of Size-Controlled Cobalt Oxide Nanoparticles Dispersed in Organically Modified Silica Glass

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Abstract: The pyrolysis of transition metal carboxylates into organically modified silica glass-ZrO_2 hybrid sol-gel films yields composite materials containing cobalt oxide nanoparticles in various proportions. The particles have sizes ranging from 5 to 10 nm, and they are homogeneously dispersed in the final materials. A reaction temperature near 250°C results in translucent films that have good mechanical properties and that could find application in nonlinear optics.

Keywords: Nanoparticles, cobalt oxide, hybrid sol-gel films.

1. INTRODUCTION

Materials containing cobalt oxide nanoparticles are interesting in relation with their potential applications in novel high-performance nonlinear optical devices [1, 2] and chemical sensors [3-6]. Co_3O_4 films prepared by a metal salt-pyrolysis method [3] (pyrolysis of spin-coated films of Co octanoate, which at temperatures above 350°C decomposes into oxide, through a variant of the Piria reaction [7]) have considerably large third-order optical nonlinearities [1]. The large third-order nonlinear susceptibility ($\chi^{(3)}$) of these films suggests that they would be useful in optical switching and optical limiting applications. Co_3O_4 nanoparticles have been made by hydrolytic [8-10], mechanochemical [11] and pyrolytic [12] methods, but there have been no attempts to prepare glasses coatings embedded with cobalt oxide nanoparticles. This is surprising because the mechanical resistance of such coatings makes them easier to handle than nanoparticle powder (which for many applications needs to be processed in a polymer or some other binder).

The sol-gel technique of polymerization of various alkoxides is known to be advantageous for preparing oxide materials in various shapes and sizes that meet optical transparency requirements. Glasses with very good optical quality have been prepared through thermal treatment of hybrid xerogels.

Co_3O_4 particles dispersed in transparent glass are especially interesting from the viewpoint of nonlinear optical applications because Co_3O_4 has a large $\chi^{(3)}$ and large figure of merit ($\chi^{(3)}/\alpha$, where α is the linear absorption coefficient of the material). Furthermore, by combining Co_3O_4 particles (refractive index $n = 1.71$) with silica glass with a smaller n (e.g., 1.457), we can reduce the light scattering at the surface of the material. We can therefore expect to increase the 3rd-order nonlinear optical effect by introducing intense incident light through the low-reflection surface of silica glass containing highly dispersed Co_3O_4 particles.

Here we show how sol-gel hybrid/metal oxide nanoparticles composites can be made by first making homogeneous xerogels incorporating cobalt octanoate and then subjecting the xerogels to a thermal treatment that converts the xerogel into a hybrid glass and produces embedded oxide nanoparticles by pyrolysis of the metal octanoate.

From the chemical point of view, the sol-gel method has another remarkable advantage for preparing highly dispersed nonlinear optical metal oxide particles in a glass matrix when it is combined with metal salt-pyrolysis method because the diffusion coefficient in the xerogel is more than 1000 times smaller than in the melt octanoate. This large difference in diffusion coefficients helps in reducing the size of the particles by suppressing the formation of large oxide particles, since aggregation is a diffusion-limited process and the movement and diffusion of the metal octanoate are very slow in the xerogel even at temperatures around 400°C.

2. MATERIALS AND METHODOLOGY

2.1. Preparation of the Primary Sols

Primary sols were prepared by the hydrolysis of a dimethyldiethoxysilane (DEDMS)-triethoxymethylsilane (TEMS) alkoxide mixture, followed by cross linking with zirconium

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propoxide (Zr(OPr)$_4$), before the addition of cobalt octanoate.

The basic sol preparation process typically included the following three steps:

1. x ml of DEDMS was mixed with ethanol (the ethanol volume was usually equal to the combined (DEDMS+TEMS) volume) + acidic water (aq HNO$_3$ pH=1). The water content was calculated to be sufficient to hydrolyze the total alkoxide mixture stoichiometrically. Unless stated otherwise, the reaction was allowed to proceed for about 1 h.

2. y ml of TEMS was added and the mixture was stirred for about 30 min.

3.   A z-gram amount of zirconium propoxide (containing 23–28% free alcohol, Fluka chemicals) was added while stirring strongly. Before the Zr(OPr)$_4$ was added it had to be dissolved for about ten times in its volume of dry CH$_2$Cl$_2$ or CH$_2$Cl-CH$_2$Cl in order to avoid local zirconium overconcentration, which could lead to an undesirable opalescence due to the quick formation and precipitation of oxopolymers. The most relevant parameter, B, is the Zr(OPr)$_4$ weight relative to the total initial Si alkoxide weight. So B = [z]/([x+y]/0.9, where 0.9 is the correction term accounting for the relative densities of the Si and Zr alkoxides. This value B is, however, close to the ratio of solution volumes, since the Zr(OPr)$_4$ solution is about 80% alkoxide and has a density of 1.05.

The sols thus obtained were processed into the composite preparation either immediately or after being stored in a freezer for more than 2 weeks.

2.2. Xerogels Preparation

Xerogels were prepared from the sols by the following method. Various amounts of cobalt octanoate (cobalt, 8% in mass) solution in toluene was mixed with the sol to prepare several kinds of composite films, differing by the amount of cobalt relative to the amount of silicon and zirconium. The mixture of the sols and the octanoate solutions yielded homogeneous solutions. Solutions with the following three concentrations, calculated on the basis of the final oxide content in the film, were made:

(I)   Co$_3$O$_4$/[SiO$_2$-ZrO$_2$ glass] =10 mass% in the final composite film after pyrolysis

(II)   Co$_3$O$_4$/[SiO$_2$-ZrO$_2$ glass] =30 mass% in the final composite film after pyrolysis

(III) Co$_3$O$_4$/[SiO$_2$-ZrO$_2$ glass] =40 mass% in the final composite film after pyrolysis

These solutions were spin-coated on a glass substrate (18x18 mm) at 2000 rpm for 100 sec. After drying for 2 hours at room temperature to give a xerogel, they were heated at 3°C/min to 380°C and then pyrolyzed at this temperature for 1 h, leaving a thin hybrid glass-nanoparticle composite film.

2.3. Glass Characterization

The composite films were characterized by the following measurements.

Absorption spectra: Shimadzu UV-3100PC double-beam spectrometer

X-ray diffraction patterns: Rigaku RINT2000 X-ray diffractometer

Refractive indices by ellipsometry: Mizojiri DHA-XA2 ellipsometer

Scanning Electron Microscopy (SEM) observation of the film surface (covered with DC-sputtered Au film 10 nm thick): Hitachi S-5000 scanning electron microscope (acceleration voltage = 20 kV)

Transmission Electron Microscopy (TEM) observation of microstructure of the film: Hitachi H-9000NA transmission electron microscope (operated at 300 kV (acceleration voltage))

3. RESULTS AND DISCUSSION

3.1. Sol Preparation

The preparation of two- or three-components DEDMS-TEMS-ZrOPr$_4$ basic sols has already been reported [13-17]. Although only a few of the possible procedures and compositions have been tried, the final glass composition seems to be influenced more by the amount of zirconium than by the DEDMS/TEMS proportion. To investigate the glass properties, we made a few test samples without adding Co octanoate.

We tried three zirconium proportions in the sols—B = 0.05, 0.1 and 0.2—and in all cases the film obtained after pyrolysis was a transparent and colourless glass. The glasses when B = 0.1 or 0.2 were very brittle, so in the rest of the work reported here we used B = 0.05 (which corresponds to about 5 % of ZrO$_2$ in the glass).

3.2. Hybrid Glasses

3.2.1. General Features and UV-Visible Spectroscopy

After pyrolysis, pale brown films were obtained. The films were uniform, hard and not brittle, which is quite surprising since without adding oxide the films were more brittle. The absorption spectra of the films (Fig. **1**) had a band below 400 nm with a shoulder band near either 600, 660, or 680 nm depending on the cobalt oxide content. Like most apparatus, our measurement system is limited at 380 nm, but despite that there is a band around 380 nm that can be discerned. These bands are characteristics of the spinel type Co$_3$O$_4$. The absorption bands were blue-shifted from those seen when a pure Co$_3$O$_4$ film was prepared by simple pyrolysis of Co octanoate, which had absorption bands near 410 nm and 720 nm [2] that could respectively be attributed to the Co^{3+} centre in the octahedral sublattice in the Co$_3$O$_4$ spinel and to the Co^{2+} centre in the tetrahedral sublattice in the Co$_3$O$_4$ spinel. The absorption bands were also blue-shifted from those of a pure Co$_3$O$_4$ film prepared by magnetron RF sputtering ($\approx$410 nm and $\approx$750 nm) [2]. This blue-shift suggests that the crystal (particle) size of Co$_3$O$_4$ in this composite film, whatever the oxide content, is smaller than those ($\approx$10 nm) in the pure Co$_3$O$_4$ films prepared by pyrolysis or by sputtering.

As shown in Fig. (**1**), the blue shift is related to the oxide content in the films and indicates that the smallest particles

are found in the most diluted sample and the largest are found in the most concentrated sample. This is what would be expected if the particles had grown by a diffusion-limited aggregation mechanism. Moreover, the fact that the particles in the composite films are smaller accounts for the slower diffusion in the hybrid glass than in the melted octanoate. This interesting feature suggests that the sizes of the particles in the xerogel films can be adjusted by changing the precursor concentration in the sol.

3.2.2. X-Ray Analysis and Ellipsometry

A composite film containing 40% Co_3O_4 displayed a weak and broad X-ray diffraction line at $2\theta = 37°$ (attributable to the (311) diffraction line of spinel-type Co_3O_4). It was difficult to obtain low noise X-ray diffraction patterns by our measuring system. The mean crystal size of Co_3O_4 particles embedded in the SiO_2-ZrO_2 glass film was estimated from the width of the diffraction line to be ≈5 nm. The composite films with lower Co_3O_4 contents (10% and 30%) of Co_3O_4 showed weaker X-ray diffraction lines at $2\theta = 37°$.
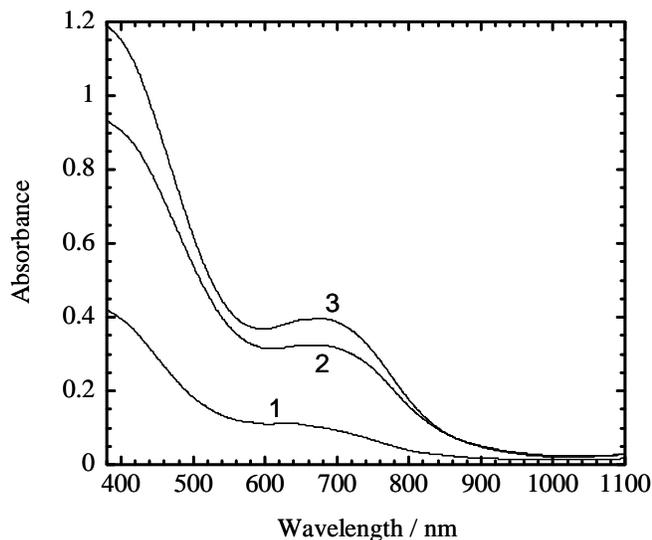

Fig. (1). UV-vis absorbance spectra of composite films containing (1) 10%, (2) 30%, and (3) and 40% cobalt oxide.

The ellipsometrically measured refractive indexes of the films were compared with values calculated assuming a linear ideal combination of the component indexes according to their relative proportions. For these calculations, the xerogels were assumed to be a blend of zirconia, silica, and the transition metal oxide and the participation of the remaining methyl groups was neglected. The refractive index of pure silica was assumed to be 1.457, that of pure zirconia was assumed to be 2.1 and that of pure cobalt oxide was assumed to be 1.71.

The measured and calculated refractive indexes of the three different xerogels, each made from the same basic sol but including various amount of cobalt oxide, are listed in Table **1**, where one sees that in each case the calculated index is very close to the measured one and that, as expected, the index of the film increases with the increasing cobalt content.
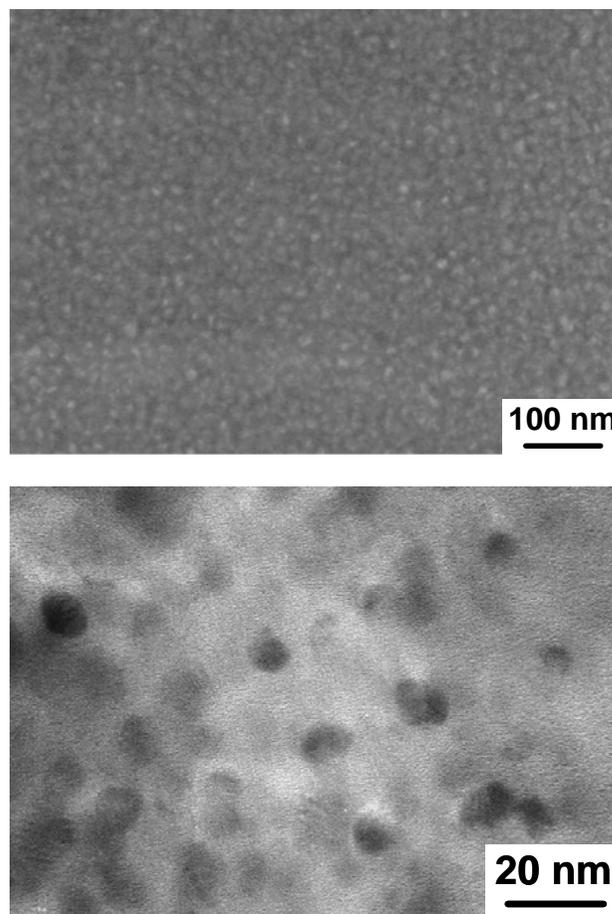

Fig. (2). SEM (top) and TEM (bottom) pictures of a composite film containing 10% cobalt oxide. The TEM picture shows the nanoparticles clearly.

3.2.3. Electron Microscopy

Figs. (**2-4**) show SEM and TEM pictures of the films. The surface of each film was smooth, uniform and almost free of cracks. In all cases the pictures show that the films contain particles with diameters ranging from <5 nm to ≈20 nm. The size of the particles seems to be correlated with the initial cobalt salt proportion, which seems to show that the growth of the oxide particles is a diffusion-limited process. It is likely that the white particles are ZrO_2 and the black ones are Co_3O_4, the contrast arising from the differences in the respective conductivities of the oxides. This brings further confirmation of the particle size in the films. Concerning the ZrO_2 particle size, results obtained in studies of closely related systems [16] show that in hybrid gels made from mixtures of silicon and zirconium alkoxide precursors, the final xerogels contain small zirconia particles with sizes ranging from 20 to 100 nm. In the case we are dealing with, the relatively small initial zirconium content would be responsible for the ZrO_2 particles being quite small. We did investigate the relation between the film composition and the size of the nanodomains in detail, but it is clear that the sizes of the particles we obtained are consistent with the smallest reported sizes [16].

The nanosize of all the particles, as well as the fact that the refraction indexes seem well correlated with the relative
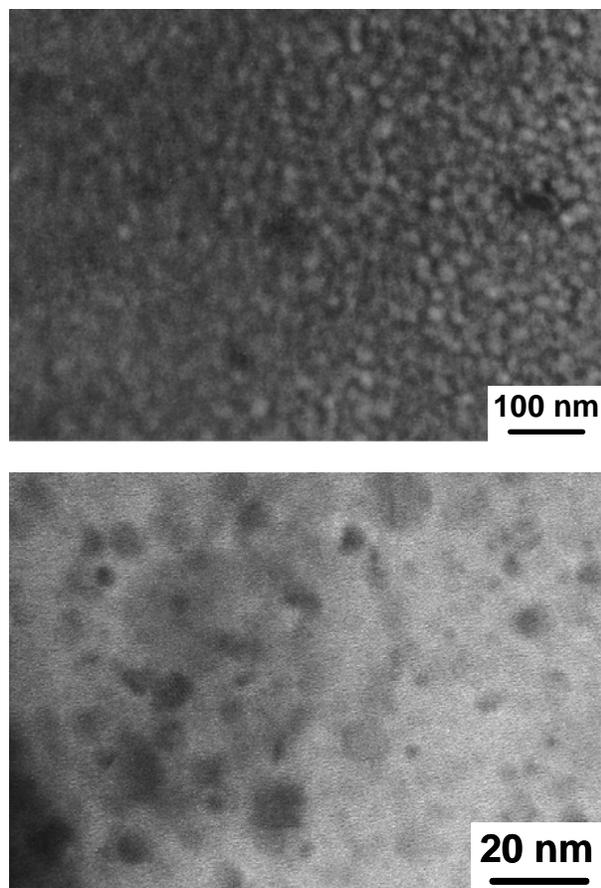
Fig. (3). SEM (top) and TEM (bottom) pictures of a composite film containing 30% cobalt oxide.

proportion of the oxides tend to show that there is little or no remaining carbon in the films. This is corroborated by the observation that in very similar gels methane evolution began at temperatures over 250°C [7] as well as by the fact that the DEDMS/TEMS ratio does not appear to influence the xerogel properties very much.

CONCLUSION

We have shown in preliminary experiments that combining the sol-gel method and metal salt pyrolysis method is an effective way to prepare uniform and optically high-quality composite films composed of size-regulated Co_3O_4 nanoparticles dispersed in organically modified silica glass. The cobalt-content-dependent blue-shift of the absorption band of the Co_3O_4 in the composite film and the good agreement between the observed and the expected refractive indexes suggest that the size of the Co_3O_4 nanoparticles in the composite film can be controlled precisely.
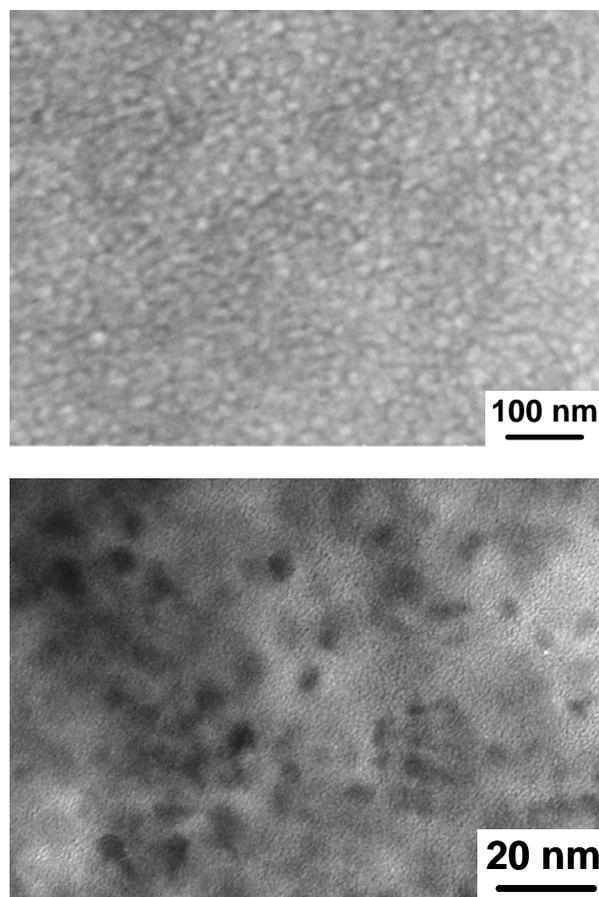
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Fig. (4). SEM (top) and TEM (bottom) pictures of a composite film containing 40% cobalt oxide.

Table 1.   Measured and Calculated Refractive Indexes of Co_3O_4–Glass Composite Films

Cobalt Oxide Content	10%	30%	40%
Measured n	1.516	1.565	1.575
Calculated n	1.514	1.552	1.575

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