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# Microstructure and optical absorption properties of Au-dispersed CoO thin films

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# 1. Introduction

Nano-composite films consisting of metal nanoparticles embedded in dielectric matrices have attracted great attention because of their enhanced nonlinear optical properties [1,2] and possible applications for all-optical switching devices [3,4]. In the past decades, the nonlinear optical properties of metal nanoparticles embedded in various dielectric matrices such as SiO<sub>2</sub> [5,6], Al<sub>2</sub>O<sub>3</sub> [7], TiO<sub>2</sub> [8], NiO [9] and ZnO [10] were much investigated which is due to a strong surface plasmon resonance (SPR) of metal nanoparticles in the visible range. The SPR frequency, a significant characteristic parameter of the nonlinear optical properties, depends on the content, size, and shape of the metal particles, as well as the dielectric properties of metal particles and the surrounding matrix material [11]. Cobalt monoxide (CoO) seems to be an attractive matrix material due to its relatively wide band gap (2.6 eV) [12] and high refractive indices (2.33) [13]. CoO and its compounds have been investigated in many areas because of their exceptionally physical and chemical properties. In the area of electric apparatus, Yu et al. [14] studied the capacitance capacity of CoO crystallites prepared by means of developing Co<sub>3</sub>O<sub>4</sub> nanoplatelets in the molten salt and Dhage et al. [15] discussed the influence of an alkali earth (Ba/Sr) element in small quantities on non-linear electrical properties of SnO2·CoO·Ta2O5 ceramic. In the application of heterogeneous catalysis, EI-Shobaky et al. [16] prepared CoO powders by the thermal decomposition of basic cobalt carbonate

# ABSTRACT

Au nanoparticles dispersed cobalt monoxide (CoO) composite films were fabricated via a chemical solution approach combined with a spin-coating processing. Au particles were spherical approximately and uniformly dispersed in the amorphous CoO matrix. The mean diameters of Au particles in the Au/CoO thin films with 40 mol% Au are about 30 nm. The optical absorption peaks due to the surface plasmon resonance (SPR) of Au particles were observed in the UV–vis absorption spectra in the wavelength range of 550–650 nm. The SPR peaks exhibit a red shift and intensify with increasing Au content from 10 to 40 mol%, but show a blue shift and weaken from 40 to 60 mol%. The band gap  $E_g$  decreases with increasing Au content.

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under a reduced pressure and found the catalytic activity of the CoO powders in the oxidation of CO. Okamoto et al. [17] investigated the effects of the starting cobalt salt on the cobalt-alumina interaction modes and cobalt dispersion in CoO/Al<sub>2</sub>O<sub>3</sub> catalysts. CoO and it-based materials were also studied in the field of magnetic materials [18,19]. However, to the best of our knowledge, CoO as the matrix of the composite nonlinear optical films has not been reported so far in the nonlinear optical area. In this study, Audispersed CoO composite thin films were successfully prepared by using a spin-coating method for the first time. The microstructure and the optical absorption properties of the thin films were investigated with a special emphasis on the influence of Au contents. An enhanced nonlinear optical absorption property was found in the Au-dispersed CoO composite films, whereby it is expected that the present Au/CoO composite films would have increased potential applications in the nonlinear optical field.

# 2. Experimental

Au/CoO composite films were prepared using a spin-coating technique with a chemical solution method. The precursor solution with a concentration of 0.2 mol/L was prepared by mixing raw materials with CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH (99.989%) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.0%) supplied by Beijing Beihua Fine Chemical Co., Ltd., China. The mixture was magnetically stirred for 5 h to obtain the homogeneous solution and then aged at room temperature for 8 h. HAuCl<sub>4</sub>·4H<sub>2</sub>O (99.99%, Beijing Beihua Fine Chemical Co., Ltd., China) was added into the precursor solution with ratios of Au/(Au + CoO) = 0, 10, 20, 30, 40, 50 and 60 mol% followed by stirring for 5 h and aging at room temperature for 8 h. The Au/CoO film was spin coated on a SiO<sub>2</sub> glass substrate with a dimension of 2 cm × 2 cm, which was ultrasonically cleaned in an acetone solution and dried in the oven in advance. The glass substrate was absorbed in a circular salver, and the aged Au/CoO Solution was dropped uniformly to the substrate. The substrate was rotated at a low rate of 200–300 rpm for 5 s, and then at a higher one of 2000–3000 rpm for 15 s. After one coating, the precursor film was first pyrolysed at 200°C for 30 s to remove the solvent and a small amount of

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Fig. 1. XRD patterns of Au/CoO thin films with different contents.

water. These sequences of coating and pyrolysis treatments were repeated 2 times for absorption measurement and 20 times for X-ray diffraction analysis. Then the pyrolysized sample was annealed at 600 °C for 30 min in pure nitrogen (99.995%) atmospheres.

The phase and crystal structure of all samples were investigated by X-ray diffraction (XRD: DMAX-RB, Rigaku Inc., Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) filtered through a Ni foil. The microstructure was observed by transmission electron microscopy (TEM: JEM-100CXII, JEOL, Japan). The surface chemical state of the prepared films was characterized by X-ray photoelectron spectroscopy (XPS: PHI-5300, PHI, USA) using Al K $\alpha$  radiation (hv = 1486.6 eV) as an X-ray source. The energies of all spectra were corrected by normalizing with respect to the C 1s peak at 285.0 eV. The Au 4f and Co 2p spectra were fitted by using the XPS data which were determined by deconvolution in the program of XPS Peak4.0. The absorption spectra were measured by UV-visible spectrophotometer (UV-2800, UNICO Instruments Co., Ltd., China).

# 3. Results and discussion

Fig. 1 shows the XRD patterns of Au/CoO thin films with 10, 30 and 50 mol% Au annealed at 600 °C for 30 min in N2. The result of the pure CoO film is also shown in Fig. 1 for comparison, which indicates the characteristic peaks of cubic crystalline CoO (PDF#43-1004) at 36.5°, 42.4° and 61.5° without other phase(s). Such diffraction peaks of the CoO phase disappear as Au was dispersed, while other three diffraction peaks at 38.2°, 44.4°, 64.6° appear, which correspond to (111), (200), (220) crystal planes of the cubic Au phase (PDF#04-0784). This result reveals that the CoO in the Au/CoO thin films may be amorphous which was restrained by dispersing Au. Okumu et al. [20] also reported that the fine dispersion of Ag in TiO<sub>2</sub> matrix delayed the crystallization of TiO<sub>2</sub>, which may be due to the fact that the presence of Ag atoms heightens the activation barrier for crystallization. The amorphous CoO in the Au/CoO thin films may be attributed to the similar behavior. The diffraction peaks of Au phase intensify with increasing Au content. The calculated Au particle sizes by the Scherrer's equation increase from 25 to 40 nm when the Au content increases from 10 to 50 mol%.

Fig. 2 shows the XPS survey spectrum of Au/CoO thin film with 40 mol% Au which was annealed at 600 °C. The Au 4f, Au 4d, Au 4p, Co 2p, Co 2s, Co LMM, Si 2p, Si 2s, O 1s and O KLL photoelectron peaks are observed besides Na KLL, Na 1s, C KVV and C 1s peaks. The appearance of Na peaks is due to the diffusion of Na atoms existed in the glass substrate into the surface after annealing. The silicon peak resulted from the SiO<sub>2</sub> substrate, and the carbon peak arose from an overlying contaminant hydrocarbon layer, which was unavoidable for the XPS analysis. The O peaks centered at binding energies of about 531 eV belong to the band of Si–O in SiO<sub>2</sub> and Co–O in CoO [21,22], which were hardly distinguishable. No other impurities are observed.



Fig. 2. XPS survey spectrum of Au/CoO thin film with 40 mol% Au annealed at 600 °C.

Fig. 3 shows the XPS spectra of Co 2p and Au 4f electrons of Au/CoO thin composite film with 40 mol% Au annealed at 600 °C. Fig. 3(a) shows two-pairs of peaks centered at the binding energies of about 780.2 and 796 eV as well as 785.7 and 802.3 eV based on the Gaussian fitting. As discussed in our previous research [23], the former pair of peaks is assigned to the  $Co^{2+} 2p_{3/2}$  and  $Co^{2+} 2p_{1/2}$  electrons and the later one is related to the satellites of the  $Co^{2+} 2p_{3/2}$  and  $Co^{2+} 2p_{1/2}$  electrons in the CoO bond [22,24]. The intense satellite peaks appear at about 5.5 and 6.3 eV beyond the  $Co^{2+} 2p_{3/2}$  and  $Co^{2+} 2p_{1/2}$  peaks. The relative integrated intensities of the satellite structure were about 40% and 84% of the main  $Co^{2+} 2p_{3/2}$  and  $Co^{2+} 2p_{1/2}$  peaks. However, the binding energies of  $Co^{2+} 2p_{3/2}$  and  $Co^{2+} 2p_{1/2}$  here are a little lower than those ( $Co^{2+} 2p_{3/2}$ , 780.5 eV;  $Co^{2+} 2p_{1/2}$ , 796.3 eV) in our previous results [23] for the pure CoO



Fig. 3. XPS spectra of Au/CoO film with 40 mol% Au annealed at 600  $^\circ C$ : (a) Co 2p, and (b) Au 4f.



Fig. 4. TEM micrograph (a) and SAED pattern (b) of Au/CoO thin film with 20 mol% Au annealed at 600 °C.

film. Fig. 3(b) manifests two peaks at 84.2 and 87.9 eV based on the Gaussian fitting which refer to Au<sup>0</sup> 4f<sub>7/2</sub> and Au<sup>0</sup> 4f<sub>5/2</sub> respectively. They are a little higher than those for metallic gold (Au<sup>0</sup> 4f<sub>7/2</sub>, 84 eV [21,25] and 83.73 eV [26]; Au<sup>0</sup> 4f<sub>5/2</sub>, 87.7 eV [21,25]), The slightly low binding energy of Co<sup>2+</sup> 2p<sub>3/2</sub> and Co<sup>2+</sup> 2p<sub>1/2</sub> and high binding energy of Au<sup>0</sup> 4f<sub>7/2</sub> and Au<sup>0</sup> 4f<sub>5/2</sub> in the Au/CoO composite film may be attributed to a charge transfer between Co<sup>2+</sup> and Au [27]. However, the Au still keeps in a metallic state and Co in a divalent state in the composite film, because of the absence of the peaks corresponding to the oxidized Au species (Au<sup>+</sup> 4f<sub>7/2</sub>, 84.7 eV [28] and 85.6 eV [29]; Au<sup>3+</sup> 4f<sub>7/2</sub>, 88.1 eV [25]) and to Co metal (Co<sup>0</sup> 2p<sub>3/2</sub>, 778.2 eV [21,24]).

Fig. 4 shows the bright-field TEM micrograph (a) and the corresponding selected area electron diffraction (SAED) pattern (b) for the Au/CoO thin film with 20 mol% Au annealed at 600 °C. As shown in Fig. 4(b), the diffraction rings from inner to outer correspond to Au crystal faces (111), (200), (220), (311) and (222), respectively. No diffraction spots for CoO crystallites are observed since Au crystallites restrain the crystallization of CoO in the Au/CoO composite film. The approximately spherical and dark black particles are considered to be Au particles and the gray matrix belongs to CoO in Fig. 4(a). The bright-field TEM micrograph and SAED pattern indicate that Au particles uniformly dispersed in the amorphous CoO matrix and the mean diameters of particles are about 30 nm, which are in well agreement with results analyzed in XRD pattern (Fig. 1).

Fig. 5(a) shows the optical absorption spectra of the Audispersed CoO thin films with different Au contents annealed at 600 °C. All samples exhibit an absorption peak in the wavelength region of 550-650 nm due to the SPR of Au nanoparticles. The SPR peaks manifest a red shift trend and intensify with increasing Au content from 10 to 40 mol%, while show a blue shift one and weaken from 40 to 60 mol%. It is well known that the position of the SPR peak for small free Au particles manifests blue shift with decreasing particle size (the quantum size effect), which can be explained by Mie and relevant Mie-like theories [30–32]. However, the blue shift is also related to another effect of a charge transfer between metal and oxide. The charge-transfer between metal and oxide in the sol-gel derived Au/Al<sub>2</sub>O<sub>3</sub> films [33] is corresponded to the blue shift of the absorption peaks as the Au particle size grew by raising annealing temperature from 300 to 800 °C. In the present study, the position of the SPR peak should be a result of the competition between the quantum size effect and the influence of the charge transfer. If the quantum size effect is stronger than that of the charge transfer between Au and Co<sup>2+</sup>, which may lead to a blue shift

of the SPR peak for the Au/CoO composite films with 40–10 mol% Au. If the effect of the charge transfer is stronger than that of the quantum size effect, which leads to the blue shift absorption band with increasing the particle size for the samples from 40 to 60 mol% Au. The dispersion threshold of the Au content is near 40 mol%. The intensity of the SPR peaks strengthen with increasing Au content from 10 to 40 mol% since more Au particles uniformly dispersed in the CoO matrix, while that weakening with more Au content may be due to the aggregation of nanoparticles and unhomogeneous distribution in the higher Au content.

Fig. 5(b) shows theoretical optical absorption spectra of Au/CoO thin films calculated by Mie theory [34]. The SPR absorption of Au



**Fig. 5.** Optical absorption spectra of Au/CoO thin films with different contents (a) and theoretical optical absorption spectra of Au/CoO thin films calculated by Mie theory (b).



Fig. 6. Relationship between  $(\alpha h \upsilon)^2$  and  $h \upsilon$  for Au/CoO thin films with different contents.

nanoclusters in the Au/CoO thin films can be predicted by the well-known Mie theory.

$$\alpha = \frac{18V_0\pi n_s^3}{\lambda} \frac{\varepsilon_{m2}}{\left[\varepsilon_{m1} + 2n_s^2\right]^2 + \varepsilon_{m2}^2},\tag{1}$$

where  $\alpha$ ,  $V_0$ ,  $n_s$ ,  $\lambda$ ,  $\varepsilon_{m1}$  and  $\varepsilon_{m2}$  are the optical absorption coefficient, the volume fraction of metal, the refraction rate of the surrounding dielectrics, the wavelength as well as the real part and imaginary part for the dielectric constant of metal, respectively. According to Mie theory, the SPR band depends on both metal species and composition of the surrounding dielectrics, i.e., the refractive indexes of the dielectric matrices as well as the volume fraction and dielectric constant of metal nanoparticles. In Fig. 5(b), the calculated SPR peaks for all samples are constantly located at 653 nm which are higher than the experimental ones. The bandwidth of the absorption peaks narrows with increasing Au content, which is much smaller than the experimental ones. Since Mie theory considers a case of perfect sphere metal particles and does not take into account the effects of the particle sizes, their distribution and the state of CoO.

To further understand the behavior of the optical absorption, the energy band gap ( $E_g$ ) was estimated by the equation [35]:

$$\alpha(\upsilon) = A \frac{(h\upsilon - E_g)^m}{h\upsilon},\tag{2}$$

where *m* is an index which determines the type of optical transition (*m*=2, 3, 1/2 and 1/3 corresponding to indirectly allowed, indirect forbidden, directly allowed and direct forbidden transitions, respectively), and *A*, *E*<sub>g</sub> and *h*v are a constant, the optical band gap energy and the incident photon energy, respectively. The dependence of  $(\alpha h v)^2$  in Fig. 6 as a function of photon energy *h*vindicates that all samples are the directly allowed nature of bandto-band transitions. The *E*<sub>g</sub> in the plot of  $(\alpha h v)^2$  and *h*v which are determined by extrapolating the linear region of the curve to the *h*v axis where  $(\alpha h v)^2 = 0$  is 1.73, 1.71, 1.64, 1.61 1.7 and 1.76 eV for the Au/CoO composite films with 10, 20, 30, 40, 50 and 60 mol% Au, respectively. The *E*<sub>g</sub> is gradually narrowed with increasing Au content up to 40 mol% causing the red shift of the SPR peaks, and then widened as the Au content is over 40 mol% as a result of blue shift, which is in well agreement with the optical absorption spectra.

### 4. Conclusions

Nanocomposite thin films Au/CoO with different Au contents were successfully prepared using the spin-coating method by the chemical solution method and annealed in a pure nitrogen (99.995%) atmosphere at 600 °C. The approximately spherical Au particles dispersed in the amorphous CoO matrix grew from 25 to 40 nm with increasing Au contents from 10 to 50 mol%. Au existed in the nature of single metal and CoO kept the oxide state in the Au/CoO thin composite film. An enhanced optical absorption peaks due to the surface plasmon resonance of Au particles achieved in the wavelength range of 550-650 nm. The peaks manifest a red shift and intensify with increasing Au content from 10 to 40 mol%, while exhibit the blue shift and weaken from 40 to 60 mol%, which are different from the theoretical ones of Au/CoO thin films calculated by Mie theory. The band gap  $E_g$  decreases with increasing Au content from 10 to 40 mol% but increases by further increasing Au content.

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