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Fabrication of chromium oxide nanoparticles by laser-induced deposition from solution

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Abstract: We have successfully deposited well-dispersed nanoscale chromium oxide particles by laser-induced solution deposition (LISD) from solution with CrCl_2 and organic solvents. The particles have narrow distributions about three sizes: 230, 350 and 400 nm and are uniform in composition and contain little contamination. We show that LISD is a new technique for producing nanoparticle chromium oxides with uniform composition, controllable size and high yield.

Author Keywords: Chromium oxide; LISD; Nanoparticles; CrCl_2

Metallic wires and dots can be obtained by reducing a metallic salt in the pores of a membrane. Electrodeposition processes in nanometer-sized pores of aluminum oxide membranes was reported more than 30 years ago [1]. Ultra-dense arrays (reaching 10^{11} cm^{-2}) of nanometer-size electrodeposited columns have been successfully produced on substrates made by electron lithography [2]. The use of plastic porous membranes has been extensively investigated and a variety of nano-materials have been successfully made by this method [3 and 4]. The reduction of metal ions in the membrane creates an assembly of wires, several micrometers in length, with a diameter chosen in the range 30 nm to a few micrometers [5, 6 and 7].

This is of great interest because magnetic systems of very small dimensions can reveal mesoscopic and quantum effects. Single electron blocking effects have

been evidenced in oxidized STM tips or substrates [8], and similar effects were reported in nanowires smaller than $0.01 \mu\text{m}^2$ [5]. Initial results on magnetoresistance measurements on nanometer diameter Ni/NiO/Co wires [6] provide evidence of an impurity in the tunnel barrier playing a role in Coulomb blockade [6 and 9], and indeed negative tunnel magnetoresistance might be observed when impurities are present in the barrier [6]. The extension of the Coulomb blockade effect to the ferromagnetic case is at its infancy, but initial measurements [10, 11 and 12] and theories [13 and 14] indicate that such systems can show enhanced magnetoresistive properties. An estimate for the spin-flip time τ_{SF} , deduced from diffusive transport bulk values is of the order of 10^{-12} s. A more relevant time scale for very small metallic particles can be found in the results of Ralph et al. [15 and 16] using the discrete electronic states of Al

nanoparticles. They gave an estimate of 10^{-8} – 10^{-9} s for the relaxation rate of excited states. Making nanoscale particle of ferromagnetic and antiferromagnetic particles is the key to future research in this area.

Chromium oxides have attracted much attention recently because of their importance both in science and technology. Band-structure calculations [17] predict that CrO_2 is a half-metallic ferromagnet — a system which is metallic for one spin direction and insulating for the opposite spin direction. This contention is supported by reflectivity measurements [18] and Andreev scattering [19 and 20]. Unfortunately, it is very difficult to fabricate CrO_2 nanoparticles by using conventional methods due to the high temperatures required and the metastability of CrO_2 phase, nor there has been much success with the fabrication of nanoparticles in the antiferromagnetic insulating Cr_2O_3 phase.

Laser-assisted deposition from solution is clearly compatible with electrochemical deposition. The laser-assisted deposition from solution (LISD) technique has been successfully used to deposit ReB_6 (Re=rareearthmetal) [21, 22, 23 and 24], copper [25 and 26], palladium [27 and 28] and more complex materials like LaNiO_3 [29]. Laser assisted deposition from a solution of silver nitrate was also used to deposit silver clusters [30]. In both the deposition of copper and palladium from solution, the metal source was a chloride [25, 26, 27 and 28], as the case in this work. We have applied this technique to fabricate nanoparticles of chromium oxide.

The deposition of chromium oxides by laser-induced solution deposition (LISD) was carried out with the laser operating in a CW mode, for which we employed an argon ion laser (the Coherent Innova 90 Series Ion Laser). CrCl_2 and $\text{Cr}(\text{CO})_6$ dissolved in solutions containing various mixtures of methanol, cyclohexane, tetrahydrofuran (THF), and diethylether. Mixtures of solvents were originally chosen on the basis of solvent pK_a , but minimization of solvent absorption of the light proved to be an important criteria. While the methanol or small amounts of “dissolved” water are believed to be a key source for oxygen in the deposition and formation processes for chromium oxides, without isotopic exchange experiments, proof is elusive. Without drying, THF contains dissolved 1–2% water. The deposition time in this experiment varies from 0.5 to 24 h and neither the samples nor the laser beam were translated during the experiment relative to one another. Both visi-

ble (laser power: 5–7 W and wavelength: 514 nm (457–528 nm)) and UV radiation (laser power: 10–100 mW and wavelength: 351 nm) were used in the experiment. The substrates for deposition were Si (1 1 1) wafers or soda-glass in all the experiments.

While the oxidation of $\text{Cr}(\text{CO})_6$ to CrO_2 and Cr_2O_3 has been successful in the gas phase [31 and 32], we did not find this source compound effective in solution deposition at room temperature. The chemical vapor deposition of Cr_2O_3 has also been successfully demonstrated using $\text{Cr}(\text{acac})_3$ [33] while deposition of highly spin-polarized CrO_2 has been successfully deposited by photolysis of chromyl chloride [34 and 35]. By trial and error, we found that chromium oxides could be deposited on Si (1 1 1) and soda-glass substrates from CrCl_2 (2.0 mg) dissolved in solvent mixtures of 1.5 ml THF and 1.5 ml cyclohexane with the laser tuned to the visible region with laser power at about 5 W and wavelength at 514 nm. Under conditions of low fluence, nanoparticles were formed (Fig. 1a) without chlorine contamination (Fig. 1c). At high fluence, deposition resulted in more uniform deposits (Fig. 1b) but include chlorine contamination and no chromium containing particles. Uniform particle sizes more readily form on silicon substrates.

As shown in Fig. 1a, with low laser fluence, the resulting deposited chromium oxide the nanoparticles are quite uniform in size and shape. After 12 h deposition, the particle sizes are narrowly distributed in sizes about 230, 350 and 400 nm or deposits that are near integer multiples of $4 \times 10^4 \text{ nm}^2$. This is shown in Fig. 1d, where plot the particle diameters, and it is clear that the diameters fall close to 230, $\sqrt{2}$ (or $\sim 1.4 \times$)230 and $\sqrt{3}$ (or $\sim 1.7 \times$)230 nm. We suggest these narrow, and widely spaced particle sizes are a result of one, two and three nucleation sites on the substrate surface: possibly catalytically active sites for the redox reaction of CrCl_2 in solution. This is one of the first examples of such uniform nanoscale CrO_x particles. The dominant role of defects in the island size distribution and island growth overlayers has been observed in other systems (Pd, for example) grown on other insulators (MgO) [36], and the particle distribution sizes do not cover the wide range observed with the formation of silver particles from laser-induced deposition from solution reported elsewhere [30]. The difficulty with the technique is that the CrO_x particles do not appear to be a necessarily single phase oxide.

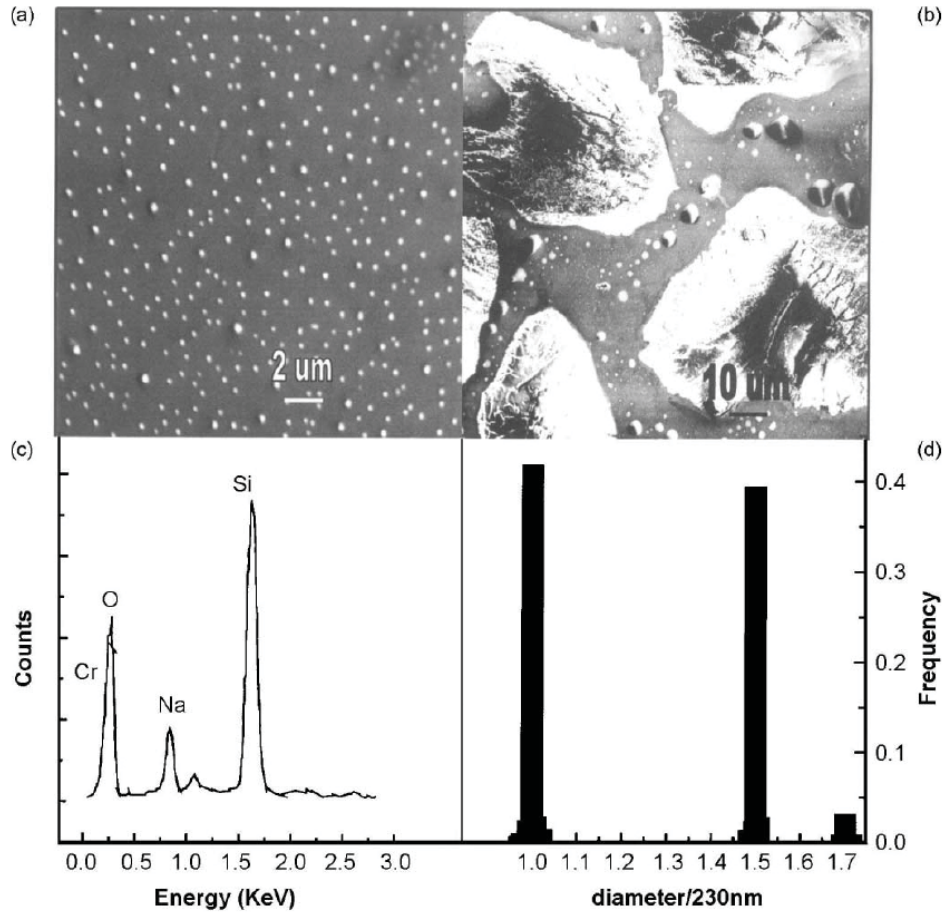


Fig. 1. (a) SEM image of CrO_x nanoparticles on soda-glass substrates obtained by LISD (wavelength at 514 nm; laser beam exposure area was about 10 mm; solute was CrCl_2 (2.0 mg) dissolved in solvents 1.5 ml THF and 1.5 ml cyclohexane) with a deposition time of 12 h. The common particle size (CrO_x) was about 230 nm diameter as well as those twice or three times in area. (b) SEM image of CrO_x films on soda-glass substrates obtained by LISD (wavelength at 514 nm; laser beam exposure area was about 10 mm; solute was CrCl_2 (2.0 mg) dissolved in solvents 1.5 ml THF and 1.5 ml cyclohexane) under conditions of high fluence. (c) Shows the EDAX spectra of the CrO_x nanoparticles as in (a). Chlorine contamination was absent and strong oxygen and chromium signals are present. (d) Shows the distribution of particle diameters relative to 230 nm.

As seen in Fig. 2, the X-ray diffraction of the nanoparticles deposited on silicon are dominated by two highly textured phases. The particles consist mostly of thermodynamic sink for chromium oxide, Cr_2O_3 , with strong (1 2 2) orientation (the diffraction line at 58.82). The lattice constant is slightly deformed, suggesting about 0.5% compressive strain. There is also a minority chromium oxide phase that could be Cr_3O_8 , Cr_2O_5 or Cr_8O_{21} with strong texture growth along the (0 1 1) direction in all cases. Given the small volume of the nanoparticles and similar chromium to oxygen ratio for

these chromium oxides, further measurements along the lines of micro-spot near edge X-ray adsorption spectroscopy are indicated.

In summary, we have successfully demonstrated that LISD is an efficacious fabrication method for producing nanoscale CrO_x particles. The advantages of the technique is the very low processing temperatures, and the compatibility with electrochemical deposition methods.

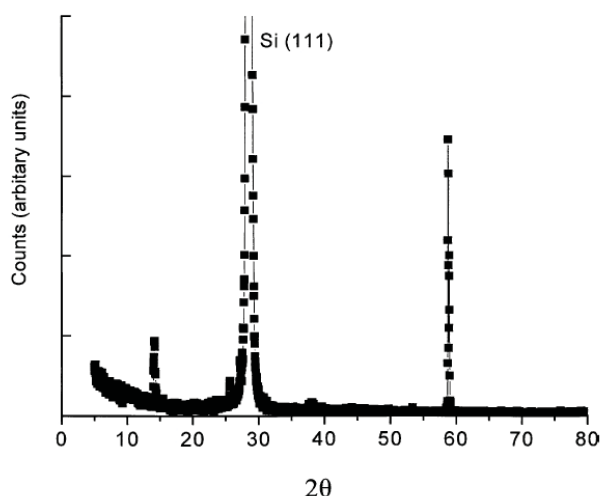


Fig. 2. The substrate silicon θ - 2θ line dominates the X-ray diffraction but Cr_2O_3 , with strong (1 2 2) orientation, is apparent in the diffraction line at 58.82° . There is also a minority chromium oxide phase that could be Cr_3O_8 , Cr_2O_5 or Cr_8O_{21} with strong texture growth along the (0 1 1) direction in all cases, with a diffraction line at about 14.15° .

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