

Small Copper Particles in a Cellulose Matrix

Emma FitzGerald, Kenneth F. Gadd,* Sally Mortimore, and William Murray

School of Science, Yeovil College (Goldcroft), Mudford Road, Yeovil, Somerset BA21 4AE, U.K.

Permeable cellulose films and filaments containing *ca.* 16% by weight metallic copper have been prepared; the particles are of colloidal dimensions (3 to 30 nm) but are far more densely packed than in conventional metal hydrosols.

The catalytic activity of metal sols is well known but their usefulness is often limited by their homogeneity with the reaction phase; it would be advantageous to support the colloidal particles on an inert material. Although the preparation of noble metal colloids is well documented, the literature on the non-noble metals is sparse. Copper sols have been characterised recently,¹ the copper particles being protected by organic polymers. We have made films and filaments which contain *ca.* 16% by weight metallic copper, of colloidal dimensions, dispersed in a cellulose matrix. This was achieved by modifying a procedure used for the regeneration of cellulose.^{2,3}

Filter paper and freshly precipitated copper(II) hydroxide were pulped with an appropriate amount of water; a deep blue, viscous solution was formed by the dropwise addition of 1,3-diaminopropane. The solution, containing *ca.* 4% and 1.6% by weight cellulose and copper respectively, was spread on a glass plate and immersed in 3 mol dm⁻³ sodium hydroxide solution (to prepare films) or exuded through a narrow glass tube into the alkali solution (to prepare filaments). Chemical analysis showed that the blue solid which formed contained copper(II) ions and doubly deprotonated glucose units (of the cellulose) in a 1:2 mole ratio. This supports the previously proposed polymeric structure in which copper(II) ions cross-link partially deprotonated cellulose molecules. The blue solid was reduced in an alkaline solution (1 mol dm⁻³ sodium hydroxide) of either sodium dithionite or hydrazine, both 0.5 mol dm⁻³, at 40–80°C. Use of sodium dithionite resulted in a brown product with a smooth surface, while reduction with hydrazine gave a blistered surface due to the evolution of nitrogen. Samples were dried *in vacuo* at 110°C after washing with water containing a little hydrazine to remove any dissolved oxygen. The product, copper(0)–cellulose, contained 16.2 ± 0.2% by weight copper, the remainder being fully protonated cellulose.

The reduction occurred *via* a yellow intermediate [containing copper(I)] which disproportionated in acid to give a brown solid containing copper(0) and fully protonated glucose units in a 1:4 mole ratio, the remaining copper going into solution as aquated copper(II) ions. Full details of the preparation, including characterisation of the blue and yellow intermediates, will be published elsewhere⁴ and will contain details of the preparation of a similar copper(0)–cellulose material using ammoniacal copper(II) hydroxide as the cellulose solvent.

The undried copper(0)–cellulose was very stable in deoxygenated water and a nitrogen atmosphere but oxidised rapidly in air (behaviour similar to that of a copper sol¹). The copper dissolved readily in dilute mineral acids in the presence of air and dissolved easily in dilute aqueous ammonia. The dried copper(0)–cellulose does not conduct electricity.

The copper(0)–cellulose films produced from a 0.5 mm thick spread cellulose solution were opaque. Samples were prepared for spectroscopic examination by squeezing an extremely thin layer of the cellulose solution in a piece of Visking tubing (cellulose). This was first placed in alkali and then alkaline sodium dithionite to yield a transparent cop-

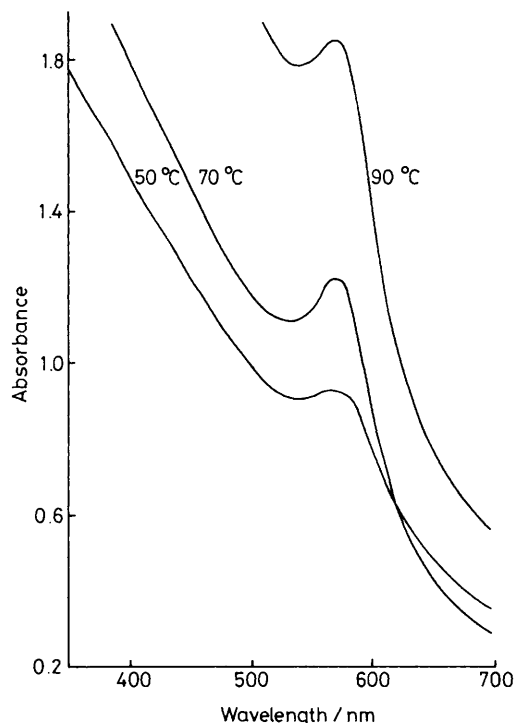


Figure 1. Absorption spectra of thin copper(0)–cellulose films sandwiched between cellulose sheets; samples were protected from the atmosphere by immersion in very dilute aqueous hydrazine, which was also used as the reference. The temperature shown is that of the sodium dithionite reduction. The thickness of samples could not be determined.

per(0)–cellulose film sandwiched between sheets of cellulose. Samples displayed subtle variations in colour, from ruby red to reddish-brown. Visible absorption spectra were recorded on a Pye Unicam SP8100 spectrophotometer. Typical spectra are shown in Figure 1; the general shape and the peak position were similar to those reported for copper sols (particle size 2–19 nm) prepared by sodium tetrahydroborate reduction.¹ Increasing absorbance with decreasing wavelength below 500 nm can be attributed to a contribution from small particle (less than 30 nm) scattering as predicted from the Mie theory.⁵ Larger particles (greater than 30 nm) are expected to exhibit an absorption maximum at rather higher wavelength, accompanied by decreasing absorbance below 500 nm, and this was observed for copper sols (particle size 20–160 nm) obtained by hydrazine reduction.¹ Caution must be exercised when comparing copper(0)–cellulose with copper sols and with predicted spectra since the copper particles are in close proximity to one another and the medium is swollen cellulose of high water content rather than water alone. However, the observed spectra do suggest copper particles of less than 30 nm in the copper(0)–cellulose samples. This is supported by electron microscopy.

Dried copper(0)-cellulose samples were finely ground and examined with a Philips 300 transmission electron microscope. Sodium dithionite reduction gave copper particles in the range 3–30 nm; the smaller sizes appeared to be discrete particles while the larger ones may be aggregates. Samples prepared by hydrazine reduction showed a similar size range but with the larger particles being more common. Examination was difficult because of the density of packing of the particles and the necessary isolation of a fragment thin enough to be transparent to the electrons. Electron diffraction patterns were consistent with the face-centred cubic structure associated with copper in the bulk metal.

The copper(0)-cellulose is being used in our laboratory as the precursor to a number of novel materials. Other metals, such as silver and platinum, have been introduced quantitatively by redox exchange reactions from aqueous solutions of suitable ions and the metal(0)-celluloses have been carbonised in a nitrogen atmosphere to yield metal-containing chars. Initial results show that the metal(0)-cellulose films are

permeable to aqueous solutes and are very effective catalysts for the decomposition of hydrogen peroxide. The chars obtained at 600 °C from copper(0)-cellulose and silver(0)-cellulose are effective dehydrogenation catalysts for primary and secondary alcohols.

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