Growth of copper oxide nanorods

Nanoforms of materials have drawn considerable interest in the recent years because of their wide range of applications in semiconductors for band tailoring, magnetic nanoparticles for giant magneto-resistance materials and CoO nanoparticles in Li batteries. In the nanoform, optical and electronic properties get modified compared to its bulk counterpart, because of large surface-to-volume ratio. The transition-metal oxides find applications in many fields like magnetic storage media, electronics, catalysis and solar-energy transformation. Amongst them, copper oxide (CuO) finds a place in several high-temperature superconductors and in photoconductive and photothermal applications. There are several routes

Figure 1. Formation of CuO nanorods at oxygen flow rate of (a) 35 ml/min, (b) 150 ml/min, (c) 300 ml/min, (d) 500 ml/min, (e) in air. f Selected area electron diffraction pattern of a single CuO nanorod.
through which CuO nanoparticles can be formed, like microwave irradiations\(^8\), alko-
thermal route\(^9\), sol-gel\(^9\) technique, one-
step solid-state reaction method at room
\(10\), electrochemical methods\(^1\),
etc. However, studies on the synthesis of
CuO nanorods are sparse. CuO nanofi-
bres have been fabricated by thermal
evaporation\(^1\), thermal decomposition of
precursor\(^1\) of Cu\(_2\)O\(_2\) or by combina-
tion of electro deposition and self-cata-
lytic mechanism.

Here we report a simple route for the
synthesis of CuO nanorods by annealing a
copper foil. This method of synthesis of
CuO nanorods was found to be con-
venient and fast. Annealing of copper
foil leads to the formation of CuO nan-
rods spread in a large area. In order to
study the effect of oxygen flow rate on the
growth of nanorods, we have carried out
the synthesis process in different oxygen
flow-rate conditions. Samples pre-
pared under similar conditions of growth
gave nanorods of similar diameter and
length, indicating that this method of
synthesis of nanorods is reproducible.

Synthesis of CuO nanorods was car-
ried out on a copper foil. The commer-
cial-grade copper foil (0.1 mm thickness) was
cleaned by dipping once in dilute
hydrochloric acid. Then the foil was
thoroughly washed in de-ionized water
and finally ultrasonically cleaned in
methanol for 15 min. The cleaned copper
foil was loaded in a silicon tube and the
tube was put in a resistive-heating hori-
zontal furnace at 500°C for 30 min. Dif-
ferent samples were prepared by annealing
at 500°C in 35, 150, 300 and 500 ml/min of
oxygen flow. Annealing of foil was also
carried out in air to know the effect of
a mixture of gases on the growth of
CuO nanorods. Samples were character-
ized in Philips XL30CP scanning electron
microscope (SEM), operated at 30 kV.
Transmission electron microscopy was
carried out on Philips CM200 microscope
operated at 200 kV. The microscope was
used both in imaging and diffraction
mode. Energy-dispersive X-ray analysis
was also carried out to confirm the ele-
mental composition of nanorods.

In order to study the influence of ox-
igen flow rate on the growth of CuO nano-
rods, different samples have been pre-
pared under oxygen flow of 35, 150, 300
and 500 ml/min and in air. Figure 1 a
shows the SEM image of the sample pre-
pared at a flow rate of 35 ml/min. The
image shows the growth of nanorods
perpendicular to the surface of the sub-
strate (copper foil). The length of the
nanorods is found to be in the range 5–
10 μm and the diameter, 100–150 mm.
The growth of these nanorods has been
seen through the pores formed on the oxide
film grown on the copper foil. Figure 1 b
shows the SEM image of the sample prepared at a flow rate of 150 ml/min. The
density of the nanorods has been found to be much more compared with the sample prepared at an oxygen flow
rate of 35 ml/min. The length of the nano-
rods in this sample ranges from 10 to
15 μm and the diameter ranges from 70
to 100 mm. The growth of nanorods in
this condition is found to be in the form
of bundles. These bundles originate from
defects in the copper foil. The porosity of the film has also in-
creased drastically. At this flow rate, hill-
and valley-type of structures have been
observed and the growth of nanorods pre-
ferentially occurs in the valley regions.

Further increasing the oxygen flow rate
to 300 ml/min reduces the density of
nanorods and the length of nanorods
reduces to < 3 μm (Figure 1 c). The diame-
ter of the nanorods remains more or less
same as in the previous case. Though the
hill- and valley-type structures have still
been observed, the porosity of the oxide
film reduces to a large extent. Oxygen
flow rate of 500 ml/min produces few
nanorods (Figure 1 d). This indicates that
flow rate of oxygen influences the growth
of CuO nanorods. In order to study the
effect of a mixture of gases on the forma-
tion of nanorods, we have annealed the
copper foil in air at 500°C for 30 min. Figure 1 e shows the SEM image of the
sample prepared at 500°C in air. As is
evident from Figure 1 e, nanorods have
been formed. The length of the nanorods
is found to be 5–10 μm and diameter,
100–125 nm. Air annealing also forms
porous oxide film on the substrate. In
order to confirm the phase of nanorods,
i.e. CuO or Cu\(_2\)O type, we have per-
formed electron-diffraction studies. Figure 1 f shows a representative electron dif-
fraction pattern taken from a single nano-
rod. The diffraction pattern was indexed with lattice parameters: \(a = 0.4684 \text{ nm}, \ b = 0.3425 \text{ nm}, \ c = 0.5129 \text{ nm} \) and \(\beta = 99.47^\circ\). The zone axis of the pattern has been found to be [\(-110\)]. In the diffraction pattern we have observed some superlattice spots along the \(110\) direction, with some streaks. This shows that some
disorder is present in the nanorods.

Further studies are underway and the re-
results will be forthcoming. Analysis of
diffraction patterns reveals that the nano-
rods are of CuO. Energy-dispersive ana-
lysis also shows the presence Cu and O,
which confirms that nanorods are of CuO
and not of Cu.

From the present study it can be con-
cluded that the proposed method for the
growth of nanorods is quite effective.
The growth of nanorods in all samples is
nearly perpendicular to the substrate.
Nanorods can also be formed by anneal-
ing the copper foil in air at 500°C for
30 min. The optimum rate of flow of
oxygen was found to be 150 ml/min. At
this flow rate, largest lengths of nanorods
have been observed.

1. Poizot, P., Lanelle, S., Grgleen, S., Dupont,
L., and Tarascon, J.-M., Nature, 2000,
407, 496–499.
409.
5. Atify, H. H., Demian, S. E., Helal, M. A.
and Mahmoud, F. A., Indian J. Pure
6. Ashida, M., Ogasawara, T., Uchida, S.,
Tokura, Y., Gonokai, M. K. and Mazum-
dav, S., Conference on laser and electro-
7. Wang, H., Xu, J. Z., Zhu, J. J. and Chen,
8. Hong, Z. S., Cao, Y. and Deng, J. F.,
10. Xu, J. F., Ji, W., Shen, Z. X., Tang,
S. H., Ye, X. R., Jia, D. Z. and Xin, X.
11. Yia, A. J., Li, J., Jian, W., Bennett, J.
1039.
12. Huang, L. S., Yang, S. G., Li, T., Gu, B.
X., Du, Y. W., Lu, Y. N. and Shi, S. Z.,
13. Xu, C. K., Liu, Y. K., Xu, G. D. and
2365.

Received 6 October 2003; revised accepted 8
December 2003

A. K. SRIVASTAVA*
PRAGYA TIWARI
ASHWANI KUMAR
R. V. NANDDEKAR

Synchrotron Utilization Division,
Centre for Advanced Technology,
Indore 452 013, India
*For correspondence
e-mail: surbindi@cat.ernet.in

CURRENT SCIENCE, VOL. 86, NO. 1, 10 JANUARY 2004 23