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Solution Based Rapid Synthesis of AgCuO$_2$ at Room Temperature

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We report a single step synthesis of AgCuO$_2$ within minutes resulting in a poly crystalline, single phasic product crystallizing in monoclinic system. Chemical composition analysis has confirmed the stoichiometry of the product with oxygen in slight excess (~ 0.1). Growth of this oxide, involved cuboidal nanoparticles in the initial stages and needle-like microstructures in the end, as shown by scanning electron microscopy. The novelty of the method lies in the stabilization of Cu in the 3+ state under ambient conditions in a rapid aqueous process.

1. Introduction

Oxide materials crystallizing in a variety of structures and exhibiting many useful physical and chemical properties have been investigated more intensively since the break-through discovery of high temperature superconductivity in perovskite related cuprates in 1986.$^{1,2}$ The salient structural features of these oxides are attributed to the abilities of the metal ions to exhibit different coordination numbers and the resultant polyhedral networks. Among the transition metal ions, copper exhibits 1+ and 2+ oxidation states, in general, and 3+ rarely, and can form square planar, square pyramidal and octahedral coordination polyhedra in cuprates.$^3$ Cu formally exists in 3+ state only in few compounds like ACuO$_2$ (A=Na, K) and LaCuO$_3$ and in superconducting cuprates, as mixed valent Cu$^{2+}$ /Cu$^{3+}$ or as [CuO$_2$]$^{4-}$. The highest T$_c$ of 164 K is held by Hg$_3$Cu oxides under high pressure.$^7$ Ag with its similarity to Hg in its chemistry and coordination can be a possible substitute for Hg in Hg cuprates. This led to the discovery of two ternary silver copper oxides, namely, Ag$_2$Cu$_2$O$_4$ with 3D structure having Ag and Cu in 1+ and 2+ oxidation states respectively and AgCuO$_2$ with layered 2D structure, notably, with Cu in 3+ state.$^8,9$ Among these, AgCuO$_2$ is an interesting layered oxide with silver in dumb-bell shaped linear (two) coordination and Cu in square planar (four) coordination. The excess charge on Ag (1+δ) and copper (2+δ) is delocalized and spread on to oxygen as well.$^{10,11}$ Due to mixed valency it is expected to exhibit semiconducting/metallic property and is therefore being explored for a variety of applications such as photovoltaics and batteries.$^{12,13}$ The synthetic procedures adopted for AgCuO$_2$ are i) wet chemical oxidation at 90 °C ii) electrochemical oxidation of Ag$_2$Cu$_2$O$_4$ with intercalation of oxygen iii) ozone oxidation of aqueous suspensions of Ag$_2$Cu$_2$O$_4$ for extended periods and iv) hydrothermal method using AgO as an oxidizing agent with CuSO$_4$ for 17h.$^{14-16}$ These methods involve either longer reaction time, elevated temperature or harsh conditions and it calls for an alternative soft chemical method, involving milder conditions as well as short reaction time. We considered it worthwhile to explore in this direction, particularly in respect of AgCuO$_2$ in which Cu formally exists in its highest oxidation state. The report by McMillan in 1962 that alkaline solution of Ag$_2$O$_2$ ions in the presence of persulfate yields the corresponding higher valent silver oxides prompted us to adopt a similar procedure under ambient conditions to prepare the ternary oxide, AgCuO$_2$ from the corresponding Ag and Cu solutions.$^{17}$ Indeed, we are successful in obtaining single phase and well-crystalline AgCuO$_2$, within 5 minutes in a single step one-pot synthesis at room temperature (RT). More importantly, AgCuO$_2$ obtained by this method is found to contain excess oxygen of 0.10 per formula unit, in which Cu is expected to be fully oxidized as Cu$^{3+}$ or as [Cu-O]$^+$. To the best of our knowledge, this is the first report on room temperature synthesis of a layered cuprate with Cu partly in 3+ state.

2. Experimental Section

2.1. Raw Materials.

Silver acetate (Aldrich) and copper acetate (Fluka), Potassium persulfate, and NaOH (Sd-Fine) were purchased and used as received with a purity of 99.9%. AgCuO$_2$ was harvested by dropping the suspension drawn from precursor solution at regular intervals of time, on glass slide followed by drying at room temperature.

2.2. Characterization.

Powder X-ray diffraction (XRD) was used to identify the phase, its purity and to determine the crystallite size. XRD was recorded using Bruker D8 –Advanced diffractometer with Cu Kα ($\lambda=1.5406$ Å) radiation.

The particle size and morphology were studied by Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscopy (TEM).The images were recorded with a FEI Nova Nano SEM 600 and low vacuum imaging was performed on the same instrument using helix detectors. Energy-dispersive spectroscopy (EDS) analysis was performed with an EDAX Genesis instrument (Mahwah, NJ) attached to the SEM.
3. Results and Discussion

The XRD patterns (Fig. 1b) reveal the formation of single phasic AgCuO$_2$. Interestingly, the sample extracted from the parent alkaline persulfate solution just after one minute of the reaction, already contained a significant amount of the product, AgCuO$_2$ with minor impurities. By the end of 5 minutes, the reaction was complete giving rise to a single phasic AgCuO$_2$. The intensities of the characteristic reflections (200), (002), (202) and (011) (Fig. 1b) of AgCuO$_2$ increased with reaction time indicating the growth of AgCuO$_2$ with increasing crystallinity. A typical XRD pattern of the product harvested from the fifth minute (Fig. 2) can be indexed to a monoclinic system with the refined lattice parameters of $a = 6.014$ (3) Å; $b = 2.818$ (5) Å; $c = 5.892$ (4) Å; $\beta = 107.98^\circ$. The JCPDS values are $a = 6.076$ Å; $b = 2.809$ Å; $c = 5.873$ Å; $\beta = 107.99^\circ$ corresponding to stoichiometric bulk AgCuO$_2$.

Fig. 1. (a) Schematic representation of RT synthesis of AgCuO$_2$. (b) XRD patterns of products formed at various time intervals. The single phasic AgCuO$_2$ formed after 5 minutes could be indexed with JCPDS 01-3070-3890. The product formed after one minute contained minor impurities, Ag$_3$O$_4$ (*) and Cu(OH)$_2$ (#). Clearly, we note a decrease in “a” parameter and an increase in “c” parameter in oxygen excess AgCuO$_2$ comparing with JCPDS data indicating oxidation of copper well over 2+ in the ab plane and intercalation of oxygen in between the layers increasing the “c” parameter. This is consistent with the observation in cuprates like La$_2$CuO$_4$.

It is indeed amazing that this simple precipitation method leads to unusual Cu 3+ along with the usual Cu 2+, which may be due to in-situ oxidation of the latter caused by the prevalent persulfate. The fact that it all completes within minutes at room temperature indicates that the reaction must be kinetically controlled. Our method therefore differs significantly from the earlier reports.

Fig. 2. Full range XRD pattern of AgCuO$_2$ harvested at fifth minute.
Fig. 3. (a) FESEM images of AgCuO$_2$ at (a) 5 min (b) 15 min (c) 30 min of synthesis showing progressive growth of cuboidal particles into needle-like structures. Inset in (a) shows the histogram of particle size distribution. (d) Scheme showing growth of cuboidal particles into needle-like structures. (e) EDS spectrum of AgCuO$_2$.

FESEM images (Fig. 3) reveal the growth of AgCuO$_2$ particles with reaction incubation. The product obtained at fifth minute mainly consisted of cuboidal nanoparticles (mean size ~ 30 nm, See Fig. 3a) and after 15 minutes, anisotropic particles - truncated larger plates, rods, and polyhedral plates, were obtained (Fig. 3b). In Fig. 3c, nanorods with larger aspect ratios, an edge length of 200–350 nm and a diameter of 20–40 nm, can be observed from the 30 min product. Fig. 3d depicts a scheme of the growth of nanoparticles into needle-like morphology characteristic of monoclinic system.

Further characterization was carried out on the fifth minute product. The large area EDS spectrum of AgCuO$_2$ (Fig. 3e) confirmed the ratio of Ag to Cu as 1:1. The oxygen content estimated by iodometric titration was found to be 2.15±0.05 per formula unit.

Fig. 4. FESEM images of AgCuO$_2$ (a-e) harvested from mother liquor from 1$^{st}$ -5$^{th}$ min. (f-j). 11$^{th}$ -15$^{th}$ min. (k-n) 30$^{th}$ min - 16h.

FESEM images (Fig. 4) revealed the growth of the product up to 16 h differing in their particle morphology. While products harvested at 1$^{st}$ - 5$^{th}$ minute consisted mostly of spherical nanoparticles (mean size of 30 nm) (Fig. 4a - e), larger particles of 100 – 250 nm (Fig. 4f-j) are observed between 11$^{th}$ – 15$^{th}$ minute. During 30$^{th}$min – 16 h (Fig. 4 k-n) anisotropic particles (truncated larger plates, rods, and polyhedral plates) were identified. In Fig. 4k, rod-shaped nanoparticles with larger aspect ratios, with an approximate mean edge length of 200–350 nm and a mean diameter of 20-50 nm, can be seen.

The growth of different morphological structures of AgCuO$_2$ could depend on the reactant to oxidant ratio, reaction time, and temperature. In the present work, with the ratio of silver to copper acetates equal to 1:1 with 1.3 g of persulfate, the growth of our AgCuO$_2$ product with time is controlled by the dehydration of the possible hydroxide precursor AgCu(OH)$_4$ at room temperature through the different crystallographic facets resulting in different nanostructures. Attempts are being made to isolate the hydroxide precursor. More importantly, cuboidal structures of AgCuO$_2$ (Fig. 4a-e) are obtained without the use of the templates. It is to be noted that a variety of nano and microstructures of Cu$_2$O and Ag$_2$O have been synthesized by wet chemical methods.

Fig. 5. (a) TEM image of AgCuO$_2$ nanoparticles. (b) Indexed SAED pattern of AgCuO$_2$ reveals polycrystalline nature of the sample. (c) and (d) HRTEM images of the different planes of AgCuO$_2$.

Fig. 5a and 5b show representative TEM micrograph of the AgCuO$_2$ nanoparticles and the corresponding Selected Area Electron Diffraction (SAED) pattern, respectively. Among the particles examined (Fig. 5a), more than 70% belonged to the size range of 30 - 40 nm. SAED pattern. (Fig. 5b) of these particles contains diffusive rings, which may be attributed to small polycrystalline grains of the product.
The diffraction features are consistent with the crystalline structure of bulk AgCuO$_2$, corresponding to the diffraction planes of (200) and (110). High-resolution TEM images (Fig. 5c and d) show lattice planes corresponding to AgCuO$_2$.

Fig. 6. Thermogram of AgCuO$_2$ under N$_2$ atmosphere.

Thermogravimetric data shown in Fig. 6, exhibits three distinct weight losses up to 350°C, the final products being Ag and CuO (confirmed by XRD, see supporting information Fig. S1). The observed total binding energies (up to stable final product formation) of 8.5%, is close to the theoretical weight loss of 8.58%, indicating that the starting composition to be AgCuO$_{2.10±0.02}$ in agreement with chemical titration (2.10±0.05).

Our soft chemical synthetic method under ambient conditions has resulted in an oxygen excess of 0.10 per formula unit $(\text{AgCuO}_{2.10})$ which gets intercalated in between the layers of AgCuO$_2$, whereas in other cuprates such as La$_2$CuO$_4$ and Sr$_2$CuO$_3$, oxygen intercalation takes place only under high pressure or in electrochemical conditions.

The least square fit (Gaussian) for the O1s peak of AgCuO$_{2.10}$ results in an oxygen excess of 0.10 per formula unit $(\text{AgCuO}_{2.10})$ which gets intercalated in between the layers of AgCuO$_2$, whereas in other cuprates such as La$_2$CuO$_4$ and Sr$_2$CuO$_3$, oxygen intercalation takes place only under high pressure or in electrochemical conditions.

The X-ray Photoelectron Spectra (XPS) of AgCuO$_{2.10}$ were recorded to obtain the binding energies of Ag, Cu and oxygen. The survey spectrum is shown Fig. 7a. Fig. 7b shows the Ag 3d core level spectrum exhibiting the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ peaks at the binding energies of 367.1 eV and 373.3 eV respectively. It may be noted that the binding energies of 3d$_{3/2}$ lies between 367.5 – 367.7 eV in the reference compound of Ag$_2$O (Ag in 1+) and around 367.1 – 367.4 eV with a satellite at 366.2 eV in the reference compound AgO corresponding to Ag in 1+ and 3+ states respectively.

Fig. 7b indicates that Ag in AgCuO$_{2.10}$ is oxidized more than 1+, possibly with a delocalization of the excess charge. The width (FWHM) of Ag 3d$_{3/2}$ in AgCuO$_{2.10}$ is found to be 1.09 eV, less than that found in Ag(I) oxide (FWHM 1.2 eV)$^{23}$ indicating that Ag in AgCuO$_{2.10}$ is oxidized more than 1+. Cu 2p 3/2 spectrum (Fig. 7c) shows a peak around 934.7 eV and a shoulder at 933.8 eV indicating the presence of Cu $^{2+}$ and $^{3+}$ respectively. These values correspond closely to Cu 2p 3/2 binding energies in CuO$^{25}$ and NaCuO$_2$.\(^{26}\)

The least square fit (Gaussian) for the O1s peak of AgCuO$_2$ (Fig. 7d) gives three components with binding energies of 528.6, 530.6 and 532.8 eV.

These values are in close agreement with earlier report$^{10}$. It is to be noted, the binding energies of O$^{2-}$, O$_2^-$ and O$_2^-$ species in oxides occur at 530.5, 532.5 – 533.5 and 534.5 – 535.5 eV respectively$^{27}$. It indicates that in our AgCuO$_{2.10}$ the excess charge on Cu (more than 2+) and Ag (more than 1+) is delocalized onto oxygen also as we observed a peak at 532.8 eV corresponding to peroxide species.

Assuming a formula of AgCuO$_2$ one would expect Ag to be in $1+\delta$ and Cu to be in $2+\delta$ ($\delta$ varying between 0 to 1). The excess charge could be delocalized on to oxygen also; however, in our AgCuO$_{2.10}$ the excess oxygen could oxidize Ag or Cu more than that found in bulk AgCuO$_2$. Since we find the evidence for the presence of peroxide, the formula along with the charges could be represented as $(\text{Ag}^{1+}\text{Cu}^{2+}\{\text{O}^{2-},\text{O}_2^-,\text{O}^-$\}$)_{(4.2+2\delta)}$.$^{27}$

Optical band gap estimated from optical absorption of AgCuO$_2$ (Fig. S2) using Tauc’s relation from the plot of $(\alpha h\nu)$ vs photon energy $(h\nu)$ was found to be 1.84 eV. Our AgCuO$_{2.10}$ product shows a conductivity value of 100 - 500 mhos. cm$^{-2}$ at room temperature consistent with an earlier report$^{28}$. However, this value of conductivity is lower than that of high temperature superconducting cuprates. Due to poor grain connectivity, the resistivity is higher than expected from complete delocalization. We are looking into the correlation of the electronic structure of AgCuO$_{2.10}$ to its properties.

4. Conclusions

Our synthetic approach based on aqueous persulfate oxidation at room temperature has successfully resulted in pure, stable, nanocrystalline AgCuO$_2$ in a few minutes. In the initial stages, the nanoparticles are found to be cuboidal in shape which grow into needle-like crystals of few µm size. The present study has significance as AgCuO$_2$ is an interesting material with low band gap and more importantly, with Cu in the unusual 3+ state. This method has also resulted in soft intercalation of oxygen (up to 0.10 per formula unit) into AgCuO$_2$ under ambient conditions, which otherwise may require high pressure. The method also results in different morphological structures of AgCuO$_2$. The present method also opens up possibilities for rapid, soft-

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chemical synthesis of many other multinary oxides.

Notes and references

Supporting Information

Optical band gap determination of AgCuO$_2$ and XRD of intermediate and final products of thermal analysis of the title oxide are given.

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