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Preparation CuO and $CuCO_3Cu(OH)_2$ Crystal Nano Particles by Using Microemulsion Method

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ABSTRACT

A microemulsion method for preparing colloidal copper nanoparticles in microemulsion is reported. The obtained copper carbonate $CuCO_3 \cdot Cu(OH)_2$ nanoparticle and copper oxide CuO nanoparticle were characterized by powder X-ray diffraction (XRD), atomic force microscopy(AFM),transmission electron microscopy (TEM) and X-ray fluorescent(XRF) analysis, the purity of material and average particle size about 10 nanometer.. A microemulsion is thermodynamically stable ,optically isotropic derision of two immiscible liquids consisting of nano-size ($CuSO_4.5H_2O$) domains of one or both liquids in the other (white oil),stabilized by an interfacial film of the surface-active molecules. The materials mixed to have new immiscible solution , add chemical materials to reduce surface tension and to reduced interfacial atomic bonds to very low level , the very fine dispersed spherical micelles in microemulsion are thermodynamically stable due to a combination of very low interfacial tension very small nanoparticles diameter of (2-5) nm. Addition another of chemical material as react agent or reduced agent and precipitate agent to product final material $CuCO_3 \cdot Cu(OH)_2$.Synthesis of monodispersed $CuCO_3 \cdot Cu(OH)_2$ nanoparticles with refractive index similar to glass plates by using ultrasonic spray pyrolysis technique by method .Yielding homogeneous ,low defect thin films of high transparency ,that can be used as color filters for liquid crystal displays .

Keywords: Microemulsion; Ultrasonic spray pyrolysis ; CuO nanoparticle ; $CuCO_3 \cdot Cu(OH)_2$ nanoparticle; Solvents; Chemical synthesis.

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تحضير اوكسيد النحاس و كربونات النحاس البلورية النانومترية باستخدام طريقة المستحلبات المايكروية

الخلاصة

استخدام طريقة المستحلبات المايكروية لتحضير جسيمات نانومترية غروية للنحاس في المستحلبات في هذا التقرير. تم تشخيص المواد المحضرة باستخدام جهاز XRD و AFM و TEM و XRF حيث أظهرت هذه الفحوصات مدى نقاوة المادة المحضرة وحجمها الحبيبي الذي كان بمعدل 10 نانومتر. المستحلبات المايكروية هي محاليل ذات وسط شفاف ومتجانس ومستقر من الناحية الثرموديناميكية. يتضمن عملها انتشار سائلين غير قابلين للامتزاج معا. احدهما يحتوي على مادة صلبة نانومترية (كبريتات النحاس المائية) وأخرى تمثل السائل الأخر(النفط الابيض) . تخلط المواد لتكوين محلول جديد غير قابل للامتزاج , حيث تضاف له مواد كيمياوية مناسبة تعمل على تقليل الشد السطحي (مثل الصابون) وأخرى لتقليل الترابط البيني مابين الذرات إلى اقل حد ممكن (كحول) ليتكون مستحلب مايكروي microemulsion يحتوي على كرات دقيقة جدا منتشرة في الوسط ومستقرة من الناحية الثرموديناميكية وذات شد بيني قليل جدا يصل قطرها من (2-5) نانومتر. و تضاف مواد كيمياوية أخرى كعوامل تفاعل او كعوامل اختزال(الهدرازين) ,لتعمل كعوامل مرسبة لتحضير المادة النهائية. تم الحصول على طبقة أحادية الانتشار من مركب $CuCO_3$ ذات الحجم النانومتري الذي انكساره للضوء مشابه لانكسار الزجاج باستخدام تقنية التبخير بالموجات فوق الصوتية على شريحة زجاجي منظفة بدقة عالية ليعطي طبقة متجانسة ذات شفافية عالية ويمكن استخدام المادة في الفلاتر اللونية في صناعة شاشات العرض البلورية السائلة.

الكلمات المرشدة: مستحلبات , رش بالموجات فوق الصوتية , اوكسيد النحاس نانومتري , كاربونات النحاس النانومترية , مذيبات , تصنيع كيمياوي .

INTRODUCTION

Microemulsions are colloidal ‘nano-dispersions’ of water in oil (or oil in water) stabilized by a surfactant film. These thermodynamically stable dispersions can be considered as truly nanoreactors which can be used to carry out chemical reactions and, in particular,to synthesize nanomaterials. The main idea behind this technique is that by appropriate control of the synthesis parameters one can use these nanoreactors to produce tailor-made products down to a nanoscale level with new and special properties. This is a very expanding area and we will describe here our particular opinion about the most important tendencies which are now growing in this field [1]. Copper carbonate , $CuCO_3 \cdot Cu(OH)_2$, as a basic salt , is used in pyrotechnics, deflagration catalyst in gas – generators , flare composition ,desulfurizer of raw oil ,wood preservative, a antidote for phosphorous toxin, insecticides, pigment (and it is still in use for artist’s colors),Fungicide for seed treatment, coloring brass black, astringent in pomade preparation, inorganic industry ,organic synthesis catalyst in organic industry, feed additive (in small amounts),Antidote for phosphorus poisoning. since the first use of microemulsion techniques for ultra-fine catalyst production in 1982 [2] , an appreciable amount of research has been performed on specific microemulsion synthesis techniques to obtain a large number of chemical compounds in nanoparticulate form much of this work has been performed by V. Pillai et. al., who have very recently reviewed the current state of the art in is area [3] . Compounds that have been produced successfully with these techniques include rare metal catalysts(Pt….) , semiconductors (CdS , ITO,….) ,carbonates (Cu , Zn ,…) , chlorides (Ag ,….) , nitrates (In,….) magnetic oxides (Fe_3O_4) , oxides(Cu , Zn , Au ,…),the produce particles of this syntheses have been incorporated in devices having improved or novel properties as a result of the nanostructure of their components. nanoparticles which are defined as particles with diameters of about (10-100 nm) or less , are technologically significant , since they are utilized to fabricate structures , coating , and devices that have novel and useful properties due to very small dimensions of their particulates of wide variety of inorganic composition is so-called (microemulsion - mediated) synthesis. A microemulsion is defined as a thermodynamically stable , optically isotropic dispersion of a two immiscible liquids consisting of nano-size domains of one or both liquids in the other , stabilized by the interfacial film of the surface–active molecules. Microemulsion usually are classified as either water-in oil (w /o) or oil-in water (o/w) depending on which is the dispersed phase. More generally microemulsions of two non-aqueous liquids of differing polarity with negligible mutual solubility can also be prepared [4]. The nature of the surface-active film is the key to microemulsion formation, by the selection of appropriate surfactant chemistry and use of relatively large amounts of surfactant microemulsion are produced spontaneously (i.e. without need for significant mechanical agitation). The very fine dispersed spherical micelles in microemulsion are thermodynamically stable due to a combination of very low interfacial tension , and a significant entropy of mixing from the very large numbers of particles produced [5].

EXPERIMENTAL

Two method for preparation colloidal copper oxide nanoparticles:

First method:

Preparation of copper carbonate nanoparticle:

Two microemulsions of equal volume:

microemulsion (1):

White Oil (kerosene)	60 wt%
Shampoo (texapon)	15.9 wt %
Ethanol	14.1 wt %
Water	10 wt %

Add to it (0.15 M) copper (II) sulfate pentahydrate salt ($CuSO_4 \cdot 5H_2O$) was 98.0% pure (Merck) .

microemulsion (2):

White Oil (kerosene)	60 wt%
Shampoo (texapon)	15.9 wt %
Ethanol	14.1 wt %
Water	10 wt %

Add to it (0.15 M) sodium carbonate (Na_2CO_3) was 99.0% pure (Merck).

The two microemulsions contained (0.15 M) dissolved reactants in the aqueous phase: microemulsion (1) contained ($CuSO_4 \cdot 5H_2O$) ,while microemulsion (2) contained (Na_2CO_3). After equilibrating , the microemulsions contained the aqueous phase as discrete monodisperse spherical micelles of about (8 nm) diameter [4]. The two microemulsions (1) and (2) were mixed, leading to exchange to the solutes within the aqueous micelles [3] . Within minutes after mixing , equilibration of solute in micelles caused the following precipitation reaction to take place:

$$CuSO_4 + Na_2CO3 \leftrightarrow CuCO_3(ppt) + Na_2SO_4$$

Due primarily to the specific microemulsion chemistry employed , nucleation of nanoparticles was slow compared to intr–molecuar exchanged processes, Thereby causing nanoparticles to nucleated and grow in very small fraction of the aqueous micelles of the new microemulsion. The microemulsion containing precipitate $CuCO_3$(ppt) nanoparticaled was passed through filter (0.2) µm to collected and washed with small volumes of organic solvents to remove adsorbed surfactant ,then was annealing . The powder copper carbonate $CuCO_3$ nanoparticles batches were examined via transmission electron microscopy (TEM) the average particle size about (10 – 50) nm.

Second method

The other methods for nanoparticle synthesis via microemulsions are modification to the first method and utilize only a single microemulsion containing a dissolved reaction. Preparation of copper oxide nanoparticle:

Copper oxide CuO colloid was prepared by reduction of aqueous (0.055M) $CuCO_3 \cdot Cu(OH)_2$ solution by using Hydrazine solution (0.15M) according to the reaction[2]:

$$N_2H_4 + Cu^{+2} + OH^{+} \leftrightarrow Cu^{o}\,(ppt) + H_2O + N_2$$

First ethylene oxide surfactant aqueous solution were add into glass vial ,then hydrazine solution was added and mixed homogeneously using magnetic stirrer for 90 min. Finally $CuCO_3 \cdot Cu(OH)_2$ was added and reaction was allowed to proceed no stirring is necessary after an initials 10 minutes stirring for homogenizing the solution . The black copper CuO were preformed at thermostatic water bath maintained at (28˚C) . It should be understand that the present invention can be carried out at any temperature in addition to the (28˚C) . Exemplified the prepared copper colloid was also kept under the same condition. The formation of copper particles involve three distinct stages:

1. Reduction of positive copper ions into copper atoms.
2. Nucleation.
3. Crystal growth by coalescence nuclei.

Since surfactant molecules are present in the solution, surfactant molecules would be adsorbed on to the surface of nuclei as soon as formed. This surfactant film will hinder the coalescence of nuclei and block the diffusion copper atom into the surface of nuclei. The powder copper oxide CuO nanoparticles batches were examined via transmission electron microscopy (TEM) and X- ray automated powder diffractometer (XRD-Shimadzu - 6000) the average particle size about (10 – 50) nm.

CHARACTERIZATION

Synthesized samples were studied by the atomic force microscopy (AFM - AA 3000 Scanning Probe Microscope, Angstron Advanced Inc.) and transmission electron microscopy (TEM -phillips model 10) to determined particle size and surface morphology of $CuCO_3 \cdot Cu(OH)_2$ and CuO powders ; X- ray automated powder diffractometer (XRD - Shimadzu - 6000) was used with Cu -Kα radiation and a pure silicon powder as a standard for studying the composition and diffraction pattern of $CuCO_3 \cdot Cu(OH)_2$ sample ; X-ray fluorescent (XRF - Oxford Instrument -2000) was used for concentration analysis of prepared $CuCO_3 \cdot Cu(OH)_2$ sample.

RESULTS AND DISCUSSION

Figure 1 (a , b) shows the (TEM) images for $CuCO_3 \cdot Cu(OH)_2$ nanoparticle and CuO nanoparticle synthesized in microemulsion process of particle size distribution and the statement of crystalline for $CuCO_3.Cu(OH)_2$. It is observed that the particles are nanosized and approximately spherical in solvent, the mean diameter of the CuO nanoparticles with microemulsion as the reaction solvent is (10 -50) nm. Figure 2 show the (AFM) high magnification micrograph, super transparent , CuO thin-film coated deposited on glass substrate, prepared by using of ultrasonic spray pyrolysis techniquethe . The thickness of thin film is about (6.68) nanometer and the Root mean square(0.228 nm) . Figure 3 shows (XRD) patterns of copper carbonate $CuCO_3 \cdot Cu(OH)_2$ powder prepared by method of microemulsion process , 2Θ(29) [6] , to calculated the particle size of powder by use (Debye-Scherr's) equation [7] that the particle size of powder a range about (30-40) nanometer. Figure 4 shows the (XRF) powder copper carbonate prepared by method of microemulsion process , represent the high purity concentration of the copper while other peaks of material could be neglected for their count rates .

CONCLUSIONS

The microemulsion method is a very versatile technique which allows the preparation of a great variety of nanomaterials just alone or in combination with other techniques. The precise control of all the parameters which can be varied affecting the final particle sizes and shapes is still a challenge, but the richness of the possibilities which can be achieved from nano- to macro- scales is a big spur to work with these tiny dispersed droplets, where the only limitation will be our imagination. System for the production of inorganic nanoparticles which system comprise a source of inorganic nanoparticles within a non-continuous micellar phase in a microemulsion containing a non-continuous micellar phase and a continuous phase . precipitating means to add a precipitating agent to the said source to precipitate the nanoparticles from the microemulsion. Ultrafiltration semipermeable membrane mean to concentrate the precipitate nanoparticles by retention and to permeate the microemulsion continuous phase not containing the precipitated nanoparticles as a permeate stream , and means to recover the precipitated nanoparticles . All the measurements of results appearance the preparation materials in scale about (10-50) nanometer.

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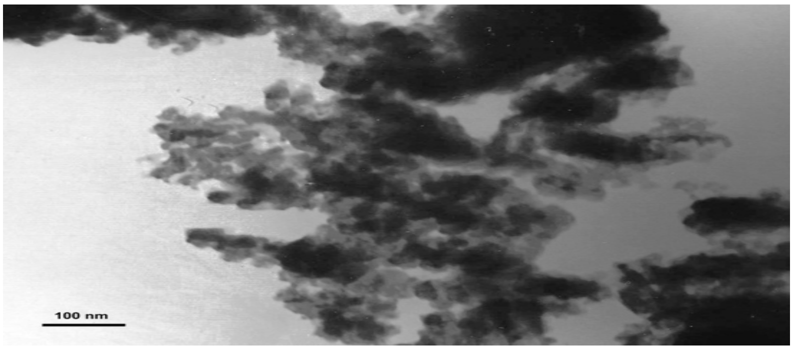
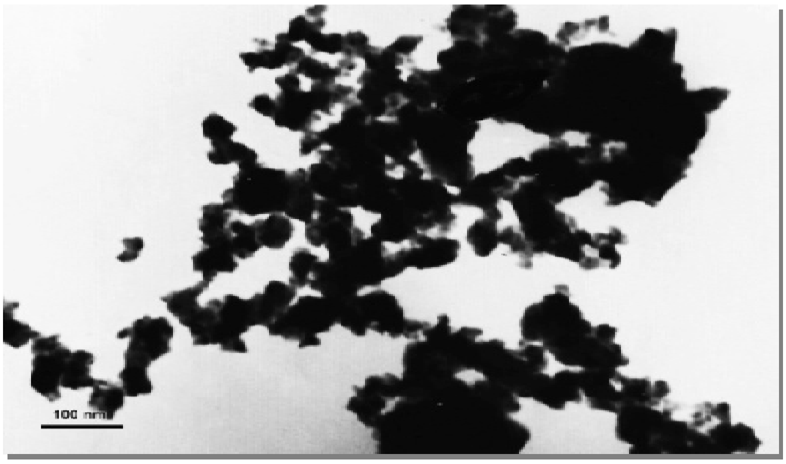


(a)

Figure (1) a - TEM image for $CuCO_3 \cdot Cu(OH)_2$ nanoparticles synthesized by method microemulsion process the particle size about (10-50 nm).



(b)

Figure (1) b -TEM image for copper CuO nanoparticle synthesized by method microemulsion process, the particle size about (10-50 nm).

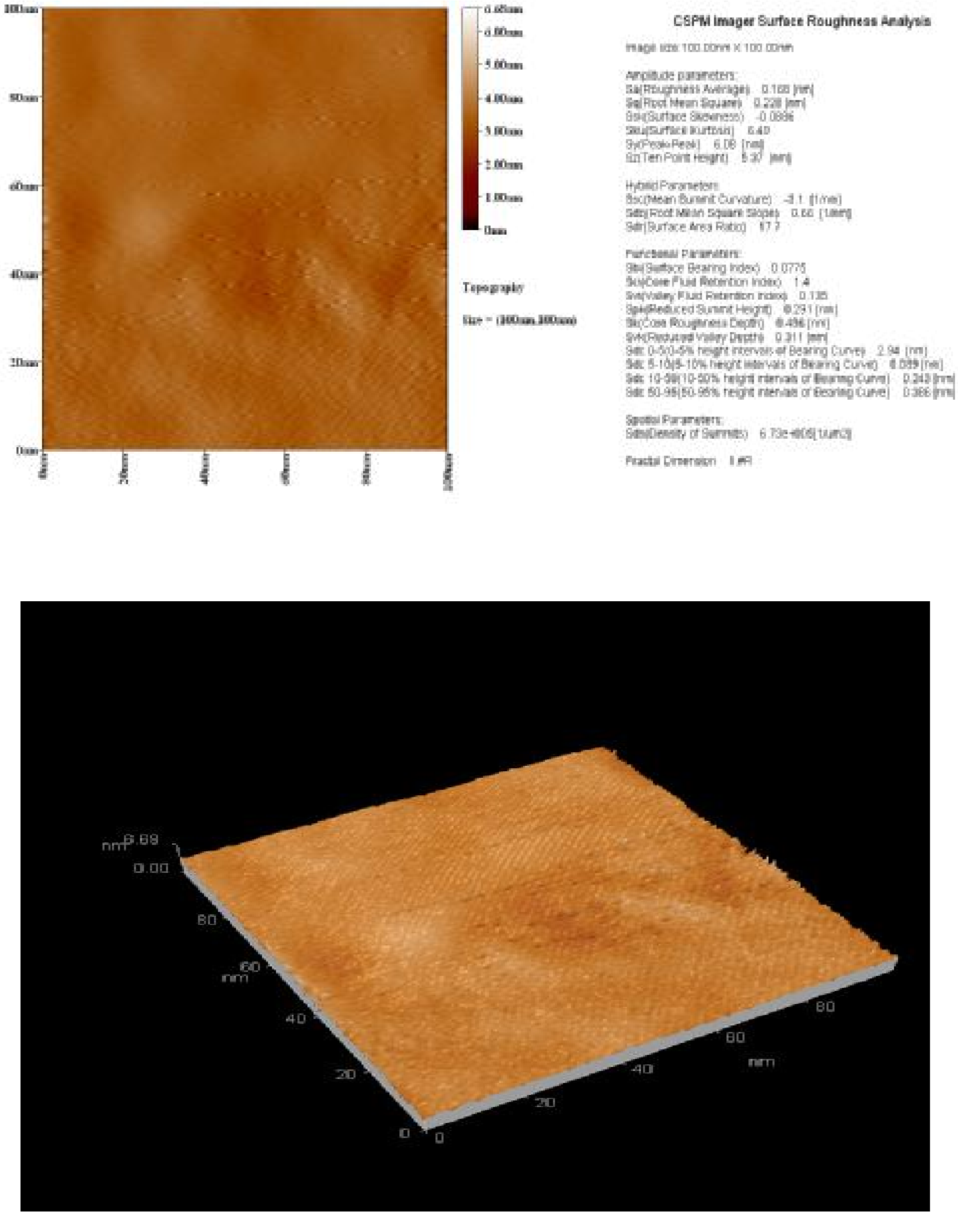
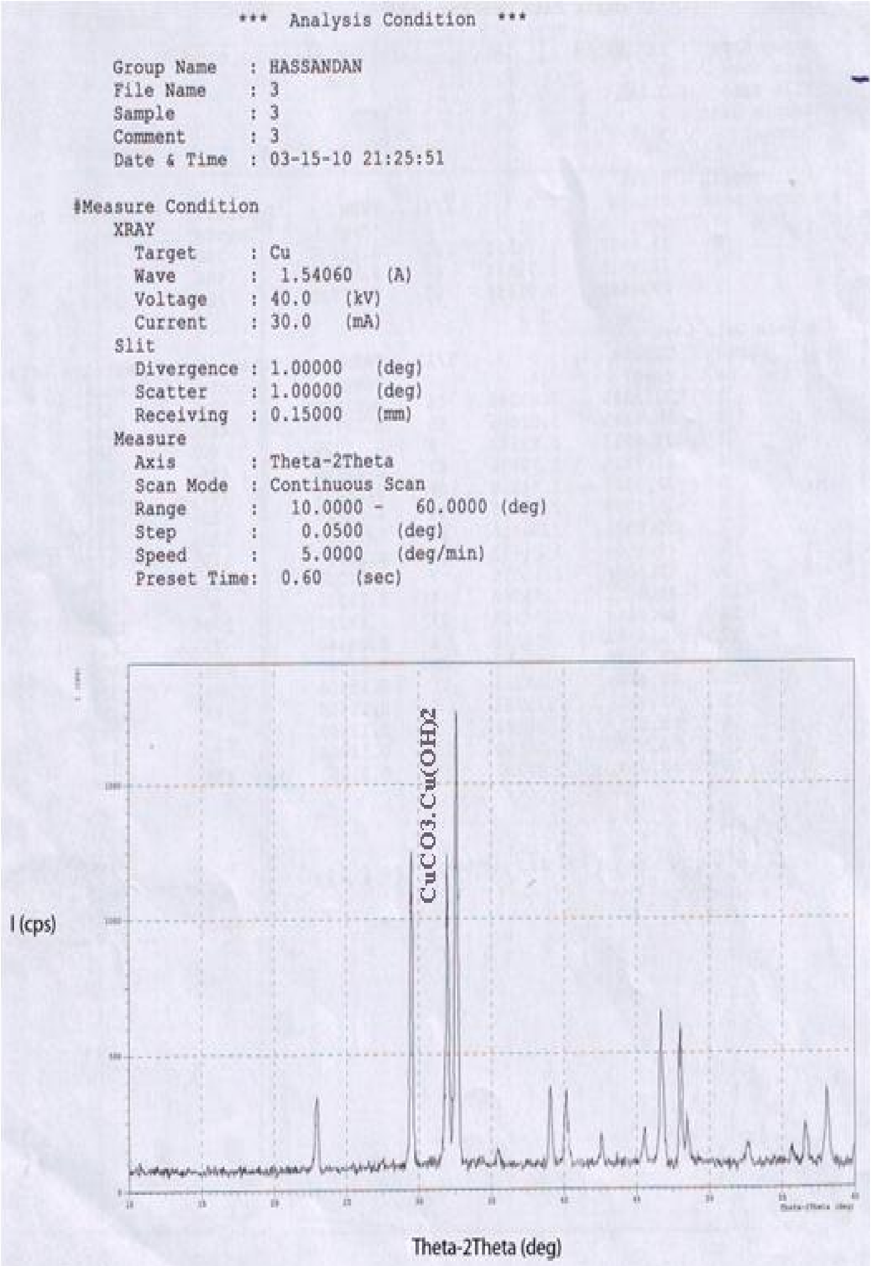


Figure (2) AFM high magnification micrograph, super transparent , CuO thin-film coated deposited on glass substrate by using of ultrasonic spray pyrolysis technique, the Root mean square (0.228 nm).



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Comment       : 3
Date & Time   : 03-15-10 21:25:51

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    Voltage     : 40.0    (kV)
    Current     : 30.0    (mA)
  Slit
    Divergence  : 1.00000    (deg)
    Scatter     : 1.00000    (deg)
    Receiving   : 0.15000    (mm)
  Measure
    Axis        : Theta-2Theta
    Scan Mode   : Continuous Scan
    Range       :   10.0000 -    60.0000 (deg)
    Step        :    0.0500    (deg)
    Speed       :    5.0000    (deg/min)
    Preset Time:   0.60    (sec)
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Figure (3) XRD patterns of copper carbonate $CuCO_3 \cdot Cu(OH)_2$ powder prepared by method of microemulsion process , 2Ɵ(29) [6].The particle size of powder by use (Debye-Scherr's) equation that the particle size of powder a range about (30-40) nanometer[7] .

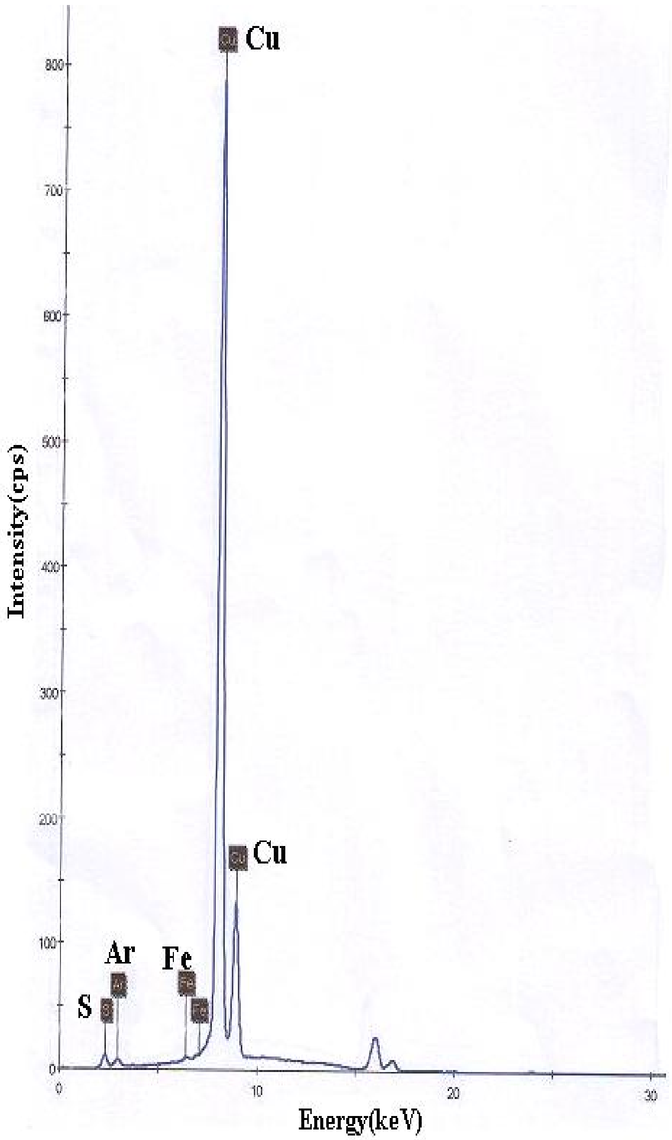

Figure (4) XRF of copper carbonate $CuCO_3 \cdot Cu(OH)_2$ powder prepared by method of microemulsion process. The high purity concentration of the copper while other peaks of material could be neglected for their count rates.