One-Step Synthesis of Copper Oxide Nanoparticles Using Pulsed Laser Ablation in Water: Influence of the Laser Wavelengths on Optical Properties

Dr.Abdulrahman K. Ali
Applied Sciences Department, University of Technology/ Baghdad
Email:akanano@yahoo.com

Received on: 6/3/2013 & Accepted on: 11/6/2013

ABSTRACT

Laser ablation has proven to be an effective method for generating nanoparticles. In this work, we have successfully produced pure cupper nanoparticles in fast and one-step method by Nd-YAG irradiation of cupper target with a 1064 and 532 nm laser wavelengths in pure water. The particle size, shape and size distributions were measured using a transmission electron microscope TEM. The UV–VIS spectroscopy has been employed for the optical properties. Nanoparticles with diameters 30 nm were observed to be formed in the colloidal solution. The UV–VIS spectrum of the material shows weak plasmon peak around 620 nm, indicating the formation of copper oxide nanoparticles. A clear blue shift is observed in the direct band gap (4.3 eV) of these nanoparticles presumably to the quantum confinement effects exerted by the nanosize.

Keywords: Copper Oxide, Pulsed, Energy gap.

تحضير جسيمات اوكسيد النحاس النانوية بخطوة واحدة بواسطة الازالة بالليزر بالماء ودراسة تأثير الطول الموجي لليزرعلى الخصائص البصرية

الخلاصة

في هذا البحث أثبت القشط بالليزر انه طريقة فعالة لتوليد الجسيمات النانوية. تم توليد جسيمات نانوية نقية من النحاس بطريقة سريعة وبخطوة واحدة وذلك بتشعيع قطعة من معدن النحاس النقي بليزر النديميوم ياك بطولين موجبين هما 1064 nm,532nm في الماء المقطر. القطر والشكل والتوزيع الكاوسي للجسيمات المتولدة تم تخمينه بواسطة المجهر الالكتروني الماسح TEM والخصائص البصرية حسبت بواسطة المطياف للمنطقة المرئية والفوق البنفسجية. وجد أن عوالق النحاس النانوية المتولدة في المحلول تمتلك معدل قطر بحدود 30 nm. طيف الامتصاص يظهر قمة امتصاص ضعيفة حول القيمة 620 nm وهذه بصمة لجسيمات اوكسيد النحاس النانوية مما يدل على تولدها. لوحظ انحراف واضح نحو الاطوال

https://doi.org/10.30684/etj.31.7B.10
2412-0758/University of Technology-Iraq, Baghdad, Iraq

الموجية القصيرة في فجوة الطاقة المباشرة (4.3 eV) وهذا يعزى الى الحصر الكمي الناتج من الحجم النانوي للجسيمات المتولدة.

INTRODUCTION

Nanoparticles possess a large fraction of surface atoms per unit volume that leads to increasing the total surface energy and hence the reactivity with atoms or molecules of the surrounding environment. Metals nanoparticles exhibit novel chemical, optical, catalysis and electronic properties are interesting materials with selectivity, specific activity which differ from the bulk properties.

Among various metal nanoparticles, copper oxide CuO nanoparticles are a narrow and direct band gap (Eg=1.2 eV) p-type semiconducting material [1,2], are of significant technological interest and promising applications because of their catalytic [3], optical [4], electrical [5] and magnetic properties [6]; it has been widely used for diverse applications such as gas sensing [7,8], Nanofluid [9], Surface-Enhanced Raman Scattering [10], as well as these materials present high antibacterial activity, low toxicity, chemical stability, long lasting action period and thermal resistance versus organic antibacterial agents [11]. In addition, copper is still a very attractive because of its abundance and cheapness.

Copper oxide nanoparticles have been synthesized through different methods such as, chemical, [16], solvo/hydrothermal method [17], arc discharge pulsed laser deposition [18, 19] and others [20]. Among them, pulsed laser ablation in liquid one of the most common dominant technologies to produce pure and stable NPs suspensions because of its low cost[21], high efficiency and precision [22].

The production of copper oxide nanoparticles using laser ablation of a solid metal in a liquid has been extensively investigated [23-28], but the preparation parameters such as laser wavelength and optical properties are not. Therefore there is a possibility that the particle size of collides can be controlled by changing the photon energy of laser (wavelength). However, no study has been carried out on the relation between energy gap and laser wavelength.

The present work reports on the synthesis, structural and morphological characterization of copper nanoparticles which prepared in water in a one step procedure in order to clarify the relation between particle size as well as optical properties and the laser wavelength.

EXPERIMENTAL

The experimental setup is shown schematically in Figure (1). The beam from a Nd:YAG laser (type HUAFEI) was focused by a lens (F = 10 cm) on the surface of a cupper target (99.99%, thickness 1.0 mm). The target was fixed in a glass cell which contains 3 ml pure water. The laser pulse duration was about 10 ns, the pulse-repetition rate 1 Hz, and the maximum energy of the 800m J/pulse. Immediately after the ablation experiment, the UV-VIS absorption spectra of cupper colloids were recorded by a spectrometer (type Metratech).A transmission electron microscope (TEM), a CM10 pw6020,Philips-Germany, was employed to take electron microphotographs of the resultant nanoparticles. The test samples were prepared by placing a drop of suspension of interest on a copper mesh. The size distributions were obtained by counting of particles in TEM images.

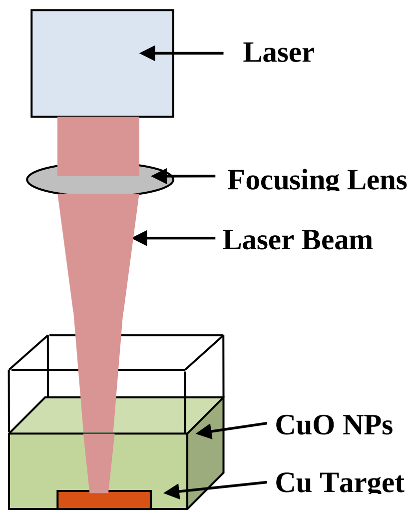

Figure (1) Schematic diagram of experimental setup.

RESULT AND DISCUSSION

Figure (2) shows the nanoparticles solutions produced by laser ablation of copper plate immersed in pure water exposed by 200 laser pulses, with laser flounce (F= 46 J/cm^2, the laser spot size is 1.22 mm), at laser wavelength of 1064, and 532 nm, respectively. The color of solution was changed and the intensity was increased when advancing in the laser shots, showing the formation of colloidal copper nanoparticles. In this experiment the green color of produced nanoparticles solution was changing in intensity corresponding to laser wavelengths. The interesting optical color is attributed to the formation of metal nanoparticles as they scatter bright intense colors. When the electromagnetic light interacts with nanoparticles solution, the free electrons of the metal nanoparticles undergo a collective vibration with respect to the positive metallic nanoparticles. This process is resonant at a particular frequency of the light and is termed the surface plasmon resonance SPR oscillation [4, 29]. This electronic oscillation can be simply visualized as a photon confined to the small size of the nanostructure. This interaction with solution decays by radiating its energy in electromagnetic wave in green color [4, 30].

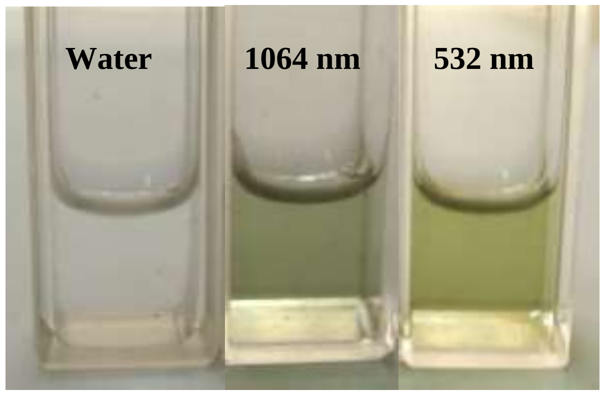

Figure (2) A Colloidal copper nanoparticles solution with varying color Intensity produced at laser wavelength of 1064, and 532 nm, respectively.

The effect of laser wavelength was examined at 1064 nm, 532 nm. Figure (3) shows absorption spectra of colloidal solutions prepared by ablating copper target in water with 532, 1064 nm laser light. The laser fluence was adjusted at 46 J/cm^2 and ablation was made for 200 pulses. The spectra consist of strong absorption due to inter-band transitions in the 300–400 nm regions and weak absorption due to plasmon band around 620 nm (the inset) independently of laser wavelengths, which indicated the formation of CuO nanoparticles; because most of the Cu particles produced by laser ablation react with surrounding water and produce copper oxide particles [11,10,22]. The plasmon resonance of colloidal copper particles which is in agreement with previously reported literatures as having a weak peak at 580–640 nm which prepared at various preparation methods [10, 11, 18, 22, and 25].

Figure (3) illustrates that the ablation efficiency at longer wavelengths was higher than that at shorter wavelengths, this can contributed to two factors: the value of the absorption coefficient of bulk copper is higher at longer wavelengths, so the intensity of absorbance peak of 1064 nm higher than at 532 nm. On the other hand, the absorbance at 1064 nm is lower than those at 532 nm in the absorption spectra of copper colloids prepared by 1064 nm light [21]. Thus, the efficiency of self-absorption by copper colloids is higher at shorter wavelengths (532 nm) than at longer wavelengths (1064 nm), leading that the ablation efficiency with shorter-wavelength light is lower than that with longer-wavelength light.

Figure (4-a) shows TEM images of particles in the colloidal solutions. The specimens for TEM experiments were prepared by depositing a drop of solution containing colloidal copper particles onto carbon-coated copper grids and letting them dry completely at room temperature. The nanoparticles thus produced were calculated to have an average diameter of 30 nm. The mean diameter and size distribution of particles are summarized in Figure (4-b).

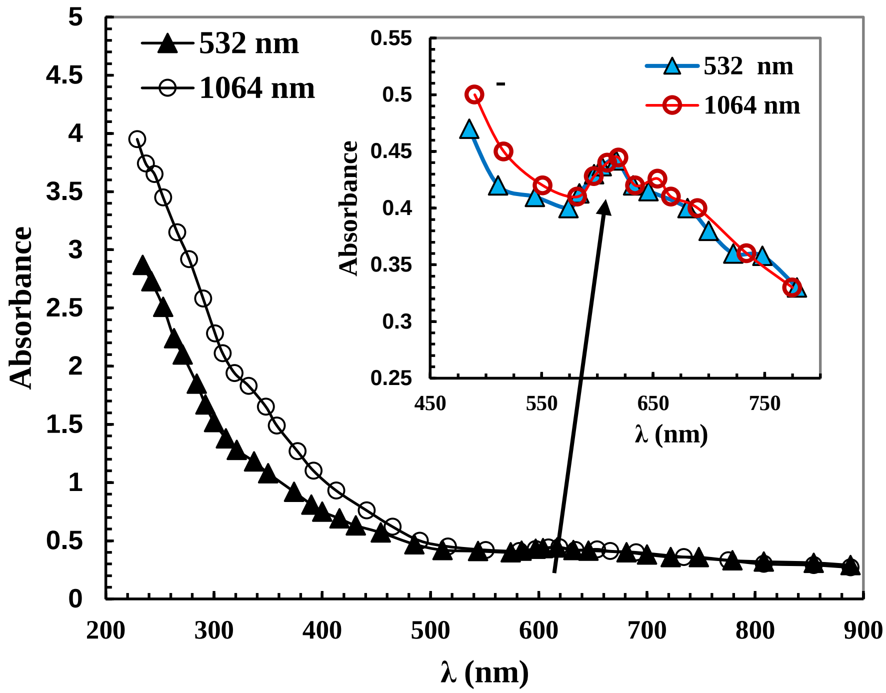

Figure (3) Absorbance spectra of the CuO nanoparticles, obtained by laser ablation of copper plates immersed in pure water exposed by 200 laser pulses, with laser fluence of 46 J/cm^2, at laser wavelength of 1064 nm and 532 nm, respectively.

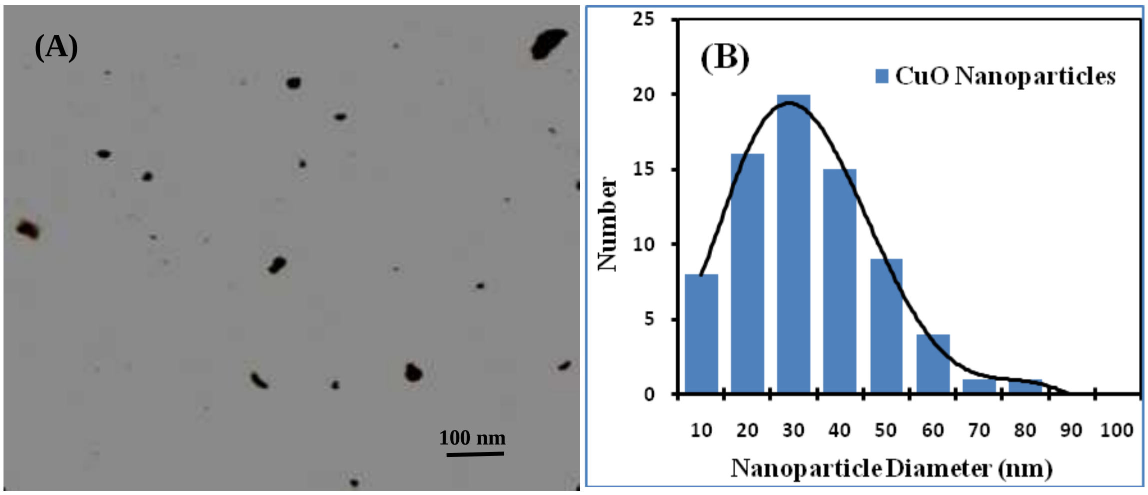

Figure (4) (A) Typical TEM image and (B) size distribution of colloidal copper nanoparticles prepared by laser ablation in water, at 1064 nm laser wavelength.

Figure (5) shows the optical band gap energy, E_g, of as synthesized colloidal solution of copper oxide, was determined from the absorbance spectra, where a steep increase in the absorption is observed due to the band–band transition. E_g is obtained using the following equation for a semiconductor $(\alpha h\nu)^n = B(E - Eg)$ [31]. Where B is a constant, Eg the band gap energy, $E = h\nu$ the photon energy, and n = 1/2 or 2, depending on whether the transition is indirect or direct, respectively. The intersection of the slope of $(\alpha h\nu)^2$ vs. hν curve on the x-axis provides band gap energy of the sample.

The energy band gap is calculated to be around 4 eV from the UV–VIS absorption spectrum, which is larger than the reported value for bulk CuO (Eg = 1.2 eV) and which in an agreement with literature for CuO quantum dots [32,31,16]. It was reported that the band gap of semiconductor materials will increase with the decrease in particle size, which leads blue shift in the direct band gap as a consequence of the quantum confinement effects [33].

From these graphs, it is clear that the direct band edge increase with decreasing wavelength. For the particle prepared at 1064, the band edge is estimated to be 3.9 eV(15% error percent), while its value for the particles at 532 nm is 4.3 eV. These changes in Eg attributed to change in particles size. It has been reported that the absorption of laser light by colloidal metal particles caused change in the size of particles [33]. Also it was reported that particle size was reduced by the self-absorption due to fragmentation [21]. Our results suggested that the self-absorption at 532 nm have a greater influence on the particle size than that at 1064 nm. As the photon energy of 532 nm higher than that at 1064 nm, this lead to the fragmentation of NPs prepared at 532 nm, so the average size of NPs prepared at 532 nm smaller than that prepared at 1064 nm.

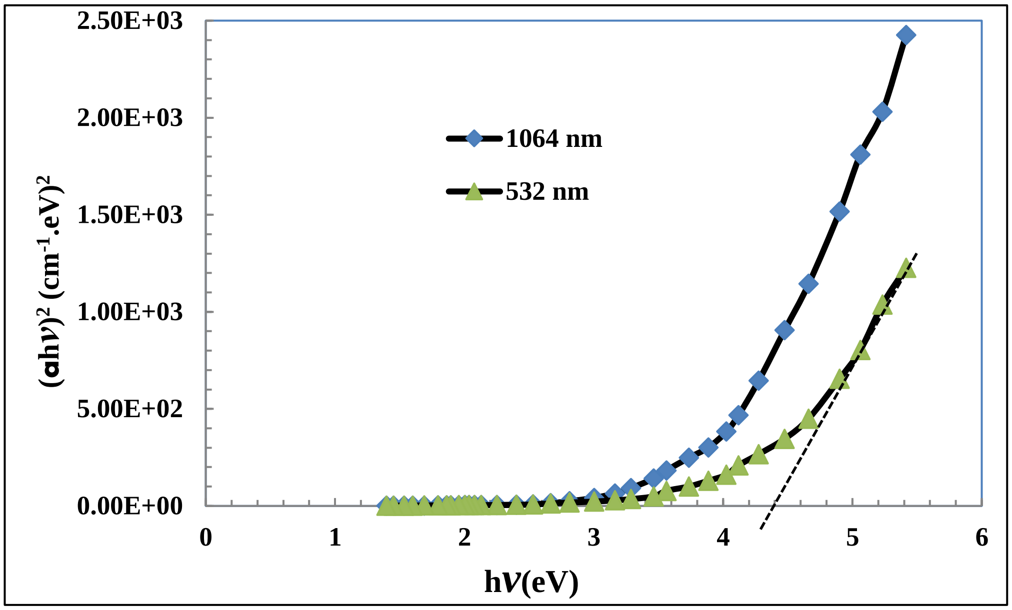

Figure (5) direct band gap estimation of CuO nanoparticles samples Prepared by laser ablation (at 1064 and 532 nm) in water.

CONCLUSIONS

In summary, we have synthesized copper oxide NPs using the method of laser ablation of the solid target in a liquid environment. Under the present conditions of ablation, The NPs generated in the colloidal solution were having average size in the range of 30 nm, depending on the laser operating parameters (energy and wavelength). The quantum confinement effect exerted by such nanocrystals found to bring significant blue-shift energy gab of the colloidal nanoparticles. Here, we demonstrate that the particle size as well as the energy gap can be controlled by changing the laser wavelength. This technique will be useful to prepared desired size colloids in solutions.
In general, the PLAL offers an alternative method for one-step generation of high purity metal-oxide NPs, which can be extended to vital applications.

REFERENCES

[1]. Wei-Tang Yao, Shu-Hong Yu, Yong Zhou, Jun Jiang, Qing-Song Wu, Lin Zhang, and Jie Jiang "Formation of Uniform CuO Nanorods by Spontaneous Aggregation: Selective Synthesis of CuO, Cu2O, and Cu Nanoparticles by a Solid-Liquid Phase Arc Discharge Process" J. Phys. Chem. B, 109, 14011-14016, 2005

[2]. Rakhshani, A. E. "Preparation, characteristics and photovoltaic properties of cuprous oxide a review" Solid-State Electron. V. 29, Issue 1, 7–17, 1986.

[3]. Yang Liu, Chai Lor, Qiang Fu, David Pan, Lei Ding, Jie Liu, and Jennifer Lu "Synthesis of Copper Nanocatalysts with Tunable Size Using Diblock Copolymer Solution Micelles" J. Phys. Chem. C, 114, 5767–5772, 2010

[4]. Fuyi Chen, Negash Alemu, and Roy L. Johnston "Collective plasmon modes in a compositionally asymmetric nanoparticle dimer" AIP ADVANCES 1, 032134, 2011.

[5]. Gunadhor S. Okram and Netram Kaurav "Size-dependent resistivity and thermopower of nanocrystalline copper" JOURNAL OF APPLIED PHYSICS 110, 023713, 2011.

[6]. Rao, G. N. Y. D. Yao, and J. W. Chen "Superparamagnetic Behavior of Antiferromagnetic CuO Nanoparticles" IEEE TRANSACTIONS ON MAGNETICS, VOL. 41, NO. 10, 3409-3411, 2005.

[7]. Davide Barreca, Giorgio Carraro, Elisabetta Comini, Alberto Gasparotto, Chiara Maccato, Cinzia Sada, Giorgio Sberveglieri, and Eugenio Tondello "Novel Synthesis and Gas Sensing Performances of CuO-TiO2 Nanocomposites Functionalized with Au Nanoparticles" J. Phys. Chem. C, 115, 10510–10517, 2011.

[8]. Alireza Aslani , Vahid Oroojpour "CO gas sensing of CuO nanostructures, synthesized by an assisted solvothermal wet chemical route" Physica B 406,144–149, 2011.

[9]. Ming-Hui Chang, Hwai-Shen Liu, Clifford Y. Tai "Preparation of copper oxide nanoparticles and its application in nanofluid" Powder Technology 207, 378–386, 2011.

[10]. Maurizio Muniz-Miranda, Cristina Gellini, and Emilia Giorgetti "Surface-Enhanced Raman Scattering from Copper Nanoparticles Obtained by Laser Ablation" J. Phys. Chem. C, 115, 5021–5027, 2011.

[11]. Mayur Valodkar, Shefaly Modi, Angshuman Pal, Sonal Thakore "Synthesis and anti-bacterial activity of Cu, Ag and Cu–Ag alloy nanoparticles: A green approach" Materials Research Bulletin 46, 384–389, 2011.

[12]. Simon H. Stelzig, Christin Menneking, Michael S. Hoffmann, Klaus Eisele, Stephan Barcikowski, Markus Klapper, Klaus Müllen "Compatibilization of laser generated antibacterial Ag- and Cu-nanoparticles for perfluorinated implant materials" European Polymer Journal 47, 662–667, 2011.

[13]. Antonio Esteban-Cubillo, Carlos Pecharroman , Eduardo Aguilar, Julio Santaren and Jose S. Moya "Antibacterial activity of copper monodispersed nanoparticles into sepiolite" J Mater Sci 41:5208–5212, 2006.

[14]. Kelechi C. Anyaogu, Andrei V. Fedorov, and Douglas C. Neckers "Synthesis, Characterization, and Antifouling Potential of Functionalized Copper Nanoparticles" Langmuir, 24, 4340-4346, 2008.

[15]. Young Hwan Kim, Don Keun Lee, Hyun Gil Cha, Chang Woo Kim, Yong Cheol Kang, and Young Soo Kang "Preparation and Characterization of the Antibacterial Cu Nanoparticle Formed on the Surface of SiO2 Nanoparticles" J. Phys. Chem. B, 110, 24923-24928, 2006.

[16]. Swarup KumarMaji, NillohitMukherjee, AnupMondal, Bibhutosh Adhikary, BasudebKarmakar "Chemical synthesis of mesoporous CuO from a single precursor: Structural, optical and electrical properties" Journal of Solid State Chemistry 183, 1900–1904, 2010.

[17] Alireza Aslani "Controlling the morphology and size of CuO nanostructures with synthesis by solvo/hydrothermal method without any additives" Physica B 406,150–154, 2011.

[18]. Chakravarty, U. P. A. Naik, C. Mukherjee, S. R. Kumbhare, and P. D. Gupta "Formation of metal nanoparticles of various sizes in plasma plumes produced by Ti:sapphire laser pulses" JOURNAL OF APPLIED PHYSICS 108, 053107, 2010.

[19]. Sy-Bor Wen and Xianglei Mao "Experimental and theoretical studies of particle generation after laser ablation of copper with a background gas at atmospheric pressure" JOURNAL OF APPLIED PHYSICS 101, 123105, 2007.

[20]. Genki Saito, Sou Hosokai, Masakatsu Tsubota, and Tomohiro Akiyama "Synthesis of copper/copper oxide nanoparticles by solution plasma" JOURNAL OF APPLIED PHYSICS 110, 023302, 2011.

[21]. Mitsuo Kawasaki "Laser-Induced Fragmentative Decomposition of Fine CuO Powder in Acetone as Highly Productive Pathway to Cu and Cu2O Nanoparticles" J. Phys. Chem. C, 115, 5165–5173, 2011.

[22]. Tilaki, R.M. A. Iraji Zad,_ S.M. Mahdavi "Size, composition and optical properties of copper nanoparticles prepared by laser ablation in liquids" Appl. Phys. A 88, 415–419, 2007.

[23]. Nath and A. Khare, A. "Size induced structural modifications in copper oxide nanoparticles synthesized via laser ablation in liquids" journal of applied physics 110, 043111, 2011.

[24]. Lin, X. Z. P. Liu, J. M. Yu, and G. W. Yang "Synthesis of CuO Nanocrystals and Sequential Assembly of Nanostructures with Shape-Dependent Optical Absorption upon Laser Ablation in Liquid" J. Phys. Chem. C, 113, 17543–17547, 2009.

[25].Kazuyuki Amikura, Takeshi Kimura, Mika Hamada, Noriko Yokoyama, Jun Miyazaki, Yasuhiro Yamada "Copper oxide particles produced by laser ablation in water" Applied Surface Science 254, 6976–6982, 2008.

[26].Manabendra Chandra, S.S. Indi, Puspendu K. Das "First hyperpolarizabilities of unprotected and polymer protected copper nanoparticles prepared by laser ablation" Chemical Physics Letters 422, 262–266, 2006.

[27].Sylvie Noel, Jorg Hermann, Tatiana Itina "Investigation of nanoparticle generation during femtosecond laser ablation of metals" Applied Surface Science 253,6310–6315, 2007.

[28].Kazakevich, P.V. A.V. Simakin, V.V. Voronov, G.A. Shafeev "Laser induced synthesis of nanoparticles in liquids" Applied Surface Science 252, 4373–4380, 2006.

[29].Haes,A."Localized Surface Plasmon Resonance Spectroscopy for Fundamental Studies of Nanoparticle Optics and Applications to Biosensors" Doctoral thesis, Northwestern University , 2004.

[30].Jain, P. K. X. Huang, I. H. EL-Sayed and M. El-Sayed "Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging, Sensing, Biology, and Medicine" American Chemical Society Acc. Chem. Res. 41, 1578–1586, 2008.

[31].Liang Cheng, Mingwang Shao, Dayan Chen, Yuzhong Zhang "Preparation, characterization, and electrochemical application of mesoporous copper oxide" Materials Research Bulletin 45, 235–239, 2010.

[32].Shama Rehman, A. Mumtaz, S. K. Hasanain "Size effects on the magnetic and optical properties of CuO nanoparticles" J Nanopart Res, 13, 2497–2507, 2011.

[33].Semaltianos, N.G. · S. Logothetidis ·W. Perrie · S. Romani · R.J. Potter · M. Sharp · P. French · G. Dearden · K.G.Watkins "II–VI semiconductor nanoparticles synthesized by laser ablation" Appl Phys A, 94, 641–647, 2009.