PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 1 (2024) pp. 79-84
Section: Physics
DOI: 10.15330/pcss.25.1.79-84

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 1 (2024) С. 79-84
Фізико-математичні науки

PACS: 78.67.-n., 78.67.Bf., 68.37.Hk., 78.40.-q. ISSN 1729-4428

R. Salome Mercy Ponrani[1,2], D. Esther Nancy[2], S.G. Rejith[3], S.C. Vella Durai[4]

Study of Structural and Optical Behaviour of Silver -Copper Bimetallic Nanoparticles

[1]Department of Physics, St.Xavier's College, Palayamkottai, Tirunelveli-627002, Tamilnadu, India, smp80jesus@gmail.com;
[2]Department of Physics, Sarah Tucker College, Tirunelveli-627007, Tamilnadu, India;
[3]Department of Physics, St.Xavier's College, Palayamkottai, Tirunelveli-627002, Tamilnadu, India;
[4]PG and Research Department of Physics, Sri Paramakalyani College, Alwarkurichi, Tenkasi-627412, Tamilnadu, India
(Affiliated to Manonmanium Sundaranar University, Tirunelveli)

Silver-based nanomaterials have proven interesting and promising material for numerous applications such as biosensor, antimicrobial, anticancer agent, catalyst, food and water treatment, energy storage devices etc. In this study, nanoparticles of Silver and Copper were prepared by chemical reduction method, using hydrazine hydrate and Sodium borohydride as reducing agent. Fine powder of Ag-Cu nanoparticles (NPs)was obtained. The structural analysis of the sample wasdone using Powder XRD, SEM and TEM images and particle size analysis by DLS.The chemical purity and the elemental compositions of synthesized NPs were studied using SEM-EDX. Optical properties of the Ag-Cu NPs were analyzed using UV-DRS spectrum and FTIR spectrum. PXRD reveals that the NPs are highly crystalline in nature. The average crystallite size is30 nm. SEM and TEM images confirm the spherical morphology, and the particle size is in nm. The DLS-particle size analyzer shows the size distribution of most of the NPs ranging from 9 nm to 100 nm. The EDX analysis reveals the percentage of elemental composition as 14.71, 9.06 and 76.23 for silver, copper and oxygen respectively. UV-DRS spectrum shows the absorption maximum occur at 371 nm. Due to the synergistic effect of silver and copper, there is blue shift in the absorption maximum. The IR spectrum discloses the metal oxide bond in the synthesized NPs.

Keywords: Nanocomposites, Silver-Copper, Reducing agent, band gap, dielectric constant, particle size.

Received 15 July 2023; Accepted 16 January 2024.

Introduction

The silver-based nanoparticles (NPs) have vast research interest in recent decades because of their physiochemical properties especially the surface plasmon resonance [1]. The surface plasmon resonance cause the high reactivity and then enhance the properties which leads AgNPs to have applications in various fields such as medical, engineering, food, health care, cosmetics, energy storageetc [2-4]. Recently, a bimetallic nanoparticle, composed of two different metals, has advantages over monometallic nanoparticles, since bimetallization expands the original single-metal physiochemical properties to novel properties due to synergistic effects [5-6]. Silver and copper based bimetallic NPs have proven promising material for biosensing and hence have found applications in nano biotechnology [4]. Due to their antimicrobial activity, Ag and Cu based nanomaterials play an important role in the treatment of several issues caused by bacteria and viruses. The green synthesis of Ag–Cu bimetallic nanoparticles and their biomedical and catalytic applications have been extensively reported [7].However, there are efficient synthesizing methods and important properties such as dielectrics, electrochemical and thermal characteristics that still need to be investigated. The aim of this study is to prepare Silver-Copper bimetallic nanoparticles and study their structural and optical behaviour. Here, chemical reduction method is used to prepare Ag-Cu NPs, because this method is simple and have high amount of yield, and to obtain better shape and size distribution. After synthesis, characteristic features of nanomaterials such as size, shape, aggregation, elemental composition and optical behaviors are evaluated using various analyzing techniques.

I. Materials and Methods

1.1. Synthesis

Analytical grade of precursor salts silver nitrate, copper nitrate and sodium borohydride are purchased. In this preparation,0.5 mole of silver nitrate and 0.2 mole of copper nitrate aqueous solution are mixed in a round bottom flask using magnetic stirrer.Then 0.1 mole Hydrazine hydrate and sodium borohydride solutions were prepared using de-ionized water and this reducing agent solution was added drop by drop to the metallic mixture so the colour of the reacting solution changes to black colour.Under vigorous stirring for three hours, nanoparticles were precipitated.5 ml of ethanol is added to this solution which can act as a stabilizer. By centrifuging, supernatant was discharged. All the reactions and processes are done at room temperature. Precipitated samples were washed in ethanol and dried in hot air oven at 80ºC nearly for two hours. The dried ultrafine nanopowder was collected in a closed vial and kept for further use.

1.2. Instrumentation

The synthesized Ag-Cu NPs were analyzed by Powder XRD, SEM, TEM, SEM-EDX, DLS-Particle size Analyser, FTIR and UV-Visible spectrum. The powder X-ray diffraction patterns was recorded on Bruker AXS D8 Advance X-ray diffractometer (Cu Kα radiation, λ=1.5406 Å). Datawas taken for the 2θ range from 5 to 80 degrees with a step of 0.02 degree. Scanning Electron Microscopic image of Ag-Cu NPs with different magnification, has taken using the instrument CAREL ZEISS EVO18. High resolution Transmission Electron Microscope (HRTEM) images was taken using Jeol/JEM 2100 and SEM-EDAX spectrograph was taken using the instrument Jeol 6390LA/OXFORD XMX N model. Make-Model Micromeritics-Nano Plus instrument is used for DLS particle size analysis. Thermo Nicolet iS50 is the instrument used for taking FTIR spectrum. UV-DRS spectrum of Ag-Cu NPs has been taken using Perkin Elmer-Lambda 35 double beam spectrophotometer.

II. Results and Discussion

2.1. Powder X-ray diffraction analysis

The recorded powder XRD pattern of Ag-Cu NPs is shown in Figure 1. The diffractogram contains high intense sharp peaks which suggest that the synthesized nanoparticles are highly crystalline in nature. There are four characteristics diffraction peaks are observed and the high intense peaks at 2θ = 33.13º and 38.18º corresponding to the elements Ag and Cu respectively, and the peaks at 2θ =29.30º and 64.54ºare due to the blended effect of both Ag and Cu in NPs. The peaks are indexed using JCPDS data files (89-6378, 89-2531 and 89-3081). The crystallographic planes for the observed peaks are assigned as (1 0 3), (1 1 1), (1 1 1) and (3 0 5). From PXRD it can be concluded that, both Ag and Cu phases are clearly identified on the samples. Also, from PXRD analysis, the average crystallite size or grain size of the Ag-Cu NPs was determined using Scherrer equation [8] which is about 30 nm.

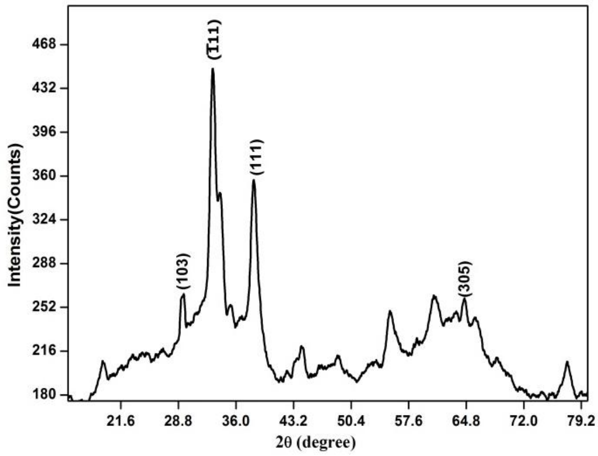

Fig. 1. Powder XRD pattern of Ag-Cu nanoparticles.

2.2. SEM and TEM Analysis

The SEM and TEM image of Ag-Cu Nps are shown in Figure 2. From the image, it can be identified that the sample comprises of well dispersed particles of spherical morphology [9]. Also, it confirms there is no agglomeration during the synthesizing process. TEM image [10] shows that the particles size rangestarts from 17 nm. These analyses support the results of PXRD analysis.

2.3. EDX analysis

Elemental compositions of Ag-Cu NPs were determined using EDX analysis and are listed in table 1. Figure 3 shows the EDX spectral graph [11] of Ag-Cu NPs. The approximate ratio of silver and copper in the sample is 5:3. The abundant presence of oxygen in the sample could be due to the oxidation of surface elements with the atmospheric air. EDX analysis confirms the results of PXRD and the purity of the sample.

Table 1.

EDX data for Ag-Cu nanopowder

Element	Line Type	Wt%	Atomic %
O	K series	36.06	76.23
Cu	K series	17.03	9.06
Ag	L series	46.91	14.71
Total:		100	100

2.4. Dynamic Light Scattering - Particle size analyzer.

Particle size of the samples was analyzed using DLS. The intensity distribution curve (figure 4) shows a single peak with wide base which indicates that the Ag-Cu NPs contains polydisperse nanoparticles ranges from 9 nm to 1000 nm. But most of the particles are <100 nm in size. DLS results are complemented by the SEM images in which we can observed that most of the particles are comparatively smaller than the micrometer size particles.

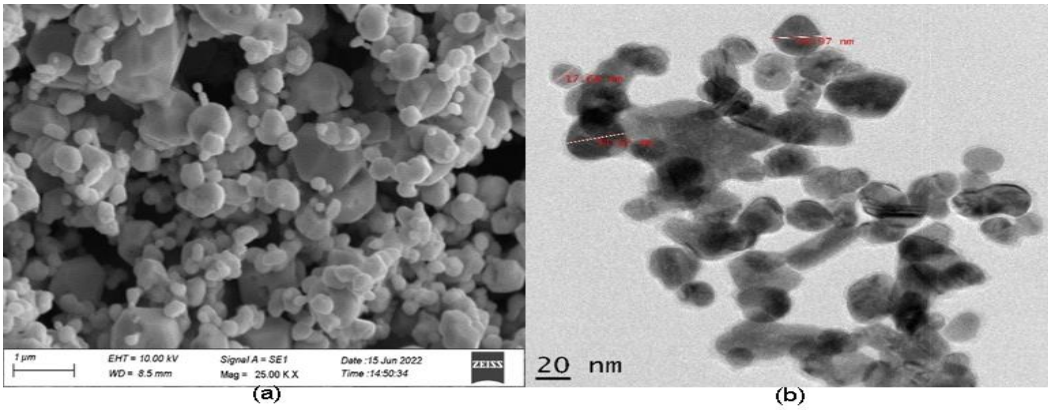

Fig. 2. a) SEM b) TEM image of Ag-Cu nanoparticles.

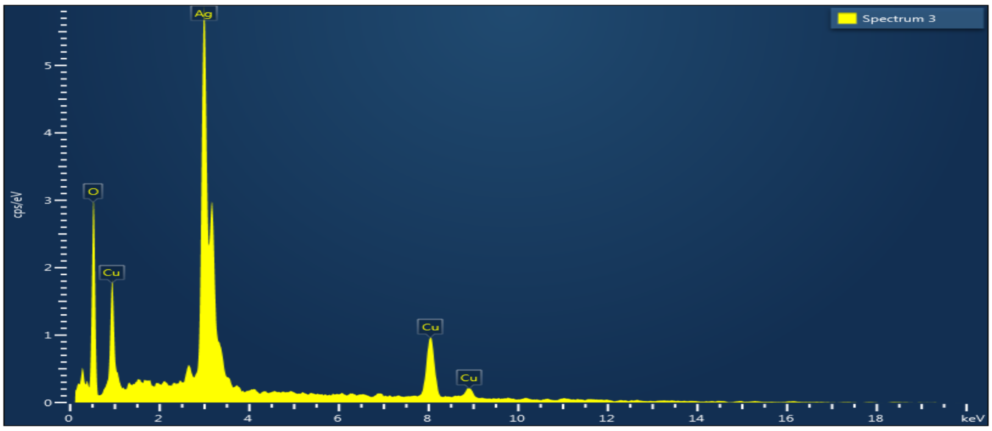

Fig. 3. EDX spectral graph of Ag-Cu nanopowder.

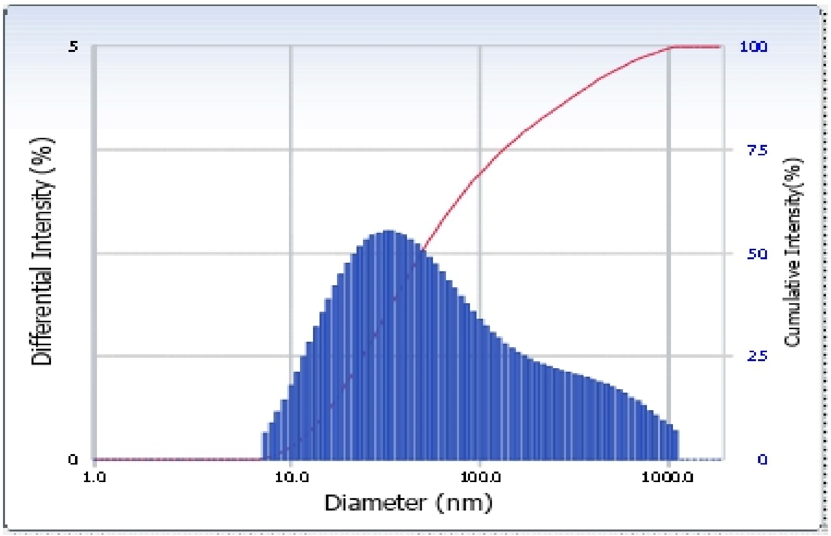

Fig. 4. DLS-Intensity distribution curve of Ag-Cu nanoparticles.

2.5. FTIR analysis

FTIR spectrum of Ag-Cu nanopowder is shown in figure 5. The broad nature of the absorption peaks reveals the presence of coupled vibrations. The combination symmetric and asymmetric stretching vibrations of O–H bond are responsible for the strong and broad absorption around the region 3400 cm^{-1}. By the results of EDX spectrum the possible elements could present in the samples are Ag, Cu and O. Therefore, the O-H bonds [11] could have been formed from the interaction of surface atoms with atmospheric water molecules or may due to the presence of water molecules in hydrate form in the prepared nanoparticles. All other observed absorption peaks at 1651 cm-^{1}, 1384 cm^{-1}, 1221 cm^{-1}, 943 cm^{-1}, 671 cm^{-1} and 523 $cm^{-1}$are mainly due to the symmetric, asymmetric stretching and bending vibrations of metal oxide bonding in the synthesized nanoparticles.

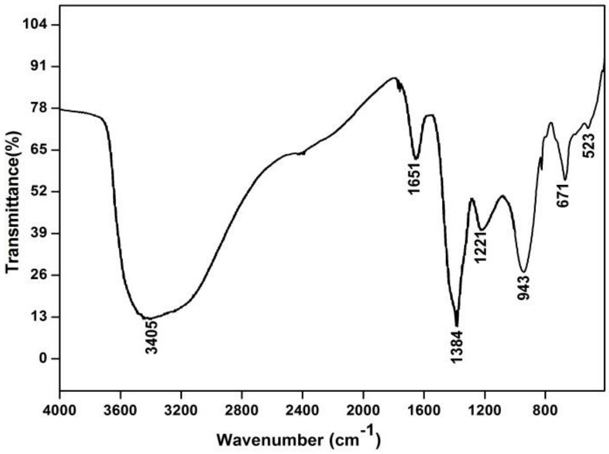

Fig. 5. FTIR spectrum of Ag-Cu nanoparticles.

2.6. UV-DRS analysis

Silver and copper nanoparticles have unique optical properties which make them strongly interact with specific wavelengths of light. They exhibit strong absorption in UV and visible region, caused due to the collective oscillation of free electrons in resonance with the light wave. In general, metals have highly reflecting surface. Along with surface reflectance, diffuse reflectance of the sample is considered for UV-DRS-Reflectance spectrum. The recorded UV-DRS reflectance and absorbance spectra of bimetallic Silver-Copper NPs are shown in figure 6 and 7 respectively.

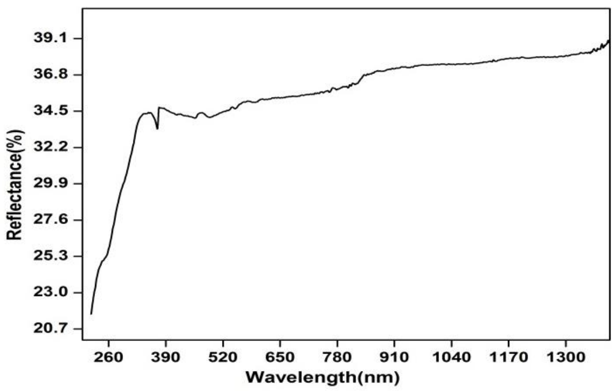

Fig. 6. UV-DRS Reflectance Spectrum of Silver-Copper bimetallic NPs.

From the reflectance spectrum, it can be observed that the light reflecting nature increasing gradually in the entire UV and visible region. In the Ag-Cu absorption spectrum, the prominent absorption peak in the near ultra-violet region articulates the enhancement of the surface plasmon resonance property of the material. The small peak absorbed around 371 nm (λ_{max}) is the characteristic absorption of the silver in the synthesized nanoparticles. The reported absorption wavelength of silver nanoparticles [12] ranging from 380 nm to 500 nm and for copper [13] is 500 nm - 600 nm. Since silver and copper both are high surface plasmon resonance material, due to their harmonic effect there is significant absorption in the entire visible region. Thus, UV-DRS reflectance spectral analysis agrees the synthesized Ag-Cu NPs are a promising material for sensors and detectors due to their high surface plasmon resonance.

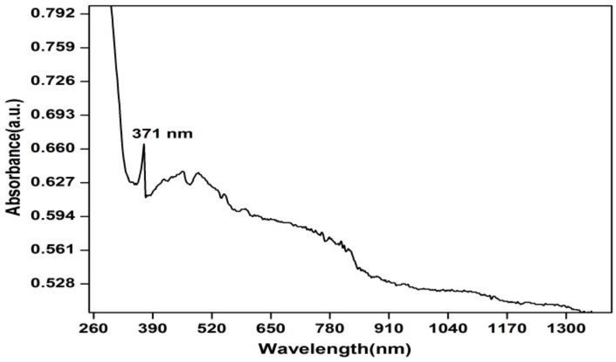

Fig. 7. UV-DRS-Absorption spectrum of Silver-Copper bimetallic NPs.

2.7. Band Gap analysis

Optical band gap energy of the synthesized nanoparticles from UV-DRS is determined by sketch the Tau's plot using Kubelka-Munk theory. The Tau's plot of bimetallic nanoparticles is given in Figure 8. The determined optical band gap energy of bimetallic Ag-Cu nanoparticle is 1.5 eV. Generally, metals have superimposed conduction and valance band, which make them a good conductor. But, when it is in nanostructures, the band gap engendered as like semiconductors. The band gap 1.5 eV infer that the semiconducting nature of the synthesized Ag-Cu nanoparticles.

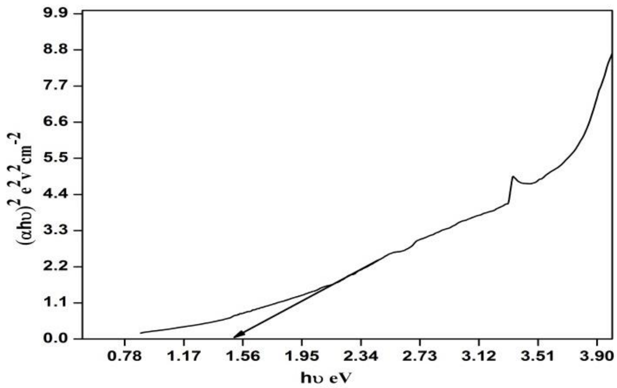

Fig. 8. Tau's plot of Silver-Copper bimetallic NPs.

2.8. Determination of Optical parameters

The empirical relation [14] between energy gap (E_g) and refractive index leads to calculate other optical parameters such as reflectance, dielectric constant and electric susceptibility. The calculated optical parameters are given in Table 2. From the table it can be infer that, the high refractive index and dielectric constant of Ag-Cu nanoparticles, makes them suitable for the photonic applications like image sensors, anti-reflective materials, electronic displays, solar cells etc. [15 -16].

Table 2.

Optical parameters of Ag-Cu Nanoparticles

Optical Parameters	**Values**
Bang gap energy	1.5 eV
Refractive index	3.307
Reflectance	0.2868
Dielectric constant	10.936
Electrical Susceptibility	9.936

Conclusion

The Ag-Cu bimetallic nanoparticles were successfully synthesized by chemical reduction method using double reductants hydrazine hydrate and sodium borohydride. The powder XRD analysis confirms the presence of crystalline phases, and mean grain size of the nanoparticles is 30 nm. The SEM and TEM images confirm the synthesized nanoparticles have spherical morphology and are poly disperse particles without agglomeration. The purity of the nanoparticle is confirmed by EDX spectrum, there is no unwanted impurity atoms from the chemicals used in synthesizing process. The DLS-particle analysis shows the distribution of different size particles in the sample and most of the particles are <100 nm in size. The results from all the structural analyses complement with each other and confirm the structural stability of the nanoparticles. The UV-DRS spectral analysis of bimetallic silver-copper nanoparticles, conclude that the synthesized nanoparticles possessing LSPR property. The synergetic effect of two metals enhanced the LSPR and making the bimetals more promising for surface plasmon resonance applications.

***R. Salome Mercy Ponrani* –** M. Sc., M. Phil., B.Ed., Research Scholar, Assistant Professor Department of Physics;
***D. Esther Nancy* –** M. Sc., Ph.D. Assistant Professor Department of Physics**;**
***S. G.Rejith* –** Assistant Professor Department of Physics**;**
***S. C. Vella Durai* –**M. Sc., M. Phil., B.Ed., Ph.D. Assistant Professor, PG and Research Department of Physics.

[1] X. F. Zhang, Z. G. Liu, W. Shen, S. Gurunathan, *Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches*, International Journal of Molecular Sciences, 2016, 17(9), 1534 (2016); https://doi.org/10.3390/ijms17091534.
[2] V. Rubbish, V. Kyrylenko, M. Durkot, L. Makar, M. Pop, A. Tarnaj, M. Trunover, S. Mudry, I. Shtablavyi, *Rapid formation methods of arrays of randomly distributed Au and Ag nanoparticles, their morphologies and optical characteristics*, Physics and Chemistry of Solid State, 22(4), 804 (2021); https://doi.org/10.15330/pcss.22.4.804-810.
[3] S. H. Lee, W. Y. Rho, S. J. Park, J. Kim, O. S. Kwon, B. H. Jun, *Multifunctional self-assembled monolayers via micro contact printing and degas-driven flow guided patterning*, Scientific Reports, 8, 16763 (2018); https://doi.org/10.1038/s41598-018-35195-9.
[4] Z.A.A. Aziz, H.M. Nasir, A. Ahmad, S.H. M. Setapar, W. L. Peng, S. C. Chuo, A. Khatoon, K. Umar, A.A. Yaqoob, M.N.M. Ibrahim, *Role of nanotechnology for design and development of cosmeceutical: application in makeup and skin care*, Frontiers Chemistry, 7, 739 (2019); https://doi.org/10.3389/fchem.2019.00739.
[5] F. Naaz, P. Lahiri, C. Kumari, H. K. Dubey, *Spectroscopic, Magnetic and Morphological studies of $MgFe_2O_4$ Nanopowder*, Physics and Chemistry of Solid State, 24(2), 392 (2023); https://doi.org/10.15330/pcss.24.2.392-402.
[6] D. Chen, Q. Yao, P. Cui, H. Liu, J. Xie, J. Yang, *Tailoring the Selectivity of Bimetallic Copper–Palladium Nanoalloys for Electrocatalytic Reduction of CO_2 to CO*, ACS Applied Energy Materials, 1, 883 (2018); https://doi.org/10.1021/jacs.5b08259.
[7] A.A.E. Mel, M. Chettab, E. Gautron, A. Chauvin, B. Humbert, J. Y. Mevellec, C. Delacote, D. Thiry, N. Stephant, J. Ding, K. Du, C. H. Choi and P. Y. Tessier, *Galvanic replacement reaction: a route to highly ordered bimetallic nanotubes*, The Journal of Physical Chemistry C, 120, 17652 (2016); https://doi.org/10.1021/acs.jpcc.6b06393.
[8] M. Liaskovska, T. Tatarchuk, V. Kotsyubynsky, H. Ersteniuk, *Zn-doped $CoFe_2O_4$ Nanoparticles Synthesized Using Ginkgo Biloba Extract: Cation Distribution*, Mossbauer Studies and Application for Water Treatment, Physics and Chemistry of Solid State, 22(4), 792 (2021); https://doi.org/10.15330/pcss.22.4.792-803.
[9] K.L. Chitturi, S. Garimella, A.K. Marapaka, K.R. Kudle, R. Merugu, *Single Pot Green Synthesis, Characterization, Antitumor Antibacterial, Antioxidant Activity of Bimetallic Silver and Copper Nanoparticles Using Fruit Pulp of Palmyra Fruit*, Journal of Bionanoscience, 12(2), 284 (2018); https://doi.org/10.1166/jbns.2018.1520.
[10] S. Delsante, G. Borzone, R. Novakovic, D. Piazza, G. Pigozzi, J. J. Rusch, M. Pilloni, G. Ennas, *Synthesis and thermo dynamics of Ag–Cu nanoparticles*, Physical Chemistry Chemical Physics, 17, 28387 (2015); https://doi.org/10.1039/C5CP02058A.
[11] N.A.N. Mohamad, N.A. Arham, J. Junaidah, A. Hadi, S. A. Idris, *Green Synthesis of Ag, Cu and AgCu Nanoparticles using Palm Leaves Extract as the Reducing and Stabilizing Agents*, IOP Conference Series: Materials Science and Engineering, 358(1), 012063 (2018); https://10.1088/1757-899X/358/1/012063.
[12] M. Umadevi, S. Shalini, M. R. Bindhu, *Synthesis of silver nanoparticle using D. carota extract*, Advances in Natural Sciences: Nanoscience and Nanotechnology, 3(2), 025008 (2012); https://10.1088/2043-6262/3/2/025008.
[13] S. Fatma, P. Kalainila, R. Sachidanandan, E. Ravindran, S. Renganathan, *Green synthesis of copper nanoparticle from Passiflora foetida leaf extract and its antibacterial activity*, Asian Journal of Pharmaceutical and Clinical Research, 10, 79-83 (2017); https://doi.org/10.22159/ajpcr.2017.v10i4.15744.
[14] R.R. Reddy, K.R. Gopal, K. Narasimhulu, L.S.S. Reddy, K.R. Kumar, C.V.K. Reddy, S.N. Ahmad, *Correlation between optical electronegativity and refractive index of ternary chalcopyrites, semiconductors, insulators, oxides and alkali halides*, Optical Matterials, 31, 209 (2008); https://doi.org/10.1016/j.optmat.2008.03.010.

[15] L. Wang, C. Darviot, J. Z. Farfan, S. Patskovsky, D. Trudel, M. Meunier, *Designable nanoplasmonic biomarkers for direct microscopy cytopathology diagnostics*, Journal of Biophotonics, 12, 201900166 (2019); https://doi.org/10.1002/jbio.201900166.

[16] S. Patskovsky, E. Bergeron, D. Rioux, M. Simard, M. Meunier, *Hyperspectral reflected light microscopy of plasmonic Au/Ag alloy nanoparticles incubated as multiplex chromatic biomarkers with cancer cells*, Analyst, 139, 5247 (2014); https://doi.org/10.1039/C4AN01063A.

Р.С.М. Понрані[1,2], Д.Е. Ненсі[2], С.Г. Реджіт[3], С.К.В. Дурай[4]

Дослідження структурної та оптичної поведінки біметалічних наночастинок срібло-мідь

[1]*Кафедра фізики, коледж Св. Ксав'єра, Палайямкоттай, Тірунелвелі-627002, Тамілнаду, Індія,* smp80jesus@gmail.com;
[2]*Кафедра фізики, коледж Сари Такер, Тірунелвелі-627007, Тамілнаду, Індія;*
[3]*Кафедра фізики, Коледж Св. Ксав'єра, Палаямкоттай, Тірунелвелі-627002, Тамілнаду, Індія;*
[4]*PG та дослідницький відділ фізики, коледж Шрі Парамакальяні, Алваркурічі, Тенкасі-627412, Тамілнаду, Індія (приєднаний до університету Манонманіум Сундаранар, Тірунелвелі)*

Наноматеріали на основі срібла є цікавими та перспективними матеріалами для багатьох застосувань, таких як біосенсори, антимікробні засоби, протиракові агенти, каталізатори, обробки їжі та води, накопичувачі енергії тощо. У цьому дослідженні наночастинки срібла та міді отримані методом хімічного відновлення, з використанням гідразингідрату та борогідриду натрію як відновника. Отримано дрібнодисперсний порошок наночастинок (НЧ) Ag-Cu. Структурний аналіз зразка проводився за допомогою порошкової XRD, аналізу SEM і TEM зображень, а також аналізу розміру частинок за допомогою DLS. Хімічну чистоту та елементний склад, а також аналізу розміру частинок за допомогою DLS. Хімічна чистота та елементний склад синтезованих наночастинок вивчали за допомогою SEM-EDX. Оптичні властивості наночастинок Ag-Cu проаналізовано за допомогою спектру UV-DRS та спектру Фур'є-трансформаційної інфрачервоної спектроскопії (FTIR). PXRD показує, що наночастинки є висококристалічними за своєю природою. Середній розмір кристалітів становить 30 нм. Зображення SEM і TEM підтверджують сферичну морфологію, а розмір частинок знаходиться в діапазоні нанометрів. DLS-аналізатор розміру частинок показує розподіл розмірів більшості наночатинок у діапазоні від 9 нм до 100 нм. Аналіз EDX показує, що відсоток елементного складу становить 14,71, 9,06 і 76,23 для срібла, міді та кисню відповідно. Спектр UV-DRS показує, що максимум поглинання спостерігається при 371 нм. Через синергетичний ефект срібла та міді спостерігається зсув спектру у бік коротших довжин хвиль. ІЧ-спектр у синтезованих наночастинках виявляє металооксидний зв'язок.

Ключові слова: нанокомпозити, Срібло-Мідь, відновник, заборонена зона, діелектрична проникність, розмір частинок.