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Nano/Micro-Structured Materials: Synthesis, Morphology and Applications

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Abstract

Materials with structural elements, clusters and crystallites or molecules with size dimension in the range 1–100 nm and/or 4–20 Å have found potential and real applications as antimicrobial agents, catalysts, nano-filters in waste water treatments and scale forming ions removal etc. These nano/micro-structured materials possess large surface area which is one of the most important properties needed in different fields of applications. In this short review, the different protocols available for the synthesis ranging from green chemistry to chemical reduction methods, structural characterization, morphology and applications of nanostructured materials such as layered double hydroxides, silver and molybdenum oxides have been discussed.

Keywords: nanomaterials, chemical reduction, green chemistry, layered double hydroxides, antimicrobial agents

1. Introduction

The synthesis of inorganic nanostructured materials, their stabilization, morphology and properties are the main issues of interest in different research groups. The interest is not only for their applications in chemical technology, catalysis, magnetic data storage and sensing [1], but also for their antimicrobial activities and waste-water treatment. More often than not, marine sediments and water environments are contaminated by urban runoffs, industrial and domestic effluents and oil spills [2]. The presence of such contaminants as polycyclic aromatic hydrocarbons (PAHs), poly chlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and heavy metals like mercury, lead and manganese poses risk to both human health and the aquatic biota [3]. Functionalized magnetic metal oxide nanoparticles [4, 5], silver nanoparticles as well as nanostructured layered double hydroxides have proven useful in the remediation of toxic waste in the water environment, inhibition of bacterial and fungi activities [6] and removal of scale forming ions from oil wells [7].

Different protocols have been employed in the synthesis of nanostructured materials by different research groups. These synthetic protocols are generally grouped into two categories: “top-down” and “bottom-up” approach. In the top-down approach (milling or attrition), bulk solid is broken into smaller and smaller

portions, until nanometer size is reached. The bottom-up method of nanoparticle synthesis involves nucleation of atoms followed by their growth in a self-assembly fashion to form the nanomaterial. Here we will look at the different nanostructured materials prepared by bottom-up methods such as hydrothermal, [8, 9] combustion synthesis [10], gas-phase methods [11, 12], microwave synthesis and sol-gel processing [13].

2. Nano/micro-structured materials

2.1 Nanostructured layered double hydroxides

Layered double hydroxides (LDHs) with the hydrotalcite-like structure are materials attracting interest to many research groups due to their use in many different fields, such as anion scavengers, catalysts, catalyst precursors, hosts for drugs controlled delivery, contaminant and radionuclide removal from acidic mine pit water etc. [14–16]. Layered double hydroxides (LDHs) are a class of anionic

Figure 1. (a) SEM micrograph of $\text{Mg-Al(OH)}_2\text{PO}_4$ 1; (b) SEM micrograph of $\text{Mg-Al(OH)}_2\text{PO}_4\text{PF}_6$ 2; (c) SEM micrograph of $\text{Ca-Al(OH)}_2\text{SO}_4$ 3; (d) SEM micrograph of $\text{Ca-Al(OH)}_2\text{PO}_4\text{PF}_6$ 4. Source: Khansi et al. [7].

clays with the structure based on brucite ($\text{Mg}(\text{OH})_2$)-like layers [17–21]. The lattice structure of LDHs with the general formula $[\text{M}_{2+1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}_n^-)_{x/n}\cdot y\text{H}_2\text{O}$, have a positively charged brucite-shaped layers, consisting of a divalent metal ion M^{2+} (e.g., Ca^{2+} , Zn^{2+} , Mg^{2+} , and Ni^{2+}) octahedrally surrounded by six OH^- hydroxyl groups [22–24]. The substitution of the M^{2+} metal with a trivalent M^{3+} cation gives rise to the periodic repetition of positively charged sheets (lamellas) alternating with charge-counter balancing A_n^- ions. According to Kovačević et al. [25], synthetic layered double hydroxides (LDHs) have been used as adsorbents and catalyst supports. The surface area and pore volume of LDHs can be increased by pillaring the interlayer with large organic and inorganic anions [19, 26, 27]. The combination of LDHs with negatively charged polymers can result in the formation of a hybrid layer component for the preparation of nano-hybrid thin films [28–30].

Figure 2.
Results for the removal of Fe^{2+} and Ca^{2+} ions from aqueous solutions by compounds 1–4. Source: Khansi et al. [7].

Figure 3.
(a) SEM micrograph of UCIM-1; (b) SEM micrograph of UCIM-2; (c) SEM micrograph of UCIM-3; (d) SEM micrograph of UCIM-4; (e) SEM micrograph of UCIM-5. Source: Ogar [37].

When LDHs which are formed by incorporating both divalent and trivalent metal ions into the octahedral lattice, are calcined at higher temperature, mixed metal oxide nanomaterials are formed with improved catalytic activity [31–33]. LDHs are also used as supports in bio-nanocomposites for medical applications [34].

Khansi et al. [7] synthesized four metal-aluminum layered double hydroxides (LDHs): $\text{Mg-Al}(\text{OH})_2\text{PO}_4$, **1**, $\text{Mg-Al}(\text{OH})_2\text{PO}_4\text{PF}_6$, **2**, $\text{Ca-Al}(\text{OH})_2\text{SO}_4$, **3** and $\text{Ca-Al}(\text{OH})_2\text{PO}_4\text{PF}_6$, **4**, by co-precipitation method followed by mild hydrothermal processing at 60°C . In **Figure 1**, we present the SEM micrographs of the as-synthesized LDHs. The synthesized nano-/microstructured LDHs of $\text{Mg-Al}(\text{OH})_2\text{PO}_4$, **1** (**Figure 1a**), $[\text{Mg-Al}(\text{OH})_2\text{PO}_4\text{PF}_6]$, **2** (**Figure 1b**) and $[\text{Ca-Al}(\text{OH})_2\text{PO}_4\text{PF}_6]$ **4** (**Figure 1d**) have their Mg-O-Al-OH and Ca-O-Al-OH layers intercalated with PO_4^{3-} and/or $[\text{PO}_4\text{PF}_6]^{4-}$ anions. Their micrographs consists of uniformed nano/microspheres of M-Al layered double hydroxides, while the Ca-O-Al-OH layer intercalated with SO_4^{2-} anions (**Figure 1c**) consisted of hexagonal nano-/microplates.

The results of the column adsorption studies showed that there is significant potential for using the synthesized nanostructured LDHs as nano filters in removing ions responsible for scale formation in oil wells. According to their report, compounds **1** and **2** removed Fe^{2+} with greater efficiency, while all the synthesized LDHs nanostructures effectively removed Ca^{2+} from the oil wells as shown in **Figure 2**.

2.2 Nanostructured metal phosphonates

A surfactant-assisted synthesis route to prepare nanometer-sized metal phosphonate particles for use as an inhibitor in porous media for scale control has been reported [35, 36]. In their method, aqueous solution of calcium chloride and zinc chloride were mixed with basic solution containing phosphonate scale inhibitors such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP) in the presence of sodium dodecyl sulfate as surfactant. Following similar procedure, Ogar [37] used hydrothermal technique in the preparation of five nanostructured metal phosphonates. In a typical synthesis, 1.5 g of sodium dodecyl sulfate (SDS) was added to 40 cm^3 of 0.25 M solution of the CaCl_2 . This was accompanied by constant stirring for 20 min ($\text{pH} = 6$). Then 25 cm^3 of 1.0 M solution of phenylphosphonic acid ($\text{pH} = 2$) was added dropwise to the above solution with constant stirring. The mixture ($\text{pH} = 3$) was allowed to stir for 1 h after which it was transferred into ACE glass tubes and heated for 8 h at a temperature of 120°C . This was followed by centrifugation at 2000 RPM for 20 min, filtration and drying of the nanomaterials in an electric incubator at 80°C . The product obtained was designated UCIM-1 (University of Calabar Inorganic Material). Similar procedure was employed in the synthesis of UCIM-2, UCIM-3, UCIM-4 and UCIM-5 with different complexing agent as aminomethylphosphonic acid (AmMePhA), 4,4'-biphenyl-bis-phosphonic acid (BBPhA) and different metal salt such as zinc acetate.

The SEM micrographs of UCIM-1 and UCIM-2 showed clusters of micro-rods (**Figure 3a** and **b**). The zinc phosphonates prepared in the presence of surfactant, UCIM-3 consisted of particles in the size range of 30–100 nm (**Figure 3c**), whereas UCIM-4 and UCIM-5 prepared without the surfactant consists of monodispersed nanoballs (**Figure 3d** and **e**). The synthesized nanostructured zinc and calcium phosphonates were applied in the removal of scale-forming ions from aqueous solution. A similar procedure reported for LDHs [7] was used. Small amount of glass wool was first introduced into the syringe followed by 0.2 g of the nanoparticles. Two molar solution of CaCl_2 was then introduced. The set-up was left for 12 h

during which the solution eluted was collected in sample bottles and analyzed using AAS. This was repeated for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The removal efficiency of Fe^{2+} and Ca^{2+} by metal phosphonate nanoparticles (UCIM-n) in percentage was calculated using the formula: efficiency (%) = C_e/C_o (C_o = initial concentration of the ions, C_e = eluted concentration of the ions after passing through the packed column).

The removal efficiency of scale forming ions in oil wells by the synthesized metal phosphonate nanoparticles was studied with the help of atomic absorption spectroscopic technique. The removal efficiency of Ca^{2+} and Fe^{2+} ions are presented in **Tables 1** and **2** respectively. The results showed that the surfactant-assisted zinc nanostructured material (UCIM-4) removed up to 92.04% of Fe^{2+} compared to UCIM-5 prepared without surfactant, which showed only 75.88% removal. The compound UCIM-4 adsorbed Ca^{2+} the most, followed by surfactant-assisted UCIM-1 Ca-nanoparticles with a very high percentage adsorption of 94.29 as presented in **Figure 4**.

2.3 Metal/bimetallic/metal-oxide nanoparticles

There are a number of interesting reports on the use of ionic liquids as a solvent and/or stabilizing agent in the synthesis of metal/metal-oxide nanoparticles. The interest is not only due to the fact that ILs can form extended hydrogen-bond networks at the liquid state, but also for their nanostructural organization which is being used as a driver for spontaneous formation of nanostructured materials [38] Taubert and co-workers [39] reported on the effects of a set of ILs based on the 1-ethyl-3-methylimidazolium cation and different anions on the formation of gold nanoparticles. They demonstrated that the nature of the ionic liquid anion was crucial in the synthesis of the gold nanoparticles. For instance, anions such as methanesulfonate (MS) and trifluoromethanesulfonate (TfO) stabilized the formation of particles in the size range of 5–7 nm at low temperature, whereas with ethyl

Nanoparticles	Initial amount (ppm)	Amount eluted (ppm)	Amount adsorbed (ppm)	Percentage adsorption
UCIM-1	7.7780	0.4438	7.3342	94.29
UCIM-2	7.7780	1.1512	6.6268	85.20
UCIM-3	7.7780	1.0251	6.7529	86.82
UCIM-4	7.7780	0.5729	7.2051	92.63
UCIM-5	7.7780	0.2399	7.5381	96.92

Table 1.
Removal efficiency of Ca^{2+} by the synthesized metal phosphonate nanoparticles (source: Ogar [37]).

Nanoparticles	Initial amount (ppm)	Amount eluted (ppm)	Amount adsorbed (ppm)	Percentage adsorption
UCIM-1	9.8526	4.1779	5.6747	57.60
UCIM-2	9.8526	5.1040	4.7486	45.46
UCIM-3	9.8526	5.3979	4.4547	45.21
UCIM-4	9.8526	0.7843	9.0683	92.04
UCIM-5	9.8526	0.2399	7.5381	96.92

Table 2.
Removal efficiency of Fe^{2+} by the synthesized metal phosphonate nanoparticles (source: Ogar [37]).

Figure 4.

Bar chart showing percentage adsorption of Ca^{2+} and Fe^{2+} by the different metal phosphonate nanoparticles. Source: Ogar [37].

sulfate (ES), polydispersed particles in the size range 15–20 nm were formed at all reaction temperature. In their report, they concluded that specific IL-gold interactions were responsible for the formation of gold particles with an IL-specific shape, size, and aggregation behavior.

Ayi et al. reported on a wet chemical approach in synthesizing titanium nanoparticles in imidazolium-based ionic liquids (ILs) under reducing conditions [40]. It was established that nanosize particles were formed with some ILs being adsorbed on the nanoparticles, thus providing the needed stabilization.

In continuation of the work on anion effects on nanoparticles formation, stable Mo and molybdenum oxide nano- and microparticles were synthesized in ILs with a variety of anions under reducing conditions by Ayi and co-workers [41]. XRD and TEM revealed a strong influence of the IL anion on the particle sizes, shapes, and crystal structures. The influence of the IL cation and the reaction temperature was found to be much less pronounced.

Very recently, Ayi's research group has used plant extracts (*Kigelia africana* fruits) to prepare silver nanoparticles and copper-silver bimetallic nanostructures and their antimicrobial potentials evaluated [42]. The aqueous extract of *Kigelia africana* was utilized in the synthesis of both metallic and bimetallic nanoparticles without additional stabilizing agent. The investigation revealed that average particle size of 10 nm were formed and stabilized by the active components of the plant extract, which were adsorbed on the surface of the particles. The synthesized particles were found to inhibit the growth of both Gram-negative and Gram-positive bacteria more than any of antibiotics tested in the study. The bimetallic nanoparticles demonstrated effectiveness against *S. aureus* with maximum ZOI of 27 mm. Walter et al., made use of 1-ethyl-3-methylimidazolium acetate (EMIMOAC) and 1-butyl-3-methylimidazolium acetate (BMIMOAC) ionic liquids to prepare cobalt nanoparticles (CoEMIMOAC or CoBMIMOAC) via chemical reduction method [43]. The SEM and UV-Vis techniques confirmed the formation of nanoparticles (**Figure 5**). There was no difference between the nanocrystals formed in EMIMOAC or BMIMOAC indicating that the cationic part of the ionic liquid did not play significant role during nucleation and growth of the particles. The inhibition zone diameter (IZD) showed moderate susceptibility of the *Staphylococcus aureus* to CoBMIMOAC (15 mm) but high susceptibility to

CoEMIMOAC with a larger inhibition zone diameter of 23 mm. Gram-negative microorganism *E. coli* is moderately susceptible to both CoEMIMOAC (14 mm), and CoBMIMOAC (15 mm) (**Figure 6**).

Figure 5.
(a) SEM micrograph of cobalt nanocrystals prepared in EMIMOAC. Source: John et al. [43]; (b) SEM micrograph of cobalt nanocrystals prepared in BMIMOAC. Source: John et al. [43].

Figure 6.
Bar chart showing nanocrystals inhibition zone diameter for *Staphylococcus aureus* and *Escherichia coli*. Source: John et al. [43].

3. Conclusion

In this short review, the different protocols available for the synthesis of nanostructured layered double hydroxides and metal phosphonates formulated as UCIM-n have been discussed with their applications in the removal of scale forming ions from aqueous solutions. Reports of the work done in our research laboratory on green chemistry involving the use of plant extracts and ionic liquids as solvent and stabilizing agents in the syntheses of metal nanoparticles along with their antimicrobial activities have been presented.

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References

- [1] Caruso F, editor. *Colloids and Colloid Assemblies: Synthesis, Modification, Organization and Utilization of Colloid Particles*. Weinheim: Wiley VCH; 2004
- [2] Goldenberg S. Dispersant 'May Make Deep-Water Horizon Oil Spill more Toxic'. *The Guardian Newspaper*. 5 May 2010
- [3] Zahir F, Rizwi SJ, Haq SK, Khan RH. Low dose mercury toxicity and human health. *Environmental Toxicology and Pharmacology*. 2005;**20**:351-360
- [4] USEP Agency. *Nanotechnology for site remediation fact sheet*. 2009
- [5] Moffat G, Williams RA, Webb C, Stirling R. Selective separations in environmental and industrial processes using magnetic carrier technology. *Minerals Engineering*. 1994;**7**(8):1039-1056
- [6] Ashishie PB, Inah BE, Ayi AA. Evaluation of antimicrobial activity of ionic liquid-assisted synthesis of monometallic silver and bimetallic copper-silver nanoparticles. *International Journal of Sciences*. 2018;**7**(5):25-31
- [7] Khansi EE, Anyama CA, Ayi AA, Onwuka JC. Use of nanostructured layered double hydroxides as nano filters in the removal of Fe^{2+} and Ca^{2+} ions from oil wells. *Advances in Materials Science and Engineering*. 2018;**2018**:1-7. DOI: 10.1155/2018/5306825
- [8] Cheng H, Ma J, Zhao Z, Qi L. Hydrothermal preparation of uniform nanosize rutile and anatase particles. *Chemistry of Materials*. 1995;**7**:663-671
- [9] Ge S, Shi X, Sun K, Li C, Uher C, Baker JR, et al. Facile hydrothermal synthesis of iron oxide nanoparticles with tunable magnetic properties. *The Journal of Physical Chemistry*. 2009;**C113**:13593-13599
- [10] Kitamura Y, Okinaka N, Shibayama T, Mahaney OOP, Kusano D, Ohtani B, et al. Combustion synthesis of TiO_2 nanoparticles as photocatalyst. *Powder Technology*. 2007;**176**:93-98
- [11] Jones AC, Chalker PR. Some recent developments in the chemical vapour deposition of electroceramics oxides. *Journal of Physics D: Applied Physics*. 2003;**36**:R80-R95
- [12] Wang W, Lenggoro IW, Terashi Y, Kim TO, Okuyama K. One step synthesis of titanium oxide nanoparticles by spray pyrolysis of organic precursors. *Materials Science and Engineering B*. 2005;**123**:194-202
- [13] Watson S, Beydoun D, Scott J, Amal R. Preparation of nanosized crystalline TiO_2 particles at low temperature for photocatalysis. *Journal of Nanoparticle Research*. 2004;**6**:193-207
- [14] Douglas G, Shackleton M, Woods P. Hydrotalcite formation facilitates effective contaminant and radionuclide removal from acidic uranium mine barren lixiviant. *Applied Geochemistry*. 2014;**42**:27-37
- [15] Douglas G. Contaminant removal from acidic mine pit water via in situ hydrotalcite formation. *Applied Geochemistry*. 2014;**51**:15-22
- [16] Balsamo N, Mendieta S, Olivab M, Eimer G, Crivello M. Synthesis and characterization of metal mixed oxides from layered double hydroxides. *Procedia Materials Science*. 2012;**1**:506-513
- [17] Cavani F, Trifirò F, Vaccaria A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catalysis Today*. 1991;**11**:173-301
- [18] Rives V. *Layered Double Hydroxides: Present and Future*. New York, NY, USA: Nova Science Publishers; 2001

- [19] Khan AI, O'Hare D. Intercalation chemistry of layered double hydroxides: Recent developments and applications. *Journal of Materials Chemistry*. 2002;**12**:3191-3198
- [20] Sideris PJ, Nielsen UG, Gan Z, Grey CP. Mg/Al ordering in layered double hydroxides revealed by multinuclear NMR spectroscopy. *Science*. 2008;**321**:113-117
- [21] Scarpellini D, Leonardi C, Mattoccia A, Di Giamberardino L, Medaglia PG, Mantini G, et al. Solution-grown Zn/Al layered double hydroxide nanoplatelets onto Al thin films: Fine control of position and lateral thickness. *Journal of Nanomaterials*. 2015;**2015**:1-8
- [22] Yang M, Tuckley E, Buffet JC, O'Hare D. Rapid efficient phase pure synthesis of Ca_2AlNO_3 layered double hydroxide. *Journal of Materials Chemistry*. 2016;**A4**:500-504
- [23] Everaert M, Warrinnier R, Baken S, Gustafsson JP, De Vos D, Smolders E. Phosphate-exchanged Mg-Al layered double hydroxides: A new slow release phosphate fertilizer. *ACS Sustainable Chemistry & Engineering*. 2016;**4**(8):4280-4287
- [24] Bao W, Wang J, Wang Q, O'Hare D, Wan Y. Layered double hydroxide nano transporter for molecule delivery to intact plant cells. *Scientific Reports*. 2016;**6**:26738
- [25] Kovačević D, Džakula BN, Hasenay D, Nemet I, Rončević S, Imre Dékány I, et al. Adsorption of arsenic on MgAl layered double hydroxide. *Croatica Chemica Acta*. 2013;**86**(3):273-279. DOI: 10.5562/cca2283
- [26] Rives V, Ulibarri MA. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. *Coordination Chemistry Reviews*. 1999;**181**(1):61
- [27] Kopka H, Beneke K, Lagaly G. Anionic surfactants between double metal hydroxide layers. *Journal of Colloid and Interface Science*. 1988;**123**:427-436
- [28] Hornok V, Erdőhelyi A, Dékány I. Preparation ultrathin membranes by layer-by-layer deposition of layered double hydroxide (LDH) and polystyrene sulfonate (PSS). *Colloid & Polymer Science*. 2005;**283**:1050-1055
- [29] Aradi T, Hornok V, Dékány I. Layered double hydroxide for ultrathin hybrid film preparation using layer-by-layer and spin coating methods. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*. 2007;**319**:116-121
- [30] Tsyganok AI, Tsunoda T, Hamakawa S, Suzuki K, Takehira K, Hayakawa T. Dry reforming of methane over catalysts derived from nickel-containing Mg-Al layered double hydroxides. *Journal of Catalysis*. 2003;**213**:191-203
- [31] Choy J-H, Choi S-J, Oh JM, Park T. Clay minerals and layered double hydroxides for novel biological applications. *Applied Clay Science*. 2007;**36**:122-132
- [32] Bhattacharjee S, Dines TJ, James AA. Synthesis and application of layered double hydroxide hosted catalysts for stereoselective epoxidation using molecular oxygen or air. *Journal of Catalysis*. 2004;**225**:398-407
- [33] Aisawa S, Ohnuma Y, Hirose K, Takahashi S, Hirahara H, Narita E. Structural characterization of arsenate ion exchanged MgAl-layered double hydroxide. *Applied Clay Science*. 2005;**28**:137-145
- [34] Yang QZ, Yang J, Zhang CK. Synthesis and properties of cordycepin intercalates of Mg-Al-nitrate layered double hydroxides. *International Journal of Pharmaceutics*. 2006;**326**:148-152

- [35] Zhang P, Shen D, Fan C, Kan AT, Tomson MB. Surfactant-assisted synthesis of metal-phosphonate inhibitor nanoparticles and its transport in porous media. In: A Conference Paper presented at the 2009 SPE International Oilfield Scale Conference in Woodland; SPE 1211552; 20-22 April 2009; Texas; 2009. pp. 1-12
- [36] Shen D, Zhang P, Kan AT, Fu G, Farrell J, Tomson MB. Control placement of scale inhibitors in the formation with stable Ca-DTPMP nanoparticles suspension and its transport porous media. In: A Conference Paper presented at the 2008 SPE International Oilfield Scale Conference in Aberdeen, UK; 28-29 May; SPE 114063; 2008
- [37] Ogar JO. Surfactant assisted synthesis of metal phosphonate nanoparticles: Structural characterization and application as oil field scale inhibitors [MSc thesis]. Nigeria: University of Calabar; 2015
- [38] Bansal V, Bhargava SK. Ionic liquids as designer solvents for the synthesis of metal nanoparticles. In: Kokorin A, editor. Ionic Liquids: Theory, Properties, New Approaches. Croatia: InTech; 2011
- [39] Khare V, Zhonghao Li Z, Alexandre Manton A, Ayi AA, Sonkaria S, Voelk A, et al. Strong anion effects on gold nanoparticle formation in ionic liquids. *Journal of Materials Chemistry*. 2010;**20**:1332-1339
- [40] Ayi AA, Khare V, Strauch P, Girard J, Fromm KM, Taubert A. On the chemical synthesis of titanium nanoparticles from ionic liquids. *Monatshefte fuer Chemie*. 2010;**141**:1273-1278. DOI: 10.1007/s00706-010-0403-4
- [41] Ayi AA, Anyama CA, Khare V. On the synthesis of molybdenum nanoparticles under reducing conditions in ionic liquids. *Journal of Materials*. 2015;**2015**:1-7. DOI: 10.1155/2015/372716
- [42] Ashishie PB, Anyama CA, Ayi AA, Oseghale CO, Adesuji ET, Labulo AH. Green synthesis of silver mono metallic and copper-silver bimetallic nanoparticles using *Kigelia africana* fruit extract and evaluation of their antimicrobial activities. *International Journal of Physical Sciences*. 2018;**13**(3):24-32. DOI: 10.5897/IJPS20174689
- [43] John WE, Ayi AA, Anyama CA, Ashishie PB, Inah BE. On the use of methylimidazolium acetate ionic liquids as solvent and stabilizer in the synthesis of cobalt nanoparticles by chemical reduction method. *Advanced Journal of Chemistry-Section A*. 2019;**2**(2):175-183