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Recent Advances in Synthesis of Active Copper-Silver (Cu-Ag) Alloyed by Expeditious of N-Arylation in Aqueous Media: A Green Approach

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Abstract
Copper-based alloy nanoparticles (NPs) have in recent times prompted research interests in the advance of economical and high-concert bimetallic catalysts with large numbers of industrial applications i.e., catalysis, development of supercapacitors, infrared-based filters, magnetic storage media, sensors, and semiconductors. The present work focused on the combination of alloyed made by Cu-Ag bimetallic nanoparticles using an electrochemical method. The outcomes revealed that the execution of the reaction at 60ºC in aqueous media and solvent-free conditions promotes a significant increase in yield. The active Cu-Ag nanoparticles were synthesized using purely green techniques for C-N, C-H, and C-C coupling. The catalytic applications of Cu-Ag bimetallic nanoparticles with different ratio have been found by N-arylation. The electrochemically derived method for the synthesis of Cu-Ag bimetallic nanoparticles has not needed thorough conditions and toxic substances.

Keywords: Active Cu-Ag alloy nanoparticles, bimetallic catalysts, N-arylation, electrochemical green NPs synthesis.

1. Introduction

Technological advancements have stimulated revolutionary advantages over conventional methods and devices that have the potential to change material design and manufacturing technology. Richard Feynman initiated Nano-sciences in 1959 which depends on the variety of strategies to reconstruct and design materials (i.e., atom by atom and molecule by molecule) at the nanoscale. These nanoscale materials have defined sizes and shapes depending upon the desired properties for target application in the fields of Science and Engineering. The recent technological advancements contribute to the hassle-free design of desired structures or devices with nanosized particles (≤ 100 nm in size). Nanotechnology is the art of designing novel materials at the Nano-domain with extraordinary physicochemical properties. The nanomaterial concepts and ideas are originally derived from interdisciplinary efforts between Chemistry, Physics, and Engineering. The structural arrangement of atoms and length scales of materials act as potential parameters to tune variation in material properties [1]. The metallic NPs can be categorized as mono-metallic, bi-metallic, and tri-metallic depending on the lots of constituent metallic parts. Recently, monometallic, bimetallic, and trimetallic materials have been used to synthesize nanomaterials with precise control over morphology and dimension. The alloy nanoparticles have more than one metal component (e.g., bimetallic and trimetallic) cross-linked together and reflect synergistic characteristics. However, certain non-metallic NPs e.g., carbon nanotubes, have organic molecules and have interesting electrical behavior.

The heterocyclic aryl-nitrogen bonds are ubiquitously utilized in industrial processes. Transition metal (e.g., silver copper, nickel, and mercury) derived transformations are mostly used for N-arylation. The Ullmann condensation reaction is generally utilized for the coupling of aryl-halides with amines [2]. Alloying of Cu (potent electrical conductivity and low electrical migration) with Ag (high electrical conductivity with high electromigration) has been reported as an significant approach to impoverish electrical performance [3]. Bimetallic Ag-Cu nanoalloys have been reported as potent antibacterial nature [4]. The bimetallic catalyst has great significance in petroleum, energy, chemicals, polymer, food, and pollution control sectors to make chemical reactions thermodynamically feasible. A catalyst is a chemical essence that increases the rate of accomplishment of chemical equilibrium. The catalyst often lowers the activation energy to make chemical reactions more favorable and faster. The catalyst is classified into heterogeneous and homogenous. The heterogeneous catalyst facilitates heterogeneous catalysis reactions wherever the catalyst and reactants are in dissimilar phases (e.g., catalysis of reactions in gases or liquid phase) using solid catalysts. The coupling reactions of amines and aryl halide derivatives in the incidence of heterogeneous catalyst such as Cu-Ag at the temperature between 60-80 ºC [5]. On the counterpart, the homogeneous catalyst boosts up the chemical reaction where the reactants and catalyst are in

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the same phase. Mostly, the industrial process drives homogeneous catalytic processes in the liquid phase e.g., ester hydrolysis by acid-base catalysts, polyethylene synthesis by organometallic catalysts, certain enzyme-catalyzed reactions, and so on [6]. The Ag-Cu bimetallic alloy NPs are characterized by UV-Visible spectroscopy, fluorescence based methods and mostly by using XRD [3].

Rahman, L. *et al.*, 2012 prepare and spectroscopic characterization of Ag-Cu alloy nanoparticles synthesized in a range of conditions and ration. The electrocatalyst mostly speeds up the electrochemical reaction. The heterogeneous electrocatalyst e.g., copper or nanoparticles, and homogeneous electrocatalyst such as enzyme-based electrocatalyst generally assist electron transfer between reactants. Electrocatalyst has tremendous opportunities in research application such as corrosion science, electro-analytical sensors, electro-organic synthesis, and energy conversion. To enhance the utility of electro-catalytic metals, it is typically dispersed as nanoparticles over the conducting support material. The performance of nano electro-catalytic metals is often depending upon certain factors e.g., the nature of electro-catalytic particles in terms of materials, surface structure, shape, size, nature of the support material surface structure, interaction between nano electro-catalytic metals, electron transfer efficacy and hold up material. The bimetallic catalysts e.g., Cu-Ag, Ni-Ag, Fe-Cu, and Fe-Co provide better catalytic activity and selectivity than that of monometallic. To enhance bimetallic catalysis, ensemble effects, and electronic effects have been proposed [7].

The idea of ensemble effect relies on the fact that catalyst selectivity relies on surface composition and electronic effect states that the modification of chemisorptions and reaction properties of adsorbents affect the most. The bimetallic catalysts have been potentially used as catalysis in electronics, photonics, labeling, and sensing due to the synergistic effects between metals. The lattice invariables of Cu (0.409 nm) and Ag (0.361 nm) are dissimilar which makes a production of Cu-Ag alloy more difficult[7]. A competitive alternative, an electrochemical reaction-based green synthesis of Cu-Ag uniform alloy nanostructures was attempted in the present research work. The research investigation explored the influences of copper predecessors on the composition and structure of the absolute product, the catalytic property of Cu-Ag bimetallic nanoparticles.

2. Material and Method

The present work was focused on the development of green synthetic processes for active Cu-Ag-promoted mild and expeditious N-arylation with aryl halide using photochemical reaction at 60-80 ºC in aqueous media and solvent. Major materials required were CuO (Merck specialties), $AgNO_3$ (Sigma-Aldrich), Graphite electrode (CRD production), DC meter-ACCESS (Model No.-ACCESS 53C, Part Number-AT_033), multimeter-electric DT33D, and AC-DC multimeter transistor probe for electronic.

2.1. Synthesis of Active Copper-Silver (Cu-Ag) Alloy

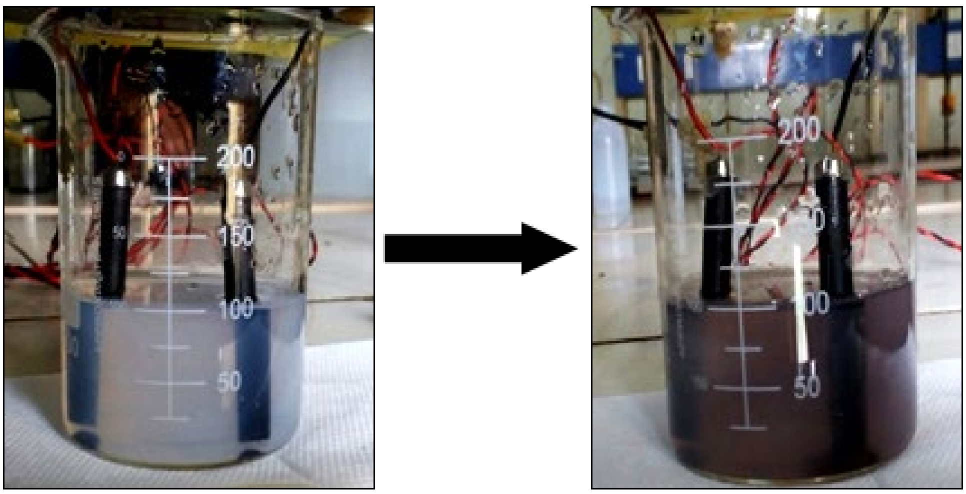
An equal concentration of CuO and $AgNO_3$ solution was prepared in deionized (DI) water. Two parallel graphite electrodes (black, 99.9% pure, 10 mm diameter, 100 mm length) were dipped in the solution at a distance of 7.0 cm and connected to a DC meter. The current supplied by the DC meter was an input voltage of AC 100-240v, 50-60Hz/100mAmp, and an output voltage of DC 5.0v/350 mAmp. After the current flow, the bubbles indicated that the movement of ions and color change of solution (black to light blue successively) confirmed the initiation of the reaction. The electrochemical reaction was completed within 5-8 hours. The prepared alloy was deposited on the anode and surface of the beaker and it was carefully separated and subjected to oven drying at 60ºC for 1 h. Setup for the synthesis of active Copper-Silver (Cu-Ag) alloy and chemical reaction are shown in Fig.1 and Fig. 2 respectively.

Electrochemical Reaction

$Cu\ (II) + 2e^- \longrightarrow Cu\ (0)\quad E_0 = -0.257$

$Ag^+ + e^- \longrightarrow Ag\ (0)\quad E_0 = +0.799$

$Cu\ (II) + Ag\ (I) \longrightarrow Cu\text{-}Ag\ (alloy)$



CuO and AgNO3 solution **Cu-Ag Nanoparticle**

Fig 1: Setup for the synthesis of active Copper-Silver (Cu-Ag) alloy

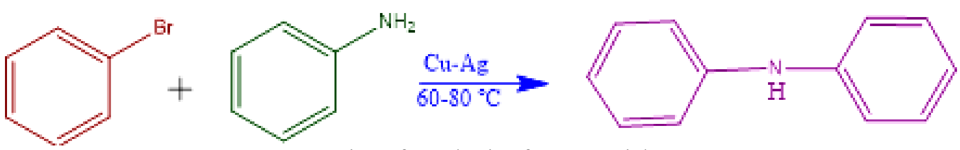


Fig 2: Reaction of Synthesis of Nanoparticle Cu-Ag

2.2. Characterization of Cu-Ag Nanoparticles

An oven-dried crystal structure of Cu-Ag alloy nanoparticles was characterized by using X-ray diffraction made of XRD, Rigaku Ultime IV with Cu Kα radiation ($\lambda = 1.54056 nm$). Scans of 2 θ were taken in the range of 30°-80° at a scanning rate of 1.2 degree per min. The signify crystallite size of the catalyst was expected by using the Williamson-Hall method by pass on to the most significant peak (111). The XRD pattern of Cu-Ag bimetallic nanoparticles was generated between angle and intensity.

2.3. Assessment of Catalytic Possessions of Cu-Ag Bimetallic Nanoparticles

Catalyst (Cu-Ag bimetallic NPs) was taken in the round bottom flask (100 ml) and added 10 ml DI water and kept in a magnetic stirrer for 0.5 h. Then, bromobenzene and organic compound (consisting of amines derivative) were gently mixed. The reaction was allowed for 7 h at 60^0C on a magnetic stirrer. The reaction progress and product formation were supervised by silica gel-layered thin-layer chromatography (TLC). After the total conversion of starting materials into a product, the catalyst was separated by Whatman filter paper, and the organic solvent was removed by Rota-vapor. Then, washed with ethanol and recrystallized. The solution was left for 4-5 days for crystal formation.

3. Results and Discussion

Present research work has emphasized the evaluation of catalytic properties and characterization of Cu-Ag bimetallic nanoparticles. In this study the synthesis of nanoparticles by Cu-Ag bimetallic through electrochemically at 60ºC. The solid crystal collected from the anode and surface of the beaker was further subjected to structural analysis after oven drying. The structural characteristics of Cu-Ag bimetallic nanoparticles were analyzed by XRD. The characteristic diffraction peaks 35.85, 38, 44, 64.35, and 78 were observed for Cu-Ag a theta with corresponds to crystallographic planes of 211, 111, 200, 220, and 311 respectively (Fig. 3). The interplanar distance $d_{(hkl)}$ was calculate using Braggs equation. The peaks were well indexed to face centered cubic (FCC) phase of crystalline Ag (JCPDS card no.4-783) and FCC phase of crystalline Cu (JCPDS card no.4-836). The peaks of nanoparticles Cu-Ag were well indexed to FCC. A noteworthy intense peak was observed at plane 111.

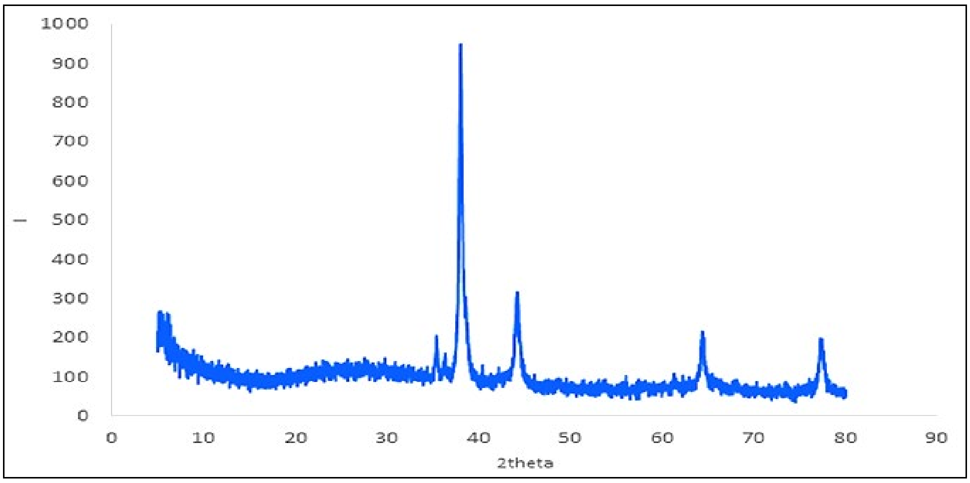


Fig 3: XRD pattern Cu-Ag bimetallic NPs

Table 1: XRD parameter of Cu-Ag bimetallic NPs

S. No.	2 Θ	λ (A^0)	$d_{(hkl)}$	($h^2+k^2+l^2$)
1.	35.85	1.54	0.900	$2^2+1^2+1^2= 6$
2.	38	1.54	1.25	$1^2+1^2+1^2= 3$
3.	44	1.54	1.11	$2^2+0^2+0^2= 4$
4.	64.35	1.54	0.855	$2^2+2^2+0^2= 8$
5.	78	1.54	0.789	$3^2+1^2+1^2= 11$

3.1. Assessment of Catalytic Properties of Cu-Ag Bimetallic NPs

The catalytic properties of Cu-Ag bimetallic nanoparticles were assessed on four different reactions. The reaction products viz., 2-Hydroxy, N-phenylbenzamide, N-phenyl pyridine, 2-Amine, N-(4-chlorophenyl), benzenamine, and N-biphenyl amine, were observed as reaction products and confirmed by TLC (Fig. 4). The reactions and products are depicted in Table 2.

Fig 4(a): 2-Hydroxy, N-phenylbenzamide

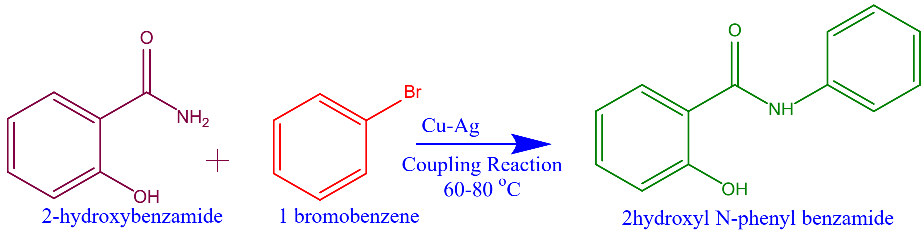
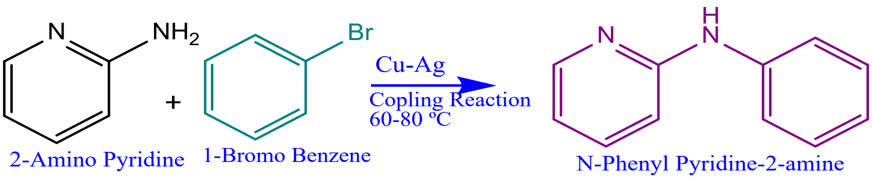
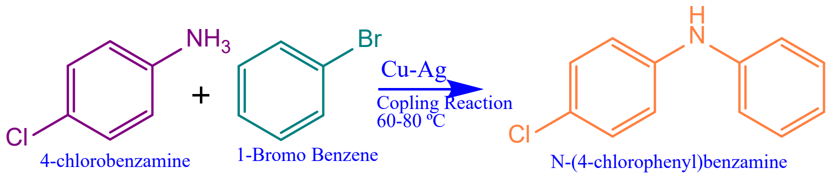
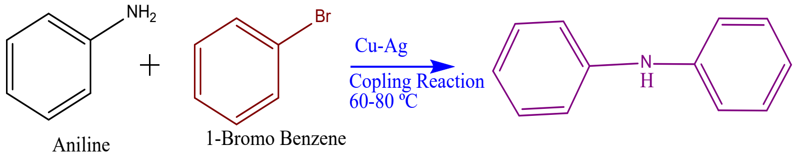
Fig 4(b): N-phenyl pyridine

Fig 4(c): N-(4-chlorophenyl), benzenamine

Fig 4(d): N-biphenyl Amine

Fig 4: TLC plates with resection products

Table 2: Application of Catalytic properties of Cu-Ag bimetallic Nanoparticles on various reactions

S. No.	Reaction and product	
1.	**2-hydroxybenzamide and bromo benzene**	
		
	Melting Point: 159°C Reaction time: 7.0 h	2-Hydroxy, N-phenylbenzamide
2.	**2-Amonopyridine and bromo benzene**	
		
	Melting Point: 109 °C Reaction time: 5.5 h	N-phenylpyridine, 2-Amine
3.	**4-chlorobenzamine and bromobenzene**	
		
	Melting Point: 76 °C Reaction time: 6.5 h	N-(4-chlorophenyl), benzenamine
4.	**Aniline and bromo benzene**	
		
	Melting Point: 53 °C Reaction time: 6.0 h	N-biphenyl Amine

Cu-Ag alloy nanoparticles have attract research interests due to its cost effective and high-performance catalytic action in numerous industrial applications along with certain biological applications. The biological application includes antimicrobial potency. Previously bimetallic Ag-Cu nanoalloys have been reported as potent antibacterial nature [4]. Kushwah *et al.* (2019) reported that the Ag-Cu nanoprticle alloy exhibited rapid photocatalysis of dye namely Methylene Blue and it is act as antibacterial agent against namely *Escherichia coli* and *Staphylococcus aureus* bacteria [8]. Chang *et al.* (2019) characterize Ag-Cu alloy nanoparticles for antimicrobial tenders [9]. N-Acylation of NPs are eagerly applied in agriculture, chemistry, biological sciences, and pharmaceutical industries [10]. The present work focused on synthesis of alloyed Cu-Ag bimetallic nanoparticles using an electrochemical method and its N-acylation for wider range of applications. The present study claimed that the execution of the reaction at 60ºC in aqueous media and solvent-free conditions promotes a significant increase in yield. The active Cu-Ag NPs were synthesized using purely green techniques for C-N, C-H, and C-C coupling in present research work. The advantage associated with electrochemically derived technique for the preparation of Cu-Ag bimetallic nanoparticles is that it has not obligatory thorough conditions and toxic agents because it is an ecofriendly for the production of active bimetallic catalysts. The transition metal-based n-arylation-mediated intermediate compounds have been reported to act as biologically active substances and have extensive application in the pharmaceutical, organic and agrochemical synthesis sectors [11]. The reaction products viz., 2-Hydroxy, N-phenylbenzamide (from 2-hydroxybenzamide and bromo benzene), N-phenyl pyridine 2-Amine (from 2-

Amonopyridene and bromo benzene), N-(4-chlorophenyl) benzenamine (from 4-chlorobenzamine and bromobenzene) and N-biphenyl amine (from aniline and bromo benzene), were observed as reaction products using Cu-Ag bimetallic NPs.

Aronson (2016) reported that the halogenated 2-Hydroxy, N-phenylbenzamide (Salicylanilide) has antiparasitic action in animal [12]. Li *et al*. (2020) claimed that the derivatives of N-phenyl-4-(pyridine-acylhydrazone) benzamide act as a effective antitumor agent for against multiple myeloma [13]. N-(4-chlorophenyl) benzenamine has certain pharmaceutical applications mentioned in Chemical book (chemical book, 2023). Researches explored that the 4-aminobiphenyl has been revealed as carcinogen (cause bladder cancer in humans) by damaging DNA (Babu, 1996) [14]. Thereby, the products synthesized by Cu-Ag nanoprticles N-acylation have possessed tremendous biological applications and could further be explored under *in-silico* examinations for biological systems.

4. Conclusion

The present research work was experimentally characterizing the structure and catalytic properties of Cu-Ag bimetallic nanoparticles. The synergistic catalytic action of Cu-Ag participate a crucial responsibility in the activation of an Amine derivative. The outcomes revealed that the bimetallic Cu-Ag nanoparticles have higher and expeditious catalytic activity compare to monometallic nanoparticles. This catalyst is used in N-arylation and their C-N bond forming occurs. The ligand-promoted bimetallic catalysis is considered an influential strategy for unreactive bond cleavage because targeted ligand coordination can modify the structural and reaction efficacy of metal catalysts along with the activation energy during catalysis. Hence, the future aspect of the present research outcome could be the study of targeted ligand coordination to enhance the catalytic efficacy of Cu-Ag bimetallic nanoparticles.

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