A facile synthesis of Cu–CuO–Ag nanocomposite and their hydrogenation reduction of *p*-nitrophenol

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Abstract

In this study, a nanocatalyst of Cu–CuO–Ag was synthesized by a facile chemical reduction method. By varying the amount of metallic precursor, different compositions of the Cu–CuO–Ag nanocomposite were synthesized, and their structural and morphological characterizations were carried out. The nanocomposites were used for the hydrogenation reduction of *p*-nitrophenol to *p*-aminophenol using sodium borohydride as the reducing agent. The catalytic activity of Cu–CuO–Ag nanocomposite had a catalytic activity that was 4.5 fold higher than that of Cu–CuO nanocomposite. The kinetic studies revealed pseudo-first order kinetics and the reduction reaction completed within four minutes. The maximum rate constant value of 0.565 min^{-1} was obtained for the composite prepared with a copper precursor to silver precursor ratio of 16:1. The developed Cu–CuO–Ag nanocomposite also showed excellent catalytic stability. There was no noticeable decrease in catalytic activity even after four cycles. Furthermore, we optimized the catalyst amount required for the reduction reaction.

Keywords Copper · Silver · *p*-nitrophenol · Catalysis

1 Introduction

Bimetallic nanoparticles based on copper such as Cu–Ni nanoparticles [1], Cu–Co nanoparticles [2], and Cu–Pd [3] have attracted increasing interest during recent years than monometallic Cu nanoparticles in catalytic reactions. Bimetallic nanostructures of Cu–Ag also gain significant attention due to their optical, electrochemical as well as electronic properties [4–6]. The major problem in the synthesis of Cu–Ag heterostructures is their high lattice mismatch (the lattice constant values of Cu and Ag are 0.409 nm and 0.361 nm respectively) which results in high interfacial energy [7]. Reports suggest that in bimetallic Cu–Ag nanostructures, mixing of copper with silver will significantly

enhance the migration of copper ions [8, 9]. Methods for the synthesis of Cu–Ag alloyed nanoparticles include wet chemical reduction, micro emulsion, sonochemical methods, and microwave methods [10–13]. Although silver is preferred for conductive metallic nanostructures, its higher material cost is not always conducive. A suitable low cost alternative to silver is copper, which is commonly available, and the electrical resistivity of copper ($1.7 \times 10^{-6} \Omega \text{ m}$) is only slightly less than that of silver ($1.6 \times 10^{-6} \Omega \text{ m}$) [14]. Stability of the Cu nanomaterials can be improved by composite formation as well as coating the surface of the Cu with Ag shell. Reports suggest that the incorporation of silver into other metallic surfaces will also effectively improve its catalytic efficiency due to the formation of metal–silver electronic junctions

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[15, 16]. Silver can be coated using immersion or electroless plating method and sono-electrochemical processes [16]. Immersion coating process proceeds by galvanic displacement reaction, but a significant disadvantage is that the as synthesized samples are not suitable for high temperature applications. Besides, the immersion coating process generates silver shell with thickness in the range of several nanometers [17, 18].

Bimetallic transition metal nanocatalysts are proven to be efficient in different catalytic reactions due to potential synergistic effects between components as well as easy engineering of size, shape, composition and stability [19]. In this context, effective designing of bimetallic nanocatalysts of copper and silver will be of particular interest. There are previous reports on the synthesis of Cu–Ag alloyed nanostructures as potential catalysts for *p*-nitrophenol reduction; however, the proposed synthesis of Cu–Ag alloyed bimetallic nanoparticles takes a long time, at least 7 h [10]. Copper–silver (Cu–Ag) mixed nanoparticles loaded on the surface of cellulose acetate and plant supported bimetallic Cu–Ag have also been proven to be better nanocatalysts for the conversion of *p*-nitrophenol to *p*-aminophenol [7]. Prior research indicates that the catalytic efficiency of metal based nanocatalysts was significantly affected by the incorporation of metal oxide materials [20–22]. In 2017, Liang et al. and coworkers developed Cu/CuO–Ag composites and studied its efficiency on the removal of organic pollutants [23]. They carried out the synthesis by a two step process involving polyvinylpyrrolidone (PVP) and cetyl trimethyl ammonium bromide (CTAB). However, the reported method requires 12 h for the completion of the synthesis of the catalytic material. To the best of our knowledge, this is the only report demonstrating the synthesis of a nanocomposite consisting of Ag, Cu and CuO. In this paper, we have developed a Cu–CuO–Ag nanocomposite with a simple chemical reduction method possessing significantly reduced reaction time. By varying the amount of metallic precursor, different compositions of the Cu–CuO–Ag nanocomposites were synthesized and their structural and morphological characterizations were carried out. Finally, the catalytic efficiency of the synthesized Cu–CuO–Ag nanocomposite was analyzed by taking the hydrogenation reduction of *p*-nitrophenol using NaBH_4 as the model reaction. Furthermore, we have also optimized the catalyst amount required for the proposed reduction reaction.

2 Materials and method

2.1 Materials used

Cupric chloride (99%, LOBA Chemie, India), Silver nitrate (99.9%, Emparta, Merck), Ethylene diamine (98%, LOBA

Chemie, India), Hydrazine hydrate (80%, Emparta, Merck, India), Sodium borohydride (95%, Emparta, Merck, India), *p*-nitrophenol (4-NP) (98%, HIMEDIA, India), and copper metal powder (99.5%, SRL Chemicals, India) were used for the synthesis and characterization of material. All the chemicals were of analytical grade without further purification and all aqueous solutions were prepared with double distilled water.

2.2 Synthesis of Cu–CuO nanocomposite

In a typical synthesis of Cu–CuO nanocomposite, about 12 mL of 0.2 M CuCl_2 solution was dissolved in 1.5 M NaOH solution. To this 7.5 mL ethylene diamine (EDA) and 3 mL hydrazine hydrate (80%) were added with continuous stirring. The mixed solution was heated to 80 °C and maintained for 60 min without stirring. The prepared solid sample was separated by filtration and dried under IR lamp for 2 h.

2.3 Synthesis of Ag/Cu/CuO nanocomposite

About 0.8978 g AgNO_3 was added to 10 mL ethylene diamine solution and allowed to dissolve for 30 min at 60 °C. The completely dissolved solution was then poured into Cu–CuO nanocomposite dispersed in ethylene diamine in a three necked flask, which was then magnetically stirred for 2 h at 80 °C. The resulting solution was then centrifuged and washed several times with water and separated by several rounds of centrifugation. Similarly, we synthesized four different compositions of Ag–(Cu–CuO) nanocomposites by varying the molar ratios of Cu and Ag precursors in the ratios 4:1, 8:1, 16:1 and 32:1. The amount of reducing agent and capping agent was kept constant for all synthesis. In the following text, the synthesized samples are designated as CA1, CA2, CA3 and CA4 respectively.

2.4 Characterization

X-ray diffractometer model D8 Advance (Bruker) with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) was used for X-ray diffraction (XRD) analysis at a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 20 to 80. Surface morphologies and EDX analysis of the products were characterized using Hitachi SU8010 scanning electron microscope. UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan) was used for the catalytic study. The high-resolution transmission electron microscope analysis of the samples was carried out using TALOS F200S G2STEM.

2.5 Catalytic reduction of *p*-nitrophenol

The catalytic performances of the synthesized samples were analyzed using the aqueous phase hydrogenation of *p*-nitrophenol by sodium borohydride. In a typical catalytic study, 7.5 mg of the prepared catalyst was dispersed in a 10 mL of aqueous *p*-nitrophenol solution (1 mM) at room temperature. Then a freshly prepared aqueous solution of NaBH₄ (3 mL, 0.04 M) was added as the reducing agent. 2 mL of the above solution was immediately transferred into a quartz cuvette, diluted with distilled water and the absorption spectra measured at regular intervals of time. The change in the absorption spectrum was monitored using a UV-Vis spectrophotometer.

3 Results and discussion

3.1 Structural and morphological study

We have synthesized Cu–CuO–Ag nanocomposite by a two-step chemical reduction method. In the first step, spherical Cu nanoparticles were synthesized using an aqueous chemical reduction method. The schematic diagram of the synthesis of Cu–CuO–Ag nanocomposites is shown in Fig. 1.

Hydrazine hydrate reduces the Cu²⁺ into metallic copper. Ethylene diamine controls the shape and size of the nanoparticles formed. Ethylene diamine also prevents the agglomeration of the nanoparticles by adsorbing on the (100) facet [24]. After synthesis, under the drying conditions, the surface of the resulting copper nanoparticles is oxidized to form a Cu–CuO nanocomposite. In the second step, the copper nanoparticles in the nanocomposite get replaced by silver ions through transmetalation reaction. The galvanic replacement of single copper ions by two silver atoms follow the reaction

This equation suggests that the amount of precursor plays a crucial role in the composition of Cu–CuO–Ag nanocomposites. We prepared four different compositions of the nanocomposite by varying the atomic ratio of copper to silver precursor. Reports suggest that in the synthesis of nanocomposites, more often, the final product will not be consistent with the feeding molar/atomic ratio due to the incomplete diffusion of second metal into the initially formed primary structure. Several factors such as reaction temperature and reaction time influence the surface diffusion process [25]. In the present study, silver is first converted to a silver-amine complex prior to addition to Cu–CuO nanoparticles. The X-ray crystallographic patterns of the synthesized Cu–CuO and Cu–CuO–Ag nanocomposites are shown in Fig. 2.

The sharp peaks in the XRD patterns suggest the crystalline nature of the synthesized nanocomposites. The XRD pattern of Cu–CuO nanocomposites shows crystalline peaks at 2 theta 43.56°, 50.8° and 74.68° corresponding to the (111), (200) and (220) planes of metallic copper (JCPDS 04–0836). The peaks at 35.63°, 38.71°, 49.01°, 58.25°, 61.70°, 66.21°, 68.08° indicate the (002), (111), (200), (202), (113), (311), (220) planes of monoclinic CuO (JCPDS 48–1548). The XRD pattern of all the Cu–CuO–Ag nanocomposites contains peaks at 38.31°, 44.28°, 64.52° and 77.43° corresponding to peaks of (111), (200), (220) and (311) phases of metallic silver (JCPDS 04–0783).

It can be found that all the Cu–CuO–Ag nanocomposites except CA1 shows XRD patterns corresponding to metallic copper and monoclinic copper oxide. The sample CA1 contains only peaks corresponding to monoclinic copper oxide and metallic silver. The absence of peaks of metallic copper can be due to the higher concentration of silver nitrate in the precursor solution. Based on previous reports, the increase in intensity of the Ag (111) peak is

Fig. 1 Schematic diagram of the formation of Cu–CuO–Ag nanocomposite

Fig. 2 XRD patterns of **a** Cu–CuO and Cu–CuO–Ag nanocomposites, **b** CA1, **c** CA2, **d** CA3 and **e** CA4 respectively

proportional to the amount of Ag in the sample, and the increase in sharpness of Ag (200) peak is proportional to the crystallinity of the Ag component. The highly intense peaks of Ag (111) at 38.31° in the sample CA1 indicates the higher amount of free silver in the sample due to dewetting process. The silver dewetting causes more fraction of elemental copper in the initially prepared Cu–CuO nanocomposite to get exposed to atmospheric oxygen resulting in its oxidation to form CuO and may be the reason for the absence of metallic copper in the CA1 sample [16]. From the XRD patterns it is clear that, in the synthesized Cu–CuO–Ag nanocomposites, the peak position of the Ag, Cu and CuO phases retains its position as in their standard JCPDS cards. This confirms the fact that the samples formed were composites and not alloys. The broadening of the Ag (200) peaks observed as we move

from sample CA1 to sample CA4 can be attributed to the Ag dewetting process [16]. Besides, the Cu–CuO and CA1 sample contains a single peak at 33.62° corresponding to the (002) plane of $\text{Cu}(\text{OH})_2$ (JCPDS 35-0505). It may be formed from the hydroxylation of the synthesized copper nanoparticles. The decrease in atomic weight percentage of silver makes the Cu, CuO and Ag peaks more distinct. As evident from the XRD patterns an increase in the concentration of silver results in an increase in the intensity of the (111) peak of silver (38.10°) and a decrease in the reflection intensity of the metallic Cu (200) (43.56°).

Figure 3 shows the SEM images of synthesized Cu–CuO and Cu–CuO–Ag nanocomposites. The samples are spherical in shape and homogeneously distributed with some particle aggregation. The EDS analysis data is given in the supplementary data (figure S1). The percentage

Table 1 Percentage composition of Copper, silver and oxygen present in the Cu–Ag nanocomposites

Sample	Copper (%)	Silver (%)	Oxygen (%)
CA1	13.2	81.3	5.5
CA2	14.6	73.1	12.30
CA3	19.2	66.2	14.6
CA4	54	9.0	37

composition of Cu, Ag and O present in the synthesized Cu–Ag nano composites obtained from energy dispersive X-ray spectroscopic analysis are shown in Table 1.

Figure 4 shows the TEM image of the as synthesized CA3 nanocomposite, which shows that the product consists of spherical nanocrystals. As shown in HRTEM image, three sets of lattice fringes at 0.236, 0.203 and 0.204 nm can be seen which can be indexed to the (111), (222) of Ag and (111) of Cu respectively.

Fig. 3 SEM images of **a** Cu–CuO and Cu–CuO–Ag nanocomposites as **b** CA1, **c** CA2, **d** CA3 and **e** CA4 respectively

3.2 Catalytic study-hydrogenation reduction of *p*-nitrophenol

The catalytic hydrogenation of *p*-nitrophenol has been extensively studied by researchers since it is a suitable model reaction for analyzing the catalytic activity of most materials [20, 26–28]. Moreover, *p*-nitrophenol is a highly toxic organic pollutant which is difficult to degrade under normal conditions. The EPA drinking water guidelines limit the percentage of nitrophenols in drinking water to 0.06 ppm. It is well reported that in the absence of a catalyst, the strong reducing agent NaBH_4 is not able to carry out the hydrogenation of *p*-nitrophenol (4-NP) [29, 30]. The UV–Visible absorption peak of pure *p*-nitrophenol is at 317 nm. The addition of NaBH_4 to the aqueous reaction solution creates basic conditions resulting in the conversion of nitrophenol to nitrophenolate ions and then the absorption peak shifts to 400 nm. But when Cu–CuO–Ag nanocomposites were added, the reduction of *p*-nitrophenol to *p*-aminophenol occurs within five minutes, and the conversion is indicated by the decrease in the absorption peak of nitrophenol at 400 nm with a simultaneous increase in the peak at 300 nm corresponding to *p*-aminophenol [30]. Also, there is visible change in the color of the solution from pale yellow to colorless. Since, in our study, the concentration of sodium borohydride was 40 times that of *p*-nitrophenol, the rate constant of the reaction can be analyzed by the pseudo-first order reaction kinetics. The rate constant values of the catalytic hydrogenation

reaction performed were obtained from the plot of $\ln C/C_0$ versus time where C/C_0 is the relative intensity of concentration at 400 nm. Figure 5 shows the UV Vis absorption plot of hydrogenation reduction of *p*-nitrophenol reduction using the commercial copper metal powder (Fig. 5a), synthesized Cu–CuO (Fig. 5b) and Cu–CuO–Ag nanocomposites (Fig. 5c–f). The time taken for the reduction of *p*-nitrophenol in solution is noticeably less when we use Cu–CuO–Ag nanocomposites compared to commercial copper powder suggesting the improved catalytic efficiency of Cu–CuO–Ag nanocomposites. Among the Cu–CuO–Ag nanocomposites, CA3 nanocomposite reduces whole of the *p*-nitrophenol in solution within 4 min and shows the maximum catalytic efficiency.

The catalytic efficiency of the prepared samples were further established by comparing the activity of commercial copper powder under the same conditions and is shown in Fig. 5a. Figure 6 displays the correlation data between the rate of decrease in the peak at 400 nm with increasing time by monitoring the UV–Vis absorption spectrum ($-\ln C/C_0$ Vs. time plot). The plot clearly demonstrates that the reaction is pseudo-first order. It is found that with 7.5 mg of the catalysts, the apparent rate constant values obtained for commercial copper powder, Cu–CuO nanocomposite, CA1, CA2, CA3 and CA4 nanocomposites were found to be 0.093, 0.125, 0.148, 0.188, 0.565 and 0.432 min^{-1} , respectively. It can be well understood that among Cu–CuO and Ag–Cu–CuO nanocomposites, the maximum catalytic activity was shown by CA3 sample for the catalytic hydrogenation

Fig. 4 **A** TEM image of CA3 nanocomposite and **a**, **b** and **c** show corresponding HRTEM image labeled as **a**, **b** and **c** area, respectively, **B** **A** selected area electron diffraction pattern of Cu–CuO–Ag nanocomposite

Fig. 5 UV absorption spectrum of hydrogenation reduction of *p*-nitrophenol using **a** commercial copper powder, **b** Cu–CuO nanocomposite, **c** CA1, **d** CA2, **e** CA3 and **f** CA4 respectively

Fig. 6 Plot of $-\ln C/C_0$ plot of commercial copper powder, Cu–CuO nanocomposite and CA1, CA2, CA3, CA4 respectively

of *p*-nitrophenol to *p*-aminophenol, which is about 4.5 fold compared to that of Cu–CuO nanocomposite.

Since the catalytic stability is an important factor that determines the efficiency of the catalyst, the recyclability of the catalyst was also monitored by carrying out four successive cycles of the catalytic hydrogenation using a definite amount of the prepared catalyst under the same experimental conditions. After each catalytic cycle, the separation of the catalyst from the reaction mixture is done by centrifugation followed by washing with distilled water several times and then used for the next cycle.

Figure 7 shows the relative rate plot of the recyclability result of hydrogenation reduction of *p*-nitrophenol with NaBH_4 catalyzed by Cu–CuO and Ag–Cu–CuO nanocomposites. It is clear that among the synthesized catalysts, the maximum recyclability was shown by CA3 nanocatalysts without any significant decrease in the catalytic efficiency even after four cycles of the hydrogenation reduction of *p*-nitrophenol and indicates the noticeable stability of the catalyst compared to all other samples. From the catalytic data, it is well understood that CA3 nanocrystals were efficient catalyst for hydrogenation reduction of *p*-nitrophenol.

The XRD patterns of the used catalyst after four cycles of the catalytic reduction reaction are shown in Fig. 8. For Cu–CuO nanocomposite, there are only peaks corresponding to monoclinic copper oxide after four cycles of the catalytic reduction reaction indicating the lower stability of the copper nanocrystals. However, a single peak at 33.6° (2θ) corresponding to $\text{Cu}(\text{OH})_2$ remains in this sample. However, for CA1, CA2 and CA3 nanocrystals, there is no change in the XRD patterns even after four cycles of the catalytic runs. In CA4, the peaks corresponding to

Fig. 7 Plot of recyclability of various catalysts for four cycles of the hydrogenation reduction of *p*-nitrophenol

monoclinic CuO at 2θ angles 32.4° , 35.6° and 38.3° are present in minute amounts. However, for all the Cu–CuO–Ag nanocatalysts, the peaks corresponding to metallic silver becomes prominent indicating the successful conversion of metallic Ag (0) to Ag^+ and back to metallic silver after catalytic reduction reaction. There is no presence of silver oxide. The higher and stable catalytic performance of the CA3 nanocrystals even after four catalytic runs indicates the stability of the nanocatalyst. However, CA2 shows a decreased catalytic performance even though its XRD patterns remain unchanged during catalytic cycles. Moreover, the decrease in apparent rate constant value for hydrogenation reduction of nitrophenol with every catalytic run may be due to the surface contamination of the sample after each catalytic cycle. At the same time, the higher stability of the CA4 nanocatalysts may be due to the more proper synergistic electronic interaction of constituent particles of the catalyst and proper interaction between the active sites with the nitrophenolate ions. This suggests that compositional effects are a crucial factor in determining the catalytic performance of these types of catalysts [30].

In order to optimize the amount of CA3 nanocatalyst required for the *p*-nitrophenol reduction reaction, we carried out the hydrogenation reaction with different amount of the catalyst. Kinetic plot ($-\ln C/C_0$ vs time) of the reduction reaction and relative rate plot of the apparent rate constant values of the hydrogenation reduction of *p*-nitrophenol in the presence of different amount of CA3 nanocrystals were given in Figs. 9 and 10 respectively. It can be observed that initially there is an increase in the

Fig. 8 XRD pattern of Cu–CuO nanocomposite, CA1, CA2, CA3 and CA4 respectively after four cycles of catalytic reduction

rate of the reaction on moving from 2.5 mg to 10 mg of the catalyst with a simultaneous increase in the rate from 0.079 to 0.632 min^{-1} . The UV absorption plot suggests that using 2.5 mg of the CA3 catalyst, reaction does not complete even after 14 min of the commencement of the reaction. With further increase in the amount of the catalyst from 10 to 12 mg, the time required for completion of the reaction remains 4 min while the apparent rate constant value decreases from 0.623 to 0.557 min^{-1} . Thus, we have concluded that 10 mg of the CA3 nano catalyst is optimum for the complete conversion of *p*-nitrophenol to *p*-aminophenol with a maximum rate constant value. The kinetic plot with a correlation coefficient value close to unity further confirms the pseudo-first order kinetics for the reaction [31].

Since most of the as synthesized Cu–CuO and Cu–CuO–Ag nanocomposite were of almost identical shape, it can be concluded that particle size of the catalyst is not the mere reason for the varying catalytic activity. The increase in catalytic reduction rate with increasing catalyst amount can be attributed to the increase in the amount of catalytically active sites available for the reduction reaction. The incorporation of silver into Cu–CuO

Fig. 9 Kinetic plot ($-\ln C/C_0$ Vs time) of the reduction reaction in the presence of different amount of CA3 nanocrystals

nanocomposite increases the catalytic activity of the samples indicating the importance of silver in the proposed catalytic reaction. The decrease in reduction rate with

Fig. 10 Relative rate plot of the apparent rate constant values of the hydrogenation reduction of *p*-nitrophenol in the presence of different amount of CA3 nanocrystals

further increase in the amount of the catalyst to 12.5 mg may be due to the decrease in the concentration of free preformed amino-phenolate ions [32].

The obtained results are compared with other metal-based catalysts reported in the literature for hydrogenation reduction of *p*-nitrophenol using the activity factor (*K*), which is defined as the values of pseudo-first order rate constants (*k*) per gram of the catalyst used. Based on the data listed in Table 2, it is clear that our synthesized CA3 nanocrystals shows high catalytic performance compared to noble metal Au-Fe₃O₄ nanocatalyst, Cu₁₈Ag alloy nanoparticles and CuO@Ag⁰ nanocatalysts. Even though, the catalytic activity factor is less compared to the previously reported Cu/CuO-Ag nanocatalyst, our new catalyst is superior in terms of low synthesis time.

The conversion of *p*-nitrophenol to *p*-aminophenol is thermodynamically favorable because of the suitable electrode potential of NaBO₂/NaBH₄ (-1.33 V) and 4-NP/4-AP (-0.76 V) under normal hydrogen electrode [36]. However, the reaction is not feasible under normal conditions due to the large kinetic barrier between the nitrophenolate and

BH₄⁻ species [23, 37]. *p*-nitrophenol gets deprotonated to nitrophenolate ions in the presence of NaBH₄. The important step in the catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol is the adsorption-desorption mechanism. The reaction commences with the adsorption of nitrophenolate and borohydride ions on the active sites of the catalyst. Then the electron transfer from the BH₄⁻ to nitrophenolate ions through the catalyst interface results in the reduction products. The desorption and diffusion of the hydrogenated products from the catalyst surface follows [38]. The *p*-nitrophenol reduction follows pseudo-first order reaction kinetics [39].

The higher catalytic rate constant of Cu-CuO compared to commercial copper powder can be due to the presence of intimate contact between the metal and metal oxide nanostructures. Reports suggest that the presence of such an interaction will always facilitate the transfer of electrons from metal to metal oxide. This occurs due to the variation in the Fermi level alignment resulting in the charge redistribution [20]. The enhancement in the catalytic reduction rate of Cu-CuO-Ag over Cu-CuO nanocomposite can be due to a combination of several reasons. In the Cu-CuO-Ag nanocomposite, Cu-CuO, Cu-Ag and Ag-CuO interfaces are present. Then using such a nanocomposite as catalysts always offers a chance of transfer of electrons and hydride ions from Cu or Ag surface to the CuO surface. Such a charge distribution results in an electron rich region around CuO and electron free region around Ag or Cu leading to the formation of a depletion layer. The presence of surplus electrons over the CuO surface will enhance the uptake of electrons by nitrophenolate ions by effectively increasing the depletion area and thus enhancing catalytic activity [23].

Besides, the high electrical conductivity of silver ($6.30 \times 10^7 \text{ Sm}^{-1}$) also favors the adsorption of the reactant species and electrons. The higher catalytic activity of Cu-CuO-Ag nanocomposite also suggests the fast desorption of *p*-aminophenol from the catalyst surface. This can be attributed to the repulsion forces arising due to the increase in proton concentration around the catalyst surface [40]. Among the Cu-CuO-Ag nanocomposite, the

Table 2 Comparison between catalytic activities with previous reports

Samples	Quality/mg	Rate constant (k)/s ⁻¹	Activity factor (K)/s ⁻¹ mg ⁻¹	Reference
Cu ₁₈ Ag alloy nanoparticles	2	0.00395	0.0019	[10]
CuO@Ag ⁰	NA	0.004	NA	[33]
Flower-like Au-Fe ₃ O ₄	2	0.0063	0.0003	[34]
Dumbbell-like Au-Fe ₃ O ₄	2	0.0105	0.0001	[34]
CuO	5	0.00237	0.00047	[35]
Cu/CuO-Ag	1.5	0.046	0.0306	[23]
CA3 nanocrystals	7.5	0.0096	0.001	Present work

variation in catalytic activity might be due to the differences in the synergistic effects of different parameters including structure effects, composite effects, and size effects [32, 41]. The catalytic performance of any catalytic system greatly depends on the atomic distribution and ratio of the constituents since even a slight alternation in the local electron density influences the catalytic activity. The enhanced catalytic activity of CA3 nanocatalyst can be attributed to the depleted layer and enhanced electron density regions created by the synergistic action of Cu, CuO and Ag interfaces. In turn this allows the CA3 nanocatalyst to facilitate the interaction between maximum number of nitrophenolate ions and catalytically active sites [42]. A decrease in the catalytic activity is observed when the copper content increases further as in CA4. The increase in copper content consequentially decreases the instances of favorable interfaces and disrupt the synergistic behavior observed in CA3 [43]. The catalytic enhancement depends on the proportion of Cu and Ag in the nanocomposites.

4 Conclusion

In summary, we have developed a facile method for the synthesis of Cu–CuO–Ag nanocomposite using a low-cost approach. The catalytic activity of the synthesized Cu–CuO–Ag nanocomposite was investigated in the catalytic reduction of *p*-nitrophenol to *p*-aminophenol. The results reveal that Cu–CuO–Ag composite nanoparticles possess higher catalytic activity than Cu–CuO nanocomposite and commercial copper. Among the Cu–CuO–Ag nanocomposite, the CA3 composite, synthesized using the copper to silver precursor ratio of 16:1 exhibited enhanced catalytic activity. The maximum rate was observed for the catalyst amount of 10 mg. The enhanced catalytic performance of Cu–CuO–Ag nanocomposite arise from the synergistic effect of Cu–CuO–Ag interfaces. An optimal amount of copper to silver ratio was observed where this synergism was maximized. Our facile synthetic method could be extended for the synthesis of other copper-based nanostructures, such as the Cu/Au and Cu/Pt bimetallic nanoparticles. The low cost, easily scalable preparation presented and insights into enhancing the catalytic activity will be useful in designing efficient catalysts for degradation of organic pollutants.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests

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