

SYNTHESIS, STRUCTURAL ANALYSIS, AND PHOTOCATALYTIC ACTIVITY OF Cu-Co AND/OR Co-Cu CORE-SHELL NANOPARTICLES

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Abstract

Bimetallic nanoparticles have been drawn much attention from many researcher due to present greater abilities than monometallic nanoparticles. The bimetallic core-shell products of Cu and Co have been prepared by aqueous reduction process, which was added copper nitrate into an aqueous mixed solution that had been contained sodium citrate, nickel sulfate, and sodium borohydride. According to the advantages of this preparation process, not only it was not complicated, fast, and performed at room temperature, but also the core and shell type could be formed and desired. If the adding time of copper nitrate was changed, we were able to obtain either Cu-Co and/or Co-Cu core-shell systems with various in their morphology. Therefore, we studied the bimetallic nanoparticles with different adding time of copper nitrate such as 1, 5, and 10 min, respectively. While, monometallic Co nanoparticles were prepared with the similar method but no added copper nitrate. The bimetallic samples were investigated by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), and Energy Dispersive X-ray Spectrometer (EDS) methods. Besides, the photocatalytic activity under UV light illumination of the bimetallic nanoparticles were observed with UV-Vis Spectrometer (UV-Vis). Compared with the monometallic nanoparticle, the bimetallic products enhanced the photocatalytic activity.

Keywords: Bimetallic Cu-Co and/or Co-Cu core-shell nanoparticles, Monometallic Co nanoparticles, Aqueous reduction process, Photocatalytic activity

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Introduction

Recently, many researches base on bimetallic nanoparticles have been produced and published. According to the co-existence and cooperative working of two metal components in nanoscale, they enhance and improve physical, chemical, optical, electrical, magnetically, and catalysis properties (Albonetti *et al.*, 2008; Tee *et al.*, 2009; Liu *et al.*, 2011; Barakat *et al.*, 2013). Therefore, they have been widely utilized in many fields, such as catalysis (Huber *et al.*, 2003; Lim *et al.*, 2009; Ibrahim *et al.*, 2016), electrochemistry (Murray, 2008; Bing *et al.*, 2010), magnetism (Sun *et al.*, 2000; Song *et al.*, 2009), and optics (Fu *et al.*, 2012; Yan *et al.*, 2012), respectively.

One of the most interesting application of bimetallic nanoparticles is using as a photocatalytic to remove and degrade of organic dyes effluents from many industrials, such as paints, textiles, printing inks, and papers (Safavi and Momeni, 2012; Sinha and Ahmaruzzaman, 2015; Hashemizadeh and Biglari, 2018). The eliminating of toxic dyes has been related to activate the suitable bimetallic nanoparticles in aqueous solution by sunlight to achieve high strongly oxidizing agents (O_2^- and OH radical), subsequently, degrade and remove organic dyes.

Nanocomposites materials base on either copper or cobalt have been derived much attention and studied for many years. Since they are not expensive, easy available, less toxicity, as well as express very interesting abilities in electric and catalysts, which have been used in various application fields such as catalysts, electrical, and sensors (Jeong *et al.*, 2011; Ansari *et al.*, 2017; Ojha *et al.*, 2017). In addition, cobalt nanoparticles have been used as recording media, magnetic sensors, magnetic memories, and magnetic composites due to their excellent in magnetic properties (Puntes *et al.*, 2001; Lim *et al.*, 2013; Thanh *et al.*, 2015). It gets even more interesting that when Cu and Co nanoparticles are combined and working together or knows as bimetallic products. Since, these bimetallic have been expressed higher and superior in physical and chemical abilities when compare with monometallic Cu or Co and the co-presence of monometallic Cu and Co nanoparticles.

It has been reported that Cu-Co nanoparticles presented high catalytic efficiency for producing high amount of alcohols from the conversion of synthesis gas (Wang *et al.*, 2012; Xiao *et al.*, 2013; Liu *et al.*, 2015). In addition, Co-Cu alloy nanoparticles embedded in carbon nanofibers (CNFs) have been expressed well electrocatalytic properties for methanol oxidation, which have

application on fuel cell. It also mentions that the catalytic ability of bimetallic alloy Co-Cu CNFs overcame pure Co and Cu nanoparticles incorporated in CNFs (Ghouri *et al.*, 2015). The fabricated bimetallic nanomaterials of tricobalt tetraoxide (Co_3O_4) and strontium carbonate ($SrCO_3$) on CNFs support, have been observed for capable of urea electrooxidation at lower onset potential with high-current density (21.33 mA/cm^2). These results implied to enhance the overall efficiency for utilizing in direct urea fuel cells. (Ghouri *et al.*, 2017) Moreover, the synthesis of Co-Cu alloy, Co, and Cu nanoparticles on carbon nanowires (CNWs) have been evaluated for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) during electrocatalytic water splitting. All the bimetallic CoCu alloy on CNWs was founded to improve electrocatalytic activity, which was obtained the optimum composition for good yields of OER and HER at $Co_{0.95}Cu_{0.05}$ CNWs (Ghouri *et al.*, 2021).

To derive and achieve the greater and desirer physical and chemical abilities of bimetallic nanoparticles, their morphology, such as shape and size, as well as, metal compositions and how they form or agglomerate are very influent parameters (Gilroy *et al.*, 2016; Srinoi *et al.*, 2018). Therefore, the understanding, control, and improve nanoparticles morphology are huge necessary and essential. Among of several bimetallic nanoparticles synthesis methods, aqueous chemical reduction process has been reported to obtain the nanoparticles with capable of precisely control of their structure (Carroll *et al.*, 2010; Phinjaroenphan *et al.*, 2020). Not only that, but it is also not complicated and expensive, do not take time, not need of specialized instruments, and perform at room temperature and atmospheric pressure, which might have potential in commercial.

Although Cu-Co nanocomposite have been emerged interesting properties and widely utilizing, there is just a few reports on the investigation of them. Hence, we presented Cu-Co and/or Co-Cu core-shell and Co nanoparticles prepared by simultaneous aqueous reduction process under ambient conditions. We also introduced a simple way to achieve and control desired core and shell type as well as their nonstructural information. Since the bimetallic nanoparticles were obtained by injecting copper nitrate into a mix solution that contained sodium citrate, cobalt sulfate, and sodium borohydride. The injecting time of copper nitrate would be the most effective parameter to control and select either Cu-Co or Co-Cu core-shell products at

different in average size of core and shell. The effect of copper nitrate injecting time on the bimetallic nanostructure will also be investigated and discussed. Moreover, the photocatalytic activity of the prepared bimetallic products in term of an organic dye degradation such as methyl orange under UV light illumination has been demonstrated and compare with the monometallic Co nanoparticles.

Materials and Methods

Sample Preparation

All chemical reagents, such as copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), trisodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), cobalt (II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), sodium borohydride (NaBH_4), and methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) were derived in analytical grade from Sigma Aldrich and used without further purification.

Synthis of Co and Cu-Co and/or Co-Cu Core-shell Nanoparticles

Monometallic Co nanoparticles could be synthesized by mixing 0.46 mM trisodium citrate and 4.6 mM nickel sulfate into 100 mL distilled water under constant stirring at room temperature. During stirring, added 8.8 mM sodium borohydride into the previous solution, then the color of combined solution was changed from clear to a dark gray and black (indicated that Co nanoparticles were started to form). The mixture solution was stirred for another 10 min to make a complete reaction, after that quenched by ethanol several times. The precipitation of Co nanoparticles could be extracted by using a centrifuge and washed with distilled water. The particles were dried in a vacuum oven at room temperature for 24 h.

Bimetallic Cu-Co and/or Co-Cu core-shell nanoparticles were obtained by using the same method as above, however the difference was the adding of copper nitrate at various times. In this synthesis process, 0.5 M copper nitrate solution was prepared as a stock solutions. After preparing the aqueous mixture solution that contained trisodium citrate, nickel sulfate, distilled water, and sodium borohydride, the copper nitrate precursor is added into the solution for the different time at 1, 5, and 10 min, respectively.

Characterization

The X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max 2,500 X-ray diffractometer with $\text{CuK}\alpha$ radiation of wavelength

0.154 nm. The high resolution transmission electron microscopy (HRTEM) were measured by a Tecnai G2 20 transmission electron microscopy. To obtained HRTEM images, all sample solution was dropping over the copper grids and let them dried in the vacuum chamber at room temperature for 24 h. The energy dispersion X-ray spectrometer (EDS) that attached with the scanning electron microscopy (SEM) was also used to characterize. The SEM samples were also prepared by placing dried nanoparticles on the carbon tape.

Photocatalytic Activity Evaluation

The photocatalytic activity of the synthesized Cu-Co and/or Co-Cu core-shell and Co nanoparticles were determined in term of the degradation rates of methyl orange (MO) by UV-Vis spectrophotometer. For 0.2 g of each nanoparticles was dispersed in 50 mL at an initial concentration of 8.15 mg/L of MO in solution. The mixture solution was stirred for 30 min in the dark (to confirm the equilibrium of adsorption and/or desorption of the nanoparticles), then irradiated under UV light with a 300-W high-pressure Hg lamp working as a UV light source. At every 30 min for the irradiation time, 5 mL of the combined solution was taken, centrifuged, and filtered. The photocatalytic activity was derived by calculating the MO concentration of the filtrate with a UV-Vis spectrometer at 463.8 nm (This wavelength corresponding to MO maximum absorption). In addition, the percentage of eliminate MO under UV light (% MO photodegradation) and the kinetic behavior of nanoparticles could be defined as shown in Equation 1 and Equation 2, respectively.

$$\text{MO photodegradation (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\% \quad (1)$$

and

$$\ln(C_0/C) = kt \quad (2)$$

where C_0 and C_t represent the MO concentration at initial time and irradiation time t in min, respectively. While k is the apparent rate constant.

Results and Discussions

The crystal phase of the bimetallic Cu and Co and monometallic Co nanoparticle products were identified by XRD analyzed as shown in Figure 1. The diffraction peaks of Co nanoparticles were obtained at around $2\theta = 41.55^\circ, 44.47^\circ, 47.45^\circ$, and 75.96° corresponding to reflection plane (100), (002), (101) and (220) of hexagonal closed packed (hcp) Co metal, according to JCDs file

no. 5-0727, respectively. In addition, there was no observed undesired oxides phases such as CoO and Co₂O₃.

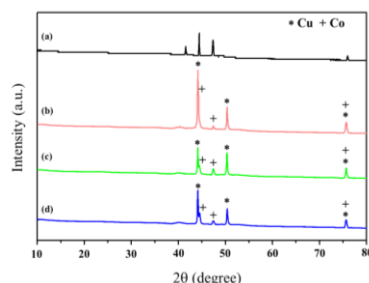


Figure 1. XRD results of the synthesized nanoparticles by aqueous reduction process; (a) Co nanoparticles; Cu-Co/Co-Cu core-shell prepared at different times of adding Cu(NO₃)₂; (b) 1 min; (c) 5 min; (d) 10 min (* Cu JCDs file no. 4-0836 (Cu) + Co JCDs file no. 5-0727 (Co))

In case of bimetallic Cu-Co samples, their XRD profiles were observed similarly regardless of injecting Cu(NO₃)₂ at 1 min (b), 5 min (c), and 10 min (d). The diffraction patterns showed double peaks, which could be extracted each diffraction peaks at around $2\theta = 43.60^\circ$ and 44.47° , respectively. The other two diffraction peaks were derived at around $2\theta = 47.45^\circ$ and 50.89° as well. Lastly, the merge peak was obtained at around $2\theta = 75.54^\circ$. These peaks were matched with the characteristic peaks from both fcc Cu ($2\theta = 43.60^\circ$ (111), 50.89° (200) and 74.81° (200), according to JCDs file no. 4-0836) and Co metals ($2\theta = 44.47^\circ$ (002), 47.45° (101) and 75.87° (220)), which suggested the presence of both Cu and Co phases. Additionally, these patterns were clean and no impurity oxide phase occurred.

Morphology and structural information of the nanoparticles were extracted by HR-TEM, as shown in Figure 2. The monometallic nanostructure of Co was observed in a spherical shape with average particles size about 20.63 ± 1.59 nm, as indicated in Figure 2(a). While, the bimetallic conformations of Cu and Co were obtained at different forms due to a huge effect from time of adding Cu(NO₃)₂. In more details, when Cu(NO₃)₂ was combined at 1 min (Cu-Co 1), the Cu core-Co shell nanoparticles were successfully formed as shown in Figure 2(b). Their average particle size was observed about 76.64 ± 6.63 nm with 41.58 ± 4.91 nm of core size and 17.53 nm of shell thickness. However, if the time of injecting Cu(NO₃)₂ increased to 5 min (Cu-Co 5), the Co core-Cu shell nanoparticles were derived instead, also shown in Figure 2(c). The average particle size of the Co core-

Cu shell was obtained larger than sample Cu-Co 1, approximately 130.09 ± 10.65 nm, with also having higher core size and shell thickness about 89.46 ± 6.83 and 20.32 nm, respectively. If the time of adding Cu(NO₃)₂ increased further to 10 min (Cu-Co 10), the core-shell system was disappeared, the cluster core of Co with small island of Cu overgrowth was revealed at this situation, as indicated in Figure 2(d). Their average total particles size were obtained about 120 nm. Experimental results indicated that morphology and structural parameters were significantly influenced by the time of adding Cu(NO₃)₂.

Moreover, increasing adding time corresponds to increase reaction time, which could generated more atoms. All the structural information are summarized and shown in Table 1. To gain more knowledge and confirmed of the type of core-shell nanoparticles, the EDS from SEM are needed to probe atomic percentage of the nanoparticle samples surface. In order to exclude the effect from Cu, all the measurements was used the carbon adhesive tapes as a sample holder. According to the EDS results, the atomic number of Co was only founded in the Co sample, while both atomic weights of Cu and Co were derived from all the Cu-Co products. These studies confirmed that the monometallic Co and bimetallic Cu-Co nanoparticles were successfully synthesized.

The atomic percentage of Co was revealed to be higher than that value of Cu for Cu-Co 1 (32.2%

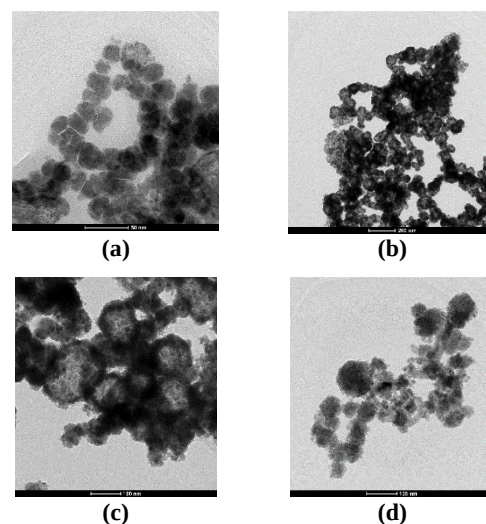


Figure 2. High resolution TEM images of the synthesized nanoparticles by aqueous reduction process; (a) Co nanoparticles; Cu-Co/Co-Cu core-shell prepared at different times of adding Cu(NO₃)₂; (b) 1 min; (c) 5 min; (d) 10 min

Table 1. XRD results of the synthesized nanoparticles by aqueous reduction process; (a) Co nanoparticles; Cu-Co/Co-Cu core-shell prepared at different times of adding $\text{Cu}(\text{NO}_3)_2$; (b) 1 min; (c) 5 min; (d) 10 min (* Cu JCDs file no. 4-0836 (Cu) + Co JCDs file no. 5-0727 (Co))

Sample	Nanostructure (observed) ^a	Particles size (nm) ^a	Diameter core size (nm) ^a	Shell thickness (nm) ^a
Co	Spherical	20.63±1.59	-	-
Cu-Co 1	Cu core-Co shell	76.64±6.63	41.58±4.91	17.53
Cu-Co 5	Co core-Cu shell	130.09±10.65	89.40±6.83	20.32
Cu-Co 10	Co cluster attached with Cu islanding	~120	-	-

Sample	Metal surface composition ^b	
	Cu	Co
	(Atomic %)	
Co	-	100.0
Cu-Co 1	32.2	67.8
Cu-Co 5	70.2	29.8
Cu-Co 10	44.1	55.9

^aNanostructure, particles size, diameter core size, and shell thickness were determined by HR-TEM

^bMetal surface composition was evaluated from EDS attached to the SEM

of Cu, 67.8% of Co) but lower than that value of Cu in case of Cu-Co 5 (70.2% of Cu, 29.8% of Co). These results suggested that Cu core with Co shell was developed at Cu-Co 1, but Co core with Cu grow around was founded at Cu-Co 5. Moreover, the atomic percentage of Co was observed to be slightly higher than that value of Cu for Cu-Co 10, it corresponded to the Co core cluster was formed with small Cu grow as islanding were obtained. The metal surface compositions of the synthesized Co and Cu-Co/Co-Cu nanoparticles were also presented in Table 1.

The structural mechanism of developed Cu-Co and/or Co-Cu core-shell, also Co nanoparticles could be explained as presented in Figure 3. The time of injecting $\text{Cu}(\text{NO}_3)_2$ into the mixture solution of cobalt sulfate, trisodium citrate and NaBH_4 would pay the most important role to control the morphology, as well as average size and type of core and shell nanoparticles. Since the reduction potential of Cu^{2+} to Cu is founded at 0.34 V, higher than that value of Co^{2+} to Co, which is obtained at -0.28 V, respectively (Gilroy *et al.*, 2016), Cu ions can be reduced and transformed to Cu atoms at faster rate than that of Co atoms. Therefore, at 1 min after NaBH_4 , the $\text{Cu}(\text{NO}_3)_2$ was injected into the solution, Cu ions could be reduced to become atoms faster than Co ions, so Cu atoms formed as a nucleation center for the Co to grow around, finally, Cu core and Co shell nanoparticles appeared. However, if the time of adding $\text{Cu}(\text{NO}_3)_2$ was increased to 5 min, Co atoms could be formed and behaved as a nucleation site instead due to they have a sufficient time to reduce and transform, then followed by Cu atoms to encapsulate, leading to Co-Cu core-shell nanoparticles was fabricated.

Not only that, more Co atoms could be produced and formed, but there atomic growth was not uniform, resulting to have higher mean particle

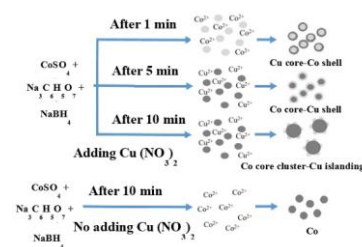


Figure 3. Schematic representation of the formation mechanism of the synthesized Co nanoparticles and Cu-Co and/or Cu-Co core-shell nanoparticles at different times of adding $\text{Cu}(\text{NO}_3)_2$ (1, 5, and 10 min) into the mixture solution; trisodium citrate, nickel sulfate, and NaBH_4

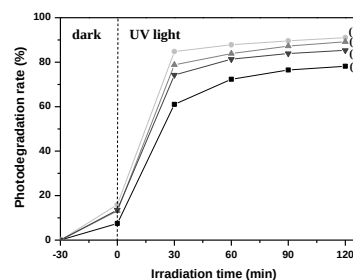


Figure 4. Photodegradation rate of MO with and without UV light irradiation by the synthesized nanoparticles; (a) Co nanoparticles; Cu-Co/Co-Cu core-shell prepared at different times of adding $\text{Cu}(\text{NO}_3)_2$; (b) 1 min; (c) 5 min; (d) 10 min

size and standard deviation. When the injecting time of $\text{Cu}(\text{NO}_3)_2$ was more increased to 10 min, a lot of Co atoms were created and formed as a large core cluster, having Cu atoms grow over as small islanding.

In addition, the photocatalytic activity of the obtained nanoparticles were evaluated by monitoring degradation rate of methyl orange (MO) under UV light irradiation as a function of time, and presented in Figure 4. It was also found that the Cu-Co 1 (b) presented the highest ability in degradation rate as it could eliminated MO up to 91.03% within 120 min. Then, Cu-Co 5 (c) and Cu-Co 10 (d) nanoparticles had lower in the degradation rate as they were able to remove MO at about 89.16% and 85.34% within 120 min, while the Co (a) samples presented the lowest ability to degrade MO at about 78.17% within the same time.

Overall, the experimental results of all the bimetallic products displayed enhancement of photocatalytic ability over the monometallic Co. Moreover, the Cu-Co core-shell (Cu-Co 1), the Co-Cu core-shell (Cu-Co 5), and the Co-Cu core-islanding (Cu-Co 10) showed high performance to eliminate MO, which was improved by about 12.9%, 11.0%, and 7.2%, respectively, as compared to the Co. The main reason for higher develop and improve photocatalytic efficiency of the bimetallic could be considered as the synergetic effect between of Cu and Co. Besides, the obtained particles size of Cu-Co core-shell (Cu-Co 1) was very small, leading to have very large active surface area.

The study of kinetic behavior of nanoparticles were shown in Figure 5. These results were fitted to pseudo first order rate equation from Langmuir isotherm. It is noted that the rate constant obtained from the Cu-Co core-shell (Cu-Co 1) was very high compared to the Co-Cu core-shell (Cu-Co 5), the Co-Cu core-islanding (Cu-Co 10) and the Co displayed its superior photo-catalytic activity.

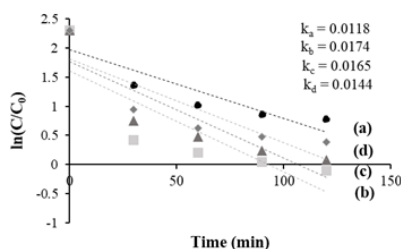


Figure 5. Rate kinetics of (a) Co nano particles; Cu-Co/Co-Cu core-shell prepared at different times of adding $\text{Cu}(\text{NO}_3)_2$; (b) 1 min; (c) 5 min; (d) 10 min

The possible mechanism of eliminate MO dyes by photocatalytic ability of Cu-Co/Co-Cu and Co metallic nanoparticles has been involved with electrons and holes induced by the UV light irradiation. This phenomena occurs when the light is absorbed by the catalyst, the electron (e^-) obtains

energy from photon and get excited to conduction band (CB) of the nanoparticles. Simultaneously, the hole (h^+) is generated in the valence band (VB). The electron (e^-) can move freely through to the catalyst surface. Then, the photogenerated electrons (e^-) are react with O_2 molecules, subsequently, receive super oxide radical ($\text{O}_2^{\cdot-}$). While photogenerated holes (h^+) are react with H_2O molecules, lastly, receive hydroxyl radical ($\text{OH}^{\cdot}$) (Saud *et al.*, 2016; Al-Meer *et al.*, 2017; Ghouri *et al.*, 2018). These radical active sites are highly strong oxidizing agents that can degrade MO. Due to the synergetic effect of Cu and Co nanoparticles, the surface electronic states of the bimetallic can be created more than those in monometallic. This result may be attributed to the high amount of electrons (e^-)-holes (h^+) pair are better generated and separated, as well as prevented them from the recombination of e^- and h^+ , leading to have high number of $\text{O}_2^{\cdot-}$ and $\text{OH}^{\cdot}$ radical.

The Cu-Co core-shell nanoparticles have been exhibited high performance in removing methyl orange dye from water. Hence, they have potential utilize as a photo-catalyst for eliminating of hazard dye effluents from industrials, such as paints, textiles, printing inks, and papers, which can serve as a promising material for water treatment.

Conclusions

Bimetallic Cu-Co and/or Co-Cu core-shell nanoparticles have been prepared with a simple aqueous reduction method, which has many advantages such as very convenient, cheap, not need to use specialized instruments, and prepare under ambient conditions. It is not all that, but this process also use only one parameter, such as the time of injecting $\text{Cu}(\text{NO}_3)_2$ after NaBH_4 , to determine and desire size and type of core and shell of the bimetallic nanoparticles. When the injecting time of $\text{Cu}(\text{NO}_3)_2$ was 1 min, Cu-Co core-shell nanoparticles were observed to be round with average particle size about 76.64 ± 6.63 nm, but if the adding time was increase to 5 min, Co-Cu core shell nanoparticles were found instead. They were still in spherical shape with larger average particle size as about 130.09 ± 10.65 nm. However, if the injecting time was longer up to 10 min, Co core cluster attached with small Cu overgrowth as islanding was obtained with approximately particle size as about 120 nm. In addition, monometallic Co nanoparticles was prepared by the same method, but without adding $\text{Cu}(\text{NO}_3)_2$.

Moreover, the Cu-Co and/or Co-Cu core-shell nanoparticles presented highly efficiency of photocatalytic activity that have been used in

the elimination of organic methyl orange (MO) dye. The improve and enhance photocatalytic ability of the bimetallic Cu and Co compare with the monometallic Co due to the synergetic effect of Cu and Co. Moreover, Cu-Co core-shell nanoparticles posed the highest ability of photocatalytic activity, which could remove MO about 91.03% after 120 min.

References

- Albonetti, S., Bonelli, R., Epoupa Mengou, J., Femoni, C., Tiozzo, C., Zacchini, S., and Trifirò, F. (2008). Gold/iron carbonyl clusters as precursors for TiO₂ supported catalysts. *Catal. Today.*, 137:483-488.
- Al-Meer, S., Ghouri, Z. K., Elsaid, K., Easa, A., Al-Qahtani, M. Th., Akhtar, M. S. (2017). Engineering of magnetically separable ZnFe₂O₄@TiO₂ nanofibers for dye-sensitized solar cells and removal of pollutant from water. *J. Alloys Compd.*, 723:477-483.
- Ansari, S. M., Bhor, R. D., Pai, K. R., Sen, D., Mazumder, S., Ghosh, K., Kolekar, Y. D., Ramana, C. V. (2017). Cobalt nanoparticles for biomedical applications: facile synthesis, physiochemical characterization, cytotoxicity behavior and biocompatibility. *Appl. Surf. Sci.* 414:171-187.
- Barakat, M., Al-Hutailah, R.I., Hashim, M.H., Qayyum, E., and Kuhn, J.N. (2013). Titania-supported silver-based bimetallic nanoparticles as photocatalysts. *Environ. Sci. Pollut. Res.*, 20:3,751-3,759.
- Bing, Y., Liu, H., Zhang, L., Ghosh, D., and Zhang, J. (2010). Nanostructured Pt-alloy electrocatalysts for PEM fuel cell oxygen reduction reaction. *Chem. Soc. Rev.*, 39:2,184-2,202.
- Carroll, K.J., Hudgins, D.M., Spurgeon, S., Kemner, K.M., Mishra, B., Boyanov, M.I., and Carpenter, E.E. (2010). One-pot aqueous synthesis of Fe and Ag core/shell nanoparticles. *Chem. Mater.*, 22:6,291-6,296.
- Fu, C.Y., Kho, K.W., Dinis, U.S., Koh, Z.Y., and Malini, O. (2012). Enhancement in SERS intensity with hierarchical nanostructures by bimetallic deposition approach. *J. Raman. Spectrosc.*, 43:977-985.
- Ghouri, Z.K., Nasser, A.M.B., and Kim, H.Y. (2015). Influence of copper content on the electrocatalytic activity toward methanol oxidation of Co_xCu_y alloy nanoparticles-decorated CNFs. *Sci. Rep.*, 5:16695.
- Ghouri, Z.K., Elsaid, K., Al-Meer, S., Nasser, A.M.B. (2017). Applicable anode based on Co₃O₄-SrCO₃ heterostructure nanorods-incorporated CNFs with low-onset potential for DUFCS. *Appl. Nanosci.*, 7:625-631.
- Ghouri, Z.K., Badreldin, A., Elsaid, K., Kumar, D., Youssef, K., and Abdel-Wahab, A. (2021). Theoretical and experimental investigations of Co-Cu bimetallic alloys-incorporated carbon nanowires as an efficient bi-functional electrocatalyst for water splitting. *J. Ind. Eng. Chem.*, 96:243-253.
- Ghouri, Z.K., Elsaid, K., Abdala, A., Al-Meer, S., and Nasser, A.M.B. (2018). Surfactant/organic solvent free single-step engineering of hybrid graphene-Pt/TiO₂ nanostructure: Efficient photocatalytic system for the treatment of wastewater coming from textile industries. *Sci. Rep.*, 8:14656.
- Gilroy, K.D., Ruditskiy, A., Peng, H.-C., Qin, D., and Xia, Y. (2016). Bimetallic nanocrystals: syntheses, properties, and applications. *Chem. Rev.*, 116:10,414-10,472.
- Hashemizadeh, S.A. and Biglari, M. (2018). Cu:Ni bimetallic nanoparticles: facile synthesis, characterization and its application in photodegradation of organic dyes. *J. Mater. Sci.: Mater. Electron.*, 29:13,025-13,031.
- Huber, G.W., Shabaker, J.W., and Dumesic, J.A. (2003). Raney Ni-Sn catalyst for H₂ production from biomass-derived hydrocarbons. *Science.*, 300:2,075-2,077.
- Ibrahim, R.K., Hayyan, M., AlSaadi, M.A., Hayyan, A., and Ibrahim, S. (2016). Environmental application of nanotechnology: air, soil, and water. *Environ. Sci. Pollut. Res.*, 23:13,754-13,788.
- Jeong, S., Song, H.C., Lee, W.W., Lee, S.S., Choi, Y., Son, W., Kim, E.D., Paik, C.H., Oh, S.H., and Ryu, B. (2011). Stable aqueous based Cu nanoparticle ink for printing well defined highly conductive features on a plastic substrate. *Langmuir* 27:3,144-3,149.
- Lim, B., Jiang, M., Camargo, P.H.C., Cho, E.C., Tao, J., Lu, X., and Xia, Y. (2009). Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. *Science.*, 324:1,302-1,305.
- Lim, J.K. and Majetich, S.A. (2013). Composite magnetic-plasmonic nanoparticles for biomedicine. *Nano. Today.*, 8:98-113.
- Liu, Z., Jackson, G.S., and Eichhorn, B.W. (2011). Tuning the CO-tolerance of Pt-Fe bimetallic nanoparticle electrocatalysts through architectural control. *Energy. Environ. Sci.*, 4:1900.
- Liu, G., Pan, D., Niu, T., Cao, A., Yue, Y., and Liu, Y. (2015). Nanoparticles of Cu-Co alloy supported on high surface area LaFeO₃ preparation and catalytic performance for higher alcohol synthesis from syngas. *RSC. Adv.*, 5:31,637-31,647.
- Murray, R.W. (2008). Nanoelectrochemistry: metal nanoparticles, nanoelectrodes, and nanopores. *Chem. Rev.*, 108:2,688-2,720.
- Ojha, N.K., Zyryanov, G.V., Majee, A., Charushin, V.N., Chupakhin, O.N., and Santra, S. (2017). Copper nanoparticles as inexpensive and efficient catalyst: a valuable contribution in organic synthesis. *Coord. Chem. Rev.*, 353:1-57.
- Phinjaroenphan, R., Boonserm, K., and Rattanasuporn, S. (2020). Preparation and characterization of bimetallic Cu-Ni and/or Ni-Cu core-shell nanoparticles with high photocatalytic activity. *Naresuan University J.: Sci. Technol.*, 29(2):54-63.
- Puntes, V.F., Krishnan, K.M., and Alivisatos, A.P. (2001). Colloidal nanocrystal shape and size control: the case of cobalt. *Science.*, 29(1):2,115-2,117.
- Safavi, A. and Momeni, S. (2012). Highly efficient degradation of azo dyes by palladium/hydroxyapatite/Fe₃ O₄ nanocatalyst. *J. Hazard. Mater.*, 201:125-131.
- Saud, P.S., Ghouri, Z.K., Hassan, M.K., Nasser, A.M.B., Kim, H.Y. (2016). Nano-designed k-CaCO₃@rGO photocatalyst for effective adsorption and simultaneous removal of organic pollutant. *J. Mater. Sci: Mater. Electron.*, 27(9).
- Sinha, T. and Ahmaruzzaman, M. (2015). Green synthesis of copper nanoparticles for the efficient removal (degradation) of dye from aqueous phase. *Energy. Environ. Sci.*, 22:24.
- Song, H.M., Kim, W.S., Lee, Y.B., Hong, J.H., Lee, H.G., and Hur, N.H. (2009). Chemically ordered FePt₃ nanoparticles synthesized by a bimetallic precursor and their magnetic transitions. *J. Mater. Chem.*, 19:3,677-3,681.
- Srinoi, P., Chen, Y.T., Vittur, V., Marquez, M.D., and Lee, T.R. (2018). Bimetallic nanoparticles: enhanced magnetic and optical properties for emerging biological applications. *Appl. Sci.*, 8:1-32.
- Sun, S., Murray, C.B., Weller, D., Folks, L., and Moser, A. (2000). Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices. *Science.*, 287:1,989-1,992.

- Tee, Y.-H., Bachas, L., and Bhattacharyya, D. (2009). Degradation of trichloroethylene by Iron-based bimetallic nanoparticles. *J. Phys. Chem. C.*, 113:9,454-9,464.
- Thanh, N.T.K. and Green, L.A.W. (2015). Functionalisation of nanoparticles for biomedical applications. *Nano. Today.*, 119:503-516.
- Wang, J., Chernavskii, P.A., Khodakov, A.Y., and Wang, Y. (2012). Structure and catalytic performance of alumina-supported copper-cobalt catalysts for carbon monoxide hydrogenation. *J. Catal.*, 286:51-61.
- Xiao, K., Bao, Z., Qi, X., Wang, X., Zhong, L., Fang, K., Lin, M., and Sun., Y. (2013). Structural evolution of CuFe bimetallic nanoparticles for higher alcohol synthesis. *J. Mol. Catal. A: Chem.*, 378:319-325.
- Yan, M., Zhang, M., Ge, S., Yu, J., Li, M., Huang, J., and Liu, S. (2012). Ultrasensitive electrochemiluminescence detection of DNA based on nanoporous gold electrode and PdCu@carbon nanocrystal composites as labels. *Analyst.*, 137:3,314-3,320.