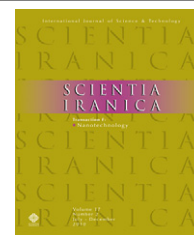




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Fluorescence emission spectra of silver and silver/cobalt nanoparticles

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Abstract Various aqueous solutions of silver and silver/cobalt nanoparticles (Ag and Ag/Co NPs) were obtained, and their fluorescence emission spectra have been studied. First, colloidal Ag NPs were prepared by an electrochemical method under different time intervals and at different rotation speeds of rotating electrode. Next, in a reduction method, Ag/Co core-shell NPs were prepared, using Ag NPs as a core. The core-shell structure of Ag/Co NPs has been demonstrated by the Transmission Electron Micrograph (TEM) and X-Ray Diffraction (XRD) pattern. The fluorescence emission spectra of Ag and Ag/Co NPs, at different ranges of excitation wavelength, were investigated, which revealed two kinds of fluorescence emission peak. The shorter emission peak was fixed at about 485 (for Ag NPs) and 538 nm (for Ag/Co NPs). For both NPs, with an increase in excitation wavelength, the latter emission peak becomes red-shifted. The effect of duration time and rotation speed of the rotating electrode, in the electrochemical preparation of Ag NPs, on its fluorescence emission spectra, has also been investigated.

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1. Introduction

Because of special optical and electronic properties of NPs, they have received much attention in many fields [1–4]. Particularly, the strong optical absorption and fluorescence of noble metallic NPs make them of special interest. However, the exact mechanism concerning factors influencing photoluminescence is still unclear; therefore, the repetition and explanation of some spectral experiments are quite difficult [5]. Fluorescence is a three-step process involving photoexcitation of an electron from ground state to excited states, followed by relaxation of the excited electron, which is accompanied by fluorescence emission [6]. Since bulk metals do not have band

gaps, and nonradiative decay can proceed back down to ground state, their fluorescence emission spectra are rather improbable [7,8]. However, NPs have large surface areas in comparison with bulk metals, and energy states are distinct, which results in a growth in fluorescence emission spectra [9,10].

The first investigation regarding the fluorescence of bulk metals was reported by Mooradian [11]. Boyd et al. studied the photoinduced fluorescence of noble metals and its enhancement on roughened surfaces [12]. The surface plasmon absorption of silver NPs and their plasmonic excited fluorescence have also been reported in [13]. Liang et al. reported the fluorescence spectra of silver NPs with different sizes dispersed in organic solvents [14]. Zheng and Dickson [15] showed that the silver clusters formed by photoreduction have strong fluorescence, while the larger NPs formed through reduction with NaBH₄ were non-fluorescent. The fluorescence emission spectra of silver nanospheres under different excitation wavelengths have also been measured [16]. Jian et al. investigated the fluorescence emission spectra of silver-coated gold colloidal nanoshells, and developed the quasi-static and local field theory to describe the fluorescence emission property [17]. The fluorescence spectrum property of gold nanochains has also been reported [18].

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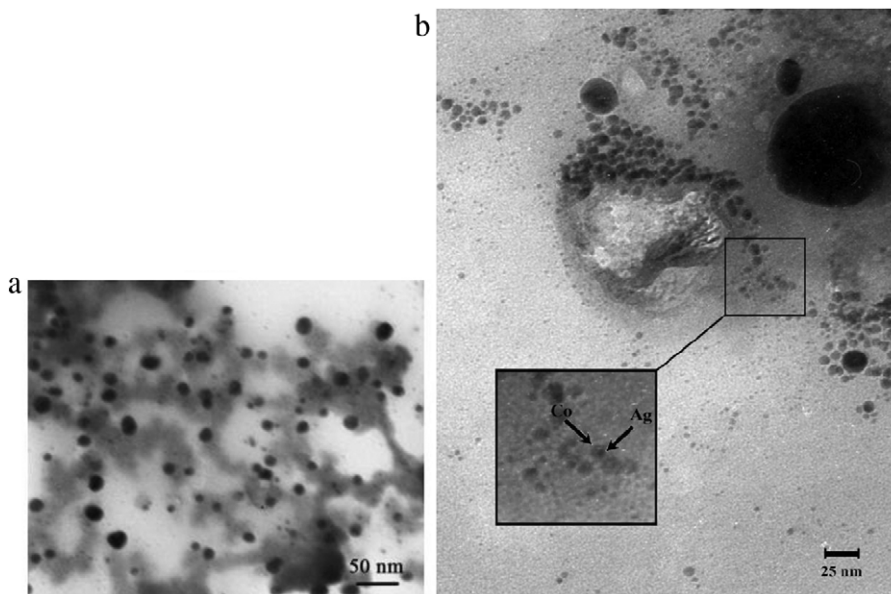


Figure 1: TEM images of (a) Ag NPs, which were synthesized at 75 s and 3000 rpm, and (b) corresponding Ag/Co NPs.

Core-shell nanoparticles show interesting optical, electronic, magnetic and catalytic properties [19–24]. Many methods have been developed for the preparation of core-shell NPs, such as microemulsion [25], electrochemical [26], radiolytic reduction [27], photolytic reduction [28], pulsed laser ablation in water [29], polyol [30], and the UV photoactivated technique [31]. Although several papers have been published about Ag/Co nanoparticles, those concerning the fluorescence emission spectra of these core/shell nanostructured materials are rare in literature.

In this paper, we have developed a simple two step method for fabrication of Ag/Co core-shell NPs. We prepared Ag NPs under different time intervals and different rotation speeds of rotating electrode. The effect of these variations on fluorescence emission spectra of Ag NPs was investigated. At different excitation wavelengths, the fluorescence emission spectra properties of Ag and Ag/Co NPs have also been studied.

2. Experimental

2.1. Materials

Materials were purchased from various chemical companies. Silver nitrate and potassium nitrate were obtained from Scharlau and Panreac, respectively. Sodium borohydride, poly(N-vinylpyrrolidone) (PVP), hexadecyltrimethylammonium bromide (CTAB), nitric acid and cobalt sulfate were also purchased from Merck. In all experiments, aqueous solutions were prepared using double-distilled water.

2.2. Apparatus

An electro analyzer system (SAMA 500) was used for the electrochemical synthesis of Ag NPs. The UV-Vis. absorption spectra were recorded, using a Varian spectrophotometer. The Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD) (Bruker D8, using Cu K_{α} radiation ($\lambda = 1.541874 \text{ \AA}$)) were used to investigate the morphology and structure of fabricated samples. TEM measurements were achieved using a Philips CM10, operating at 100 kV. For this measurement, the

sample was prepared by dropping a diluted prepared solution of the product onto a copper grid and letting it evaporate. The photoluminescence was recorded on a Varian spectrophotometer. The fluorescence spectra were accomplished on a $1 \times 1 \text{ cm}$ quartz cell at various excitation wavelengths.

2.3. Preparation of silver and silver/cobalt NPs

Ag NPs were synthesized by “Controlled Current Coulometry” (CCC), electrochemical method, using a Pt rotating electrode. A solution mixture of AgNO_3 and KNO_3 was applied as an electrolyte and PVP as a stabilizer. Ag NPs were prepared during different time intervals of electrolysis (35, 75, 300 and 600 s), and different rotating speeds of cathode electrode (500, 1000, 1500, 2000 and 3000 rpm) at 1 A, at room temperature. The color change of the electrolyte around the cathode to yellow reveals the formation of Ag NPs.

Then, Ag/Co core-shell NPs were prepared by the reduction method, using Ag NPs as a core. For this purpose, a solution containing CoSO_4 and CTAB was added to the colloidal Ag NPs solution. Then, NaBH_4 , as a reducing agent, was added. The color change to dark brown indicated the formation of Ag/Co NPs.

3. Results and discussion

In this study, we have investigated the fluorescence emission spectra of Ag and Ag/Co NPs. First, Ag and Ag/Co NPs were prepared. In Figure 1, TEM images of Ag NPs that were synthesized at 75 s and 3000 rpm, and related Ag/Co NPs are shown; the XRD pattern of the Ag/Co NPs is shown in Figure 2. The core-shell structure of the fabricated Ag/Co NPs is confirmed by its TEM image. In core-shell NPs, whose heavier metal is a shell, only the peaks of heavier metal are observed in the XRD pattern [32]. For this purpose, the XRD pattern of the related Ag/Co NPs was investigated. As determined by X-ray diffraction (Figure 2), peaks fitted on 38.15 , 44.3 , 64.50 , 77.47 and 81.62° indicate the existence of Ag, and bands fitted on 41.10 , 43.78 , 46.84 and 74.89° show the presence of cobalt. From these results, we conclude that Ag is core and Co is

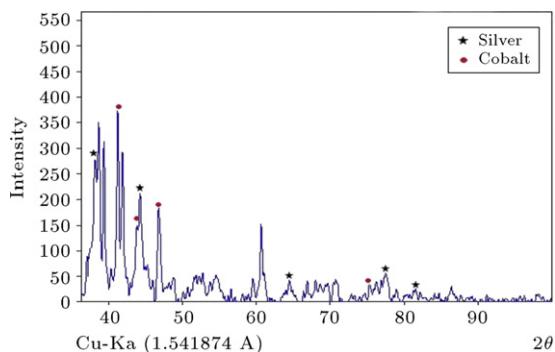


Figure 2: XRD pattern of Ag/Co NPs obtained from Ag NPs, which were synthesized at 75 s and 3000 rpm.

shell; so the dark solid core of particles belongs to Ag, and the bigger grayish sphere surrounding them belongs to Co atoms. However, TGA analysis and electrochemical techniques have also been applied as proof of the core-shell structure of these fabricated Ag/Co NPs [33].

Ag NPs were prepared by an electrochemical method at different time intervals and rotation speeds of the rotating electrode. The UV–Vis. spectra of these synthesized NPs were investigated (Figure 3). The Ag NPs characteristic plasmon resonance absorption band was detected at about 405 nm. We observed that as the time of Ag NPs synthesis was increased, the concentration of Ag NPs was also enhanced, so, we had to dilute Ag NPs, which were synthesized over 600 s, in order to study its UV–Vis. absorption spectrum. Therefore, its intensity decreased in comparison with Ag NPs prepared over 300 s (Figure 3).

Then, the fluorescence emission spectra of various solutions of Ag NPs were investigated. For this purpose, the Ag NPs that were prepared over different time intervals and at different rotation speeds of rotating electrode were excited at 420 nm. As reported previously [34], the rotation speed of the rotating electrode has a significant effect on the particle size and degree of aggregation, and at higher rotational speed, the synthesis of smaller nanoparticles is favorable. We also observed that enhancement in the rotation speed of the rotating electrode is accompanied by a decrease in the size of the prepared Ag NPs. It was also observed that the fluorescence emission peak slightly blue-shifted with a decrease in the size of Ag NPs (Figure 4).

As shown in Figure 5, the fluorescence emission peak of Ag NPs, which was prepared over 75 s was detected at about 485 nm at a certain rotation speed of rotating electrode (for example, 500 rpm). By increasing the time of synthesis to 600 s, interaction between Ag NPs increases, due to the

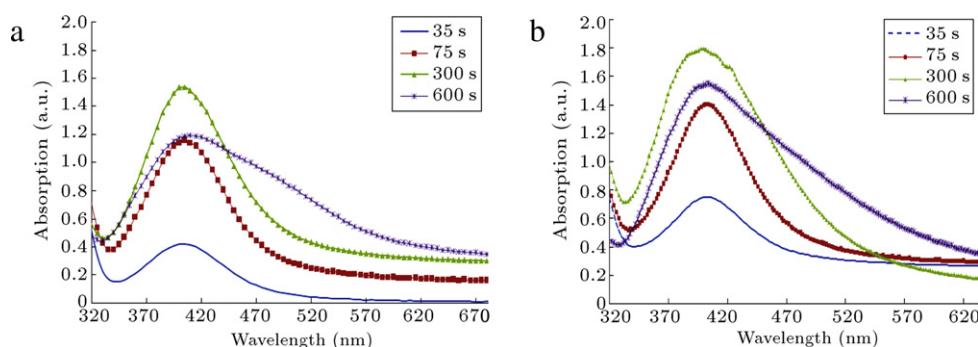


Figure 3: UV–Vis. absorption spectrum of Ag NPs, which were synthesized at different times (35, 75, 300 and 600 s) in (a) 500 and (b) 3000 rpm.

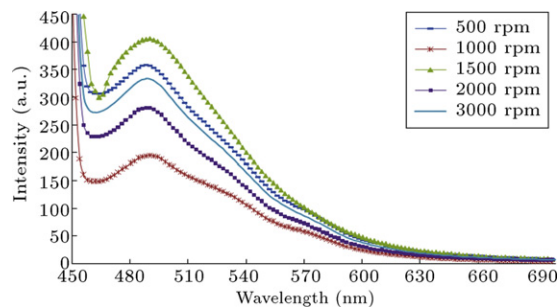


Figure 4: Fluorescence emission spectra of Ag NPs synthesized during 75 s at different rotation speeds (500, 1000, 1500, 2000 and 3000 rpm), excited at 420 nm.

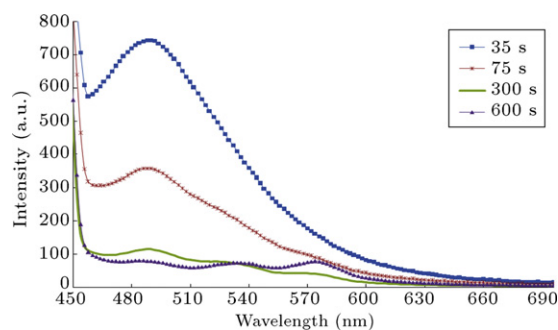


Figure 5: Fluorescence emission spectra of Ag NPs, which were prepared during different times (35, 75, 300, and 600 s), and 500 rpm, excited at 420 nm.

concentration enhancement of NPs. As a result, the energy level becomes broader and splits. Therefore, two emission peaks were observed for Ag NPs that were prepared over 300 and 600 s.

The fluorescence properties of Ag and Ag/Co NPs under different excitation wavelengths were also investigated (Figures 6 and 7). As the excitation wavelength changed from 380 to 410 nm for Ag NPs, and from 400 to 440 nm for Ag/Co NPs, two kinds of fluorescence emission peak were observed. The shorter emission wavelength was fixed at about 485 and 538 nm for Ag and Ag/Co NPs, respectively, and the longer emission wavelengths were red-shifted, along with the increase in excitation wavelength. These two fluorescence emission peaks are attributed to relaxation from the electronic motion of surface plasmon, and a recombination of sp electrons with holes in the d band, respectively. The reason for the observed red-shift in fluorescence spectra can be elucidated by the following explanation. As the excitation wavelength increases, the electrons will

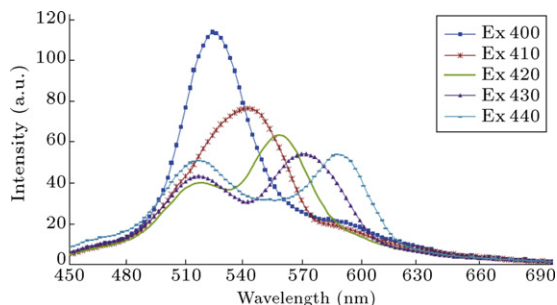


Figure 6: Fluorescence emission spectra of Ag/Co NPs, which were prepared by Ag NPs that were synthesized during 75 s at 500 rpm, excited at 400–440 nm.

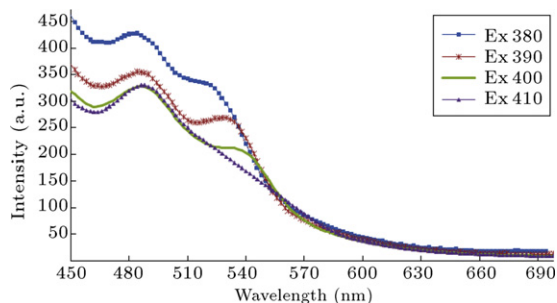


Figure 7: Fluorescence emission spectra of Ag NPs, which were prepared at 75 s and 500 rpm, excited at 380–410 nm.

be stimulated to the lower energy level, so relaxation of these electrons will be emitted at longer wavelengths.

As shown in Figure 6, in fluorescence emission peaks of Ag/Co NPs at excitation wavelengths smaller than 420 nm, the shorter emission peak cannot be seen. It has been covered with the longer one, and as the excitation wavelength increases, the latter peak become red-shifted and two peaks become more distinct. However, for Ag NPs in excitation wavelengths higher than 400 nm, the longer emission peak has been covered by the shorter one (Figure 7).

4. Conclusion

In this study, we have prepared Ag and Ag/Co NPs, and the fluorescence emission spectra of these NPs have been investigated. The Ag NPs have been prepared by an electrochemical method over different time intervals and at different rotation speeds of rotating electrode. The UV–Vis. and fluorescence emission spectra of these synthesized NPs were studied, and the effect of the duration time of synthesis and the rotation speed of the rotating electrode on their fluorescence emission spectra, at 420 nm excitation wavelength, was investigated. It was observed that as the duration time of Ag NPs synthesis increased, the fluorescence peak splits and with an increase in the rotation speed of the rotating electrode, the peak becomes slightly blue-shifted. Then, during a reduction method, Ag/Co NPs were obtained from Ag NPs. The core-shell structure of Ag/Co NPs was also demonstrated by TEM image and XRD pattern. The fluorescence emission spectra of Ag and Ag/Co NPs at different excitation wavelengths were studied, and for both NPs, two kinds of emission peak were observed. For Ag NPs, it was observed that at excitation wavelengths higher than 400 nm, the latter emission peak was hidden by the shorter one. However, for Ag/Co NPs, by increasing excitation wavelength, the emission fluorescence peak will be distinct.

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References

- [1] Ung, T., Luis, M., Marzan, L. and Mulvaney, P. "Gold nanoparticle thin films", *Colloids Surf. A*, 202, pp. 119–126 (2002).
- [2] Lazarides, A.A., Lance Kelly, K., Jensen, T.R. and Schatz, G.C. "Optical properties of metal nanoparticles and nanoparticle aggregates important in biosensors", *J. Mol. Struct.*, 529, pp. 59–63 (2000).
- [3] Benfield, R.E., Grandjean, Kroll, D.M., Pugin, R., Sawitowski, T. and Schmid, G. "Structure and bonding of gold metal clusters, colloids, and nanowires studied by EXAFS, XANES, and WAXS", *J. Phys. Chem. B*, 105, p. 1961 (2001).
- [4] Ji, C.X. and Searson, P.C. "Synthesis and characterization of nanoporous gold nanowires", *J. Phys. Chem. B*, 107, pp. 4494–4499 (2003).
- [5] Zhang, A., Zhang, J. and Fang, Y. "Photoluminescence from colloidal silver nanoparticles", *J. Lumin.*, 128, pp. 1635–1640 (2008).
- [6] Siwach, O.P. and Sen, P. "Synthesis and study of fluorescence properties of Cu nanoparticles", *J. Nanopart. Res.*, 10, pp. 107–114 (2008).
- [7] Chen, S., Ingram, R.S., Hostetler, M.J., Pietron, J.J., Murray, R.W., Schaaff, T.G., Khoury, J.T., Alvarez, M.M. and Whetten, R.L. "Gold nanoelectrodes of varied size: transition to molecule-like charging", *Science*, 280, pp. 2098–2101 (1998).
- [8] Ingram, R.S., Hostetler, M.J., Murray, R.W., Schaaff, T.G., Khoury, J.T., Whetten, R.L., Bigioni, T.P., Guthrie, D.K. and First, P.N. "28 kDa alkanethiolate-protected Au clusters give analogous solution electrochemistry and STM Coulomb staircases", *J. Am. Chem. Soc.*, 119, p. 9279 (1997).
- [9] Mohamed, M.B., Volkov, V., Link, S. and El-Sayed, M.A. "The lightning gold nanorods: fluorescence enhancement of over a million compared to the gold metal", *Chem. Phys. Lett.*, 317, p. 517 (2000).
- [10] Wilcoxon, J.P., Martin, J.E., Parsapour, F., Wiedenman, B. and Kelley, D.F. "Photoluminescence from nanosize gold clusters", *J. Chem. Phys.*, 108, p. 9137 (1998).
- [11] Mooradian, A. "Photoluminescence of metals", *Phys. Rev. Lett.*, 22, pp. 185–187 (1969).
- [12] Boyd, G.T., Yu, Z.H. and Shen, Y.R. "Photoinduced luminescence from the noble metals and its enhancement on roughened surfaces", *Phys. Rev. B*, 33, p. 7923 (1986).
- [13] Abdullah, A. and Annapoorni, S. "Fluorescent silver nanoparticles via exploding wire technique", *Pramana J. Phys.*, 65, pp. 815–819 (2005).
- [14] Liang, H.C., Rong, M.Z., Zhang, M.Q. and Zeng, H.M. "Individual water-soluble dendrimer-encapsulated silver nanodot fluorescence", *Acta Phys. Sinica*, 51, p. 50 (2002).
- [15] Zheng, J. and Dickson, R.M. "Individual water-soluble dendrimer-encapsulated silver nanodot fluorescence", *J. Am. Chem. Soc.*, 124, pp. 13982–13983 (2002).
- [16] Jian, Z., Xiang, Z. and Yongchang, W. "Electrochemical synthesis and fluorescence spectrum properties of silver nanospheres", *Microelectron. Eng.*, 77, pp. 58–62 (2005).
- [17] Jian, Z., Yongchang, W. and Yimin, L. "Fluorescence spectra characters of silver-coated gold colloidal nanoshells", *Colloids Surf. A*, 232, pp. 155–161 (2004).
- [18] Jian, Z., Liqing, H., Yongchang, W. and Yimin, L. "Fluorescence spectrum properties of gold nanochains", *Physica E*, 25, pp. 114–118 (2004).
- [19] Liu, M. and Guyot-Sionnest, P. "Synthesis and optical characterization of Au/Ag core/shell nanorods", *J. Phys. Chem. B*, 108, pp. 5882–5888 (2004).
- [20] Hodak, J.H., Henglein, A., Giersig, M. and Hartland, G.V. "Laser-induced inter-diffusion in AuAg core-shell nanoparticles", *J. Phys. Chem. B*, 104, pp. 11708–11718 (2000).
- [21] Sun, S., Murray, C.B., Weller, D., Folks, L. and Moser, A. "Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices", *Science*, 287, p. 1989 (2000).
- [22] Saravanan, P., Srinivasa Rao, K., Premkumar, M. and Singh, A.K. "Spherical granular structures of Ag/Co nanoparticles: synthesis, characterization and magnetic properties", *J. Alloys Compd.*, 509, pp. 3880–3885 (2011).
- [23] Wu, S.Y., Yang, C.C., Tsao, F.C., Huang, P.J., Chung, M.K. and Li, W.-H. "Tunneling magnetoresistance in Ag/Co nanoparticles composites", *J. Magn. Mater.*, 294, pp. e83–e86 (2005).
- [24] Wang, L., Clavero, C., Huba, Z., Carroll, K.J., Carpenter, E.E., Gu, D. and Lukaszew, R.A. "Plasmonics and enhanced magneto-optics in core-shell Co–Ag nanoparticles", *Nano Lett.*, 11, pp. 1237–1240 (2011).
- [25] Garcia-Torres, J., Vallés, E. and Gómez, E. "Synthesis and characterization of Co@Ag core-shell nanoparticles", *J. Nanopart. Res.*, 12, pp. 2189–2199 (2010).

- [26] Zhu, J., Wang, Y., Huang, L. and Lu, Y. "Resonance light scattering characters of core-shell structure of Au–Ag nanoparticles", *Phys. Lett. A*, 323, pp. 455–459 (2004).
- [27] Xue, C., Millstone, J.E., Li, S. and Mirkin, C.A. "Plasmon-driven synthesis of triangular core-shell nanoprisms from gold seeds", *Angew. Chem. Int. Ed.*, 46, pp. 8436–8439 (2007).
- [28] Mulvaney, P., Giersig, M. and Henglein, A. "Electrochemistry of multilayer colloids: preparation and absorption spectrum of gold-coated silver particles", *J. Phys. Chem.*, 97, pp. 7061–7064 (1993).
- [29] Compagnini, G., Messina, E., Puglisi, O., Cataliotti, R.S. and Nicolosi, V. "Spectroscopic evidence of a core-shell structure in the earlier formation stages of Au–Ag nanoparticles by pulsed laser ablation in water", *Chem. Phys. Lett.*, 457, pp. 386–390 (2008).
- [30] Tsuji, M., Hikino, S., Tanabe, R., Matsunaga, M. and Sano, Y. "Synthesis of Ag/Cu alloy and Ag/Cu alloy core Cu shell nanoparticles as a polyol method", *Cryst. Eng. Comm.*, 12, pp. 3900–3908 (2010).
- [31] Mallik, K., Mandal, M., Pradhan, N. and Pal, T. "Seed mediated formation of bimetallic nanoparticles by UV irradiation: a photochemical approach for the preparation of "core-shell" type structures", *Nano Lett.*, 1, pp. 319–322 (2001).
- [32] Xu, Z., Hou, Y. and Sun, S. "Magnetic core/shell Fe₃O₄/Au and Fe₃O₄/Au/Ag nanoparticles with tunable plasmonic properties", *J. Am. Chem. Soc.*, 129, pp. 8698–8699 (2007).
- [33] Parang, Z., Keshavarz, A., Farahi, S., Elahi, S.M., Ghoranneviss, M. and Nasser, A. "Preparation and investigation of optical, thermal, and electrochemical properties of Ag/Co nanoparticles", *Nano*, 7, pp. 12500061–12500069 (2012).
- [34] Ma, H., Yin, B., Wang, S., Jiao, Y., Pan, W., Huang, S., Chen, S. and Meng, F. "Synthesis of silver and gold nanoparticles by a novel electrochemical method", *Chem. Phys. Chem.*, 5, pp. 68–75 (2004).

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