

Research Article

Facile Interpretation of Catalytic Reaction between Organic Dye Pollutants and Silver Nanoparticles with Different Shapes

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In this study, various shapes of silver nanoparticles (Ag NPs) were synthesized via simple methods in aqueous solution. The size and shape of Ag NPs were measured by TEM image and DLS, and the crystalline form of Ag NPs was confirmed by XRD. From ATR-IR and zeta potential, the Ag NPs were found to be well surrounded by PVP. In addition, the catalytic activity of Ag NPs was evaluated using model dyes. Unlike the conventional catalysts, the model dyes with absorption peaks that did not overlap with the SPR peaks of the Ag NPs were selected to evaluate the catalytic activity without removal of the Ag NPs from the dye solution.

1. Introduction

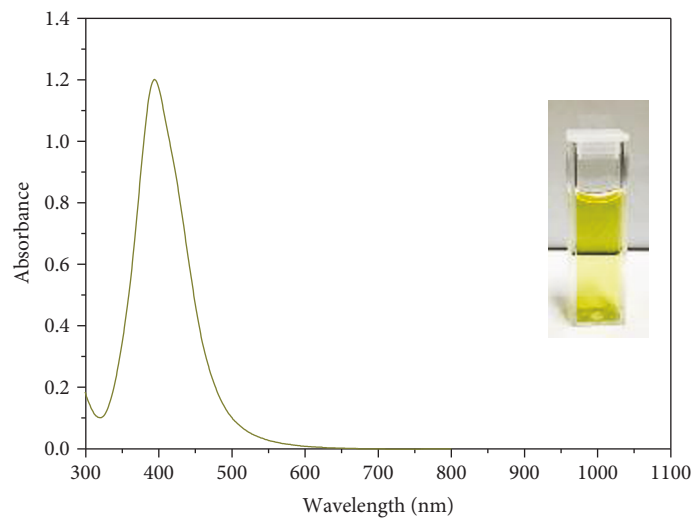
In recent years, metal nanoparticles (NPs) have received considerable attention because of their attractive properties and interesting applications [1–3]. They are widely used in various fields including sensors, catalysts, functional materials for devices, and imaging [4–11]. Among them, silver nanoparticles (Ag NPs) are being studied extensively for their potential in catalysts, antibacterial agents, biological diagnostics, electronics, and surface-enhanced Raman scattering [12–16]. In particular, the catalytic properties of Ag NPs are of interest to many researchers because of their high reactivity.

Environmental pollution caused by organic pollutants has emerged as a serious problem. Among the many organic pollutants, it is important to address the problem of organic dye contamination caused by the development of industries such as paper, fiber, plastic, and paint [17]. The release of wastewater, which contains an excess of organic dyes, can interfere with sunlight penetration and with photosynthesis of the plant. In addition, some synthetic dyes can pose a serious threat to the human body [12, 18]. Thus, a variety of techniques has been used for the removal of contaminants

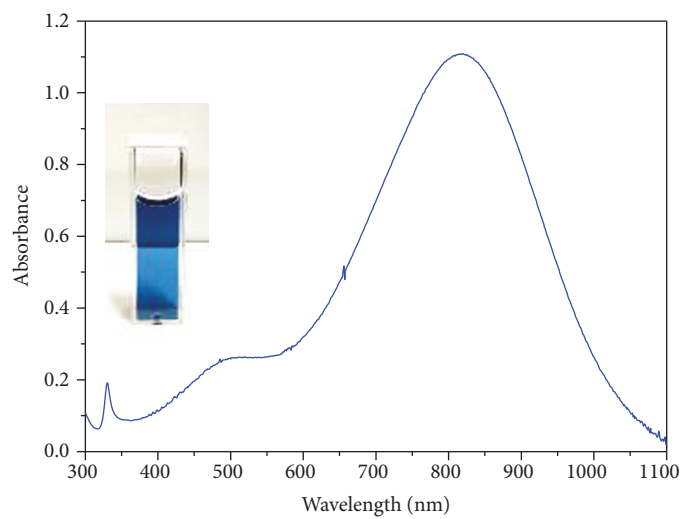
such as adsorption, catalytic degradation, membrane filtrations, and chemical oxidation [19, 20].

Much research has been focused on the catalytic decompositions of organic dyes using Ag NPs as a catalyst. However, it is impossible to interpret directly the catalytic reaction from a mixture of organic dyes and NPs because of a severe overlapping between the surface plasmon resonance (SPR) peak of Ag NPs and the absorption peak of dyes. Therefore, the catalytic activity has been investigated by either incorporating Ag NPs into a polymer matrix, such as nanofibers, or removing Ag NPs in the solution by centrifugation [12, 21–23].

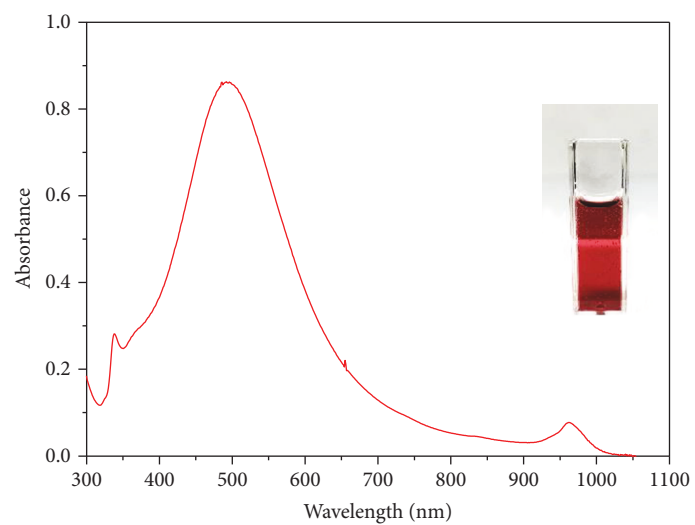
In this study, the shape-controlled Ag NPs were synthesized by simple methods in aqueous solution in order to vary the SPR peak position according to the shape of the Ag NPs. The synthesized Ag NPs were nanospheres, nanodisks, and nanotriangular plates, abbreviated as Ag NSs, Ag NDs, and Ag NTs, respectively. The morphology and crystalline structure of the Ag NPs were observed, and their catalytic activities for the model dyes were evaluated. In order to measure the catalytic activity in real time without the removal of Ag NPs from the dye solution, the catalytic activity was evaluated by selecting a model dye with an



(a)



(b)



(c)

FIGURE 1: SPR spectra of Ag NPs using UV-Vis spectroscopy: (a) Ag NSs, (b) Ag NTs, and (c) Ag NDs. The solution color is inserted.

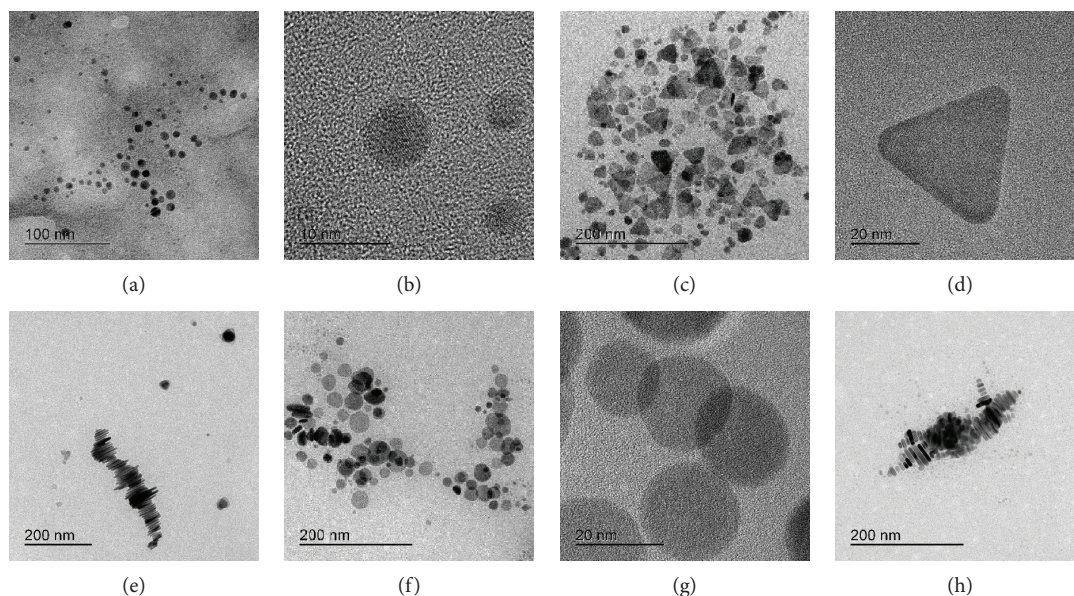


FIGURE 2: TEM images of Ag NPs with different shapes: (a, b) Ag NSs, (c–e) Ag NTs, and (f–h) Ag NDs.

TABLE 1: Zeta potential and DLS of Ag NPs with different shapes.

	Ag NSs	Ag NDs	Ag NTs
Zeta potential value	-13.8 mV	-29.2 mV	-28.6 mV
DLS size	38.54 nm	50.55 nm	51.11 nm

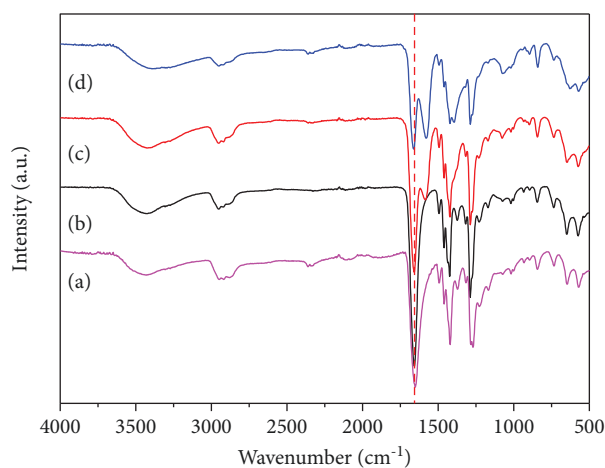


FIGURE 3: ATR-IR spectra of (a) PVP and various types of Ag NP: (b) Ag NSs, (c) Ag NTs, and (d) Ag NDs.

absorption peak position that does not significantly overlap with the SPR absorption peak of Ag NPs.

2. Materials and Methods

2.1. Materials. Silver nitrate (AgNO_3), a precursor of Ag NPs, was purchased from Kojima Co. Ltd. (purity 99.9%, Sayama, Japan). Poly(vinyl pyrrolidone) (PVP) (Mw 40,000, Sigma-Aldrich, MO, USA) as a stabilizer and NaBH_4 (Samchun

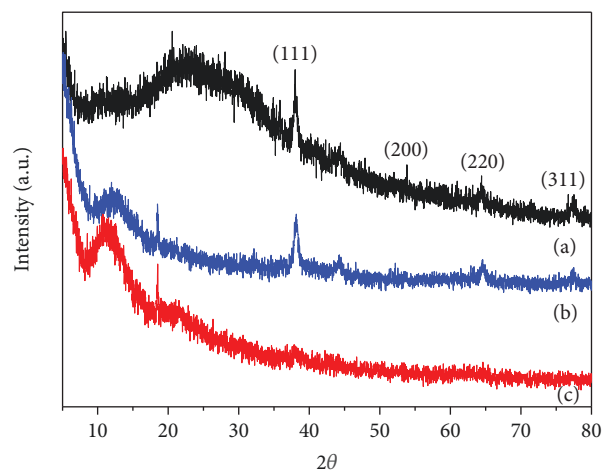


FIGURE 4: XRD patterns of Ag NPs with three shapes: (a) Ag NSs, (b) Ag NTs, and (c) Ag NDs.

Pure Chemical, Pyeongtaek, Korea), which is a strong reducing agent, were used. Tribasic sodium citrate anhydrate (Na_3CA) and hydrogen peroxide (H_2O_2) (30%), which play an important role in controlling the shape of Ag NPs, were obtained from Sigma-Aldrich (MO, USA) and Junsei Chemical Co. Ltd. (Tokyo, Japan), respectively. The solvent of all materials was distilled water.

2.2. Preparation of Ag NPs with Different Shapes. The Ag NPs were synthesized as three types, nanosphere, nanodisk, and nanotriangular plate, and each detailed synthesis was as follows. First, Ag NSs were synthesized by simply mixing a precursor, a reducing agent, and a stabilizer. 1.5 ml and 0.14 ml of PVP (0.7 mM) and NaBH_4 (100 mM), respectively, were added to the 25 ml of AgNO_3 solution (0.1 mM). The

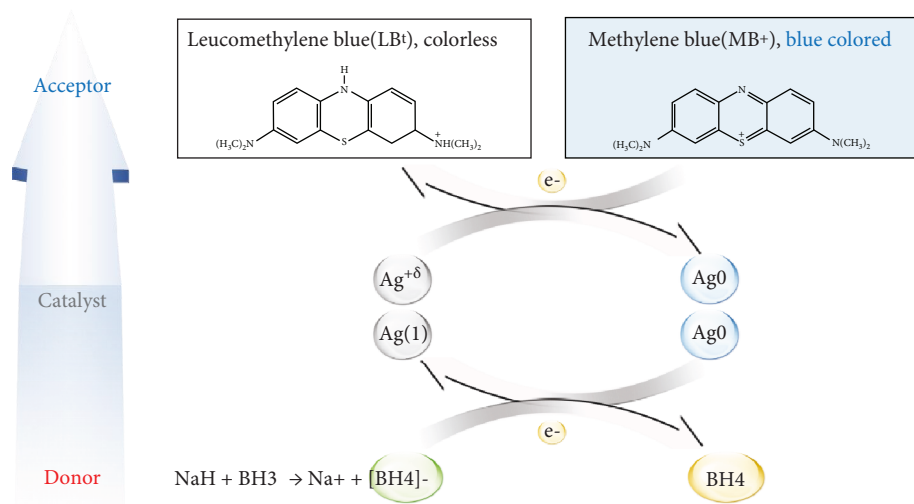
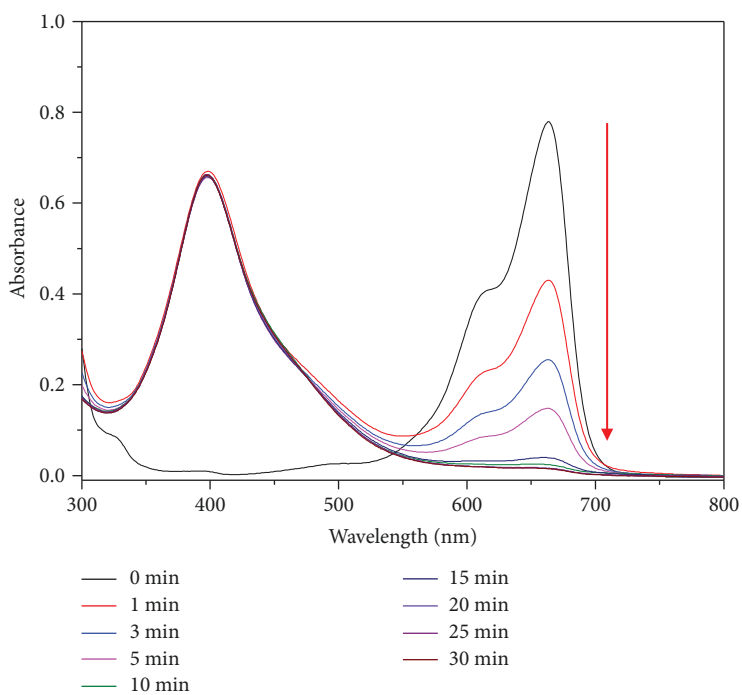
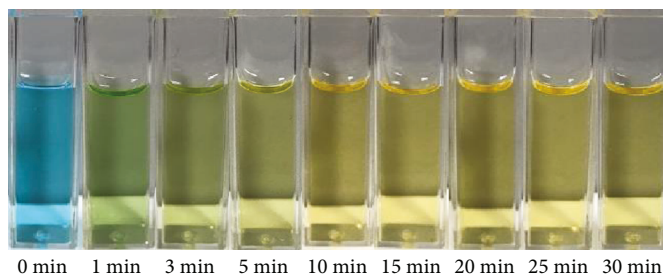


FIGURE 5: The scheme of the catalytic mechanism of Ag NPs.



(a)



(b)

FIGURE 6: Catalytic activity of Ag NSs for MB according to reaction time: (a) UV-Vis spectra and (b) solution color.

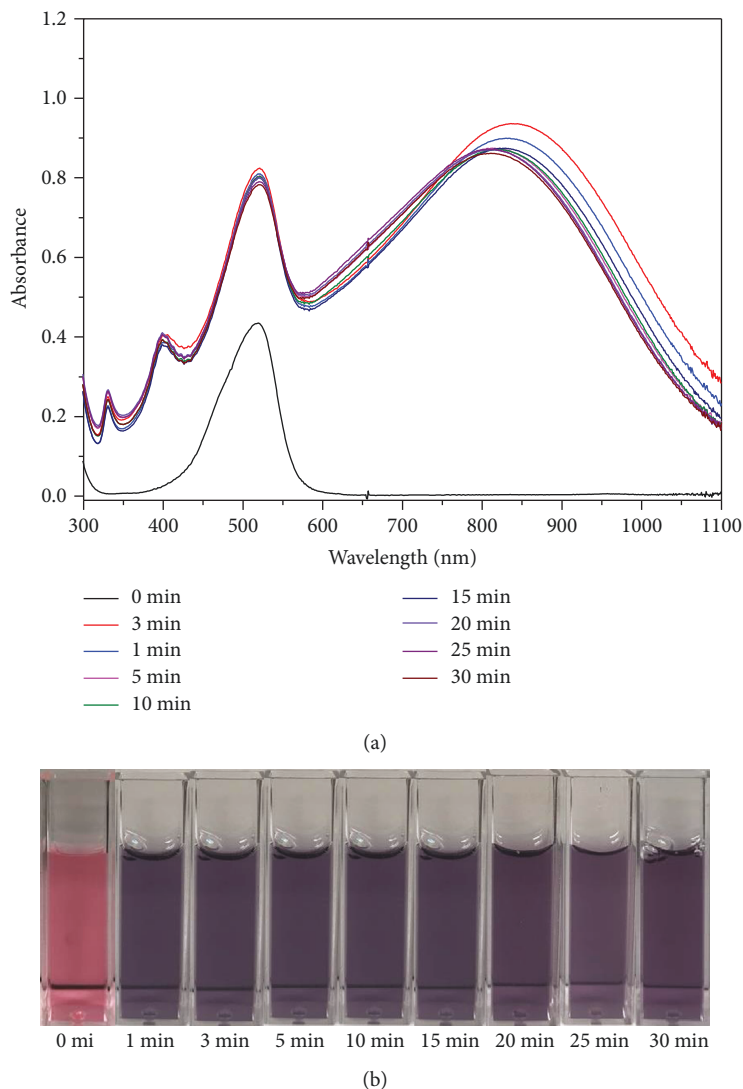


FIGURE 7: Catalytic activity of Ag NTs for SO according to reaction time: (a) UV-Vis spectra and (b) solution color.

solution turned yellow immediately after mixing. In the second method, Ag NTs were synthesized in almost the same way as for the Ag NSs. Na_3CA (1.5 ml, 30 mM) and H_2O_2 (90 μl) were added to a mixed solution of AgNO_3 , PVP, and NaBH_4 . The solution color of yellow gradually became blue through red, and violet on mild stirring. Finally, Ag NDs were synthesized via a two-step synthesis. In the first step, the NaBH_4 solution (100 mM) and 0.06 g of PVP were added to the AgNO_3 solution (0.1 mM). After PVP was completely dissolved, 240 μl of H_2O_2 and 1.8 ml of Na_3CA (100 mM) were added. The change in solution color was observed after sufficient stirring, when the solution gradually changed to blue from the surface to the bottom. When the mixed solution was heated in a water bath (95°C), Ag NDs were synthesized and the solution turned red.

All samples were obtained by ultracentrifugation (13,000 rpm, 10 min) (Supra 30K, Hanil Science Co. Ltd., Daejeon, Korea), purged with argon gas, then lyophilized (FD8508, IlshinBio, Yangju, Korea).

2.3. Catalytic Activity. Methylene blue (MB) (Samchun Pure Chemical, Pyeongtaek, Korea) and safranin O (SO) (Sigma-Aldrich, MO, USA) dyes were used as model dyes for the catalytic experiments. The concentration of the dye used was 2×10^{-5} M. After adding 0.01 g of the dried Ag NPs to 10 ml of each dye solution, the change in absorbance and color with time was examined. At this time, Ag NTs were used together with SO, and Ag NSs and Ag NDs were used together with MB, so that the SPR spectra of the Ag NPs and the absorption peaks of the dyes did not overlap each other.

2.4. Characterizations. The SPR absorption spectra of Ag NPs were recorded using a UV-Vis spectrophotometer (US 8453, Agilent Technologies, CA, USA) with a variable wavelength between 200 and 1,100 nm and a 1 cm optical path at room temperature. For the transmission electron microscopy (TEM) (Tecnai G2 F30, FEI Company, OR, USA) images, the samples were prepared by dropping the solution containing Ag NPs onto the carbon-coated copper grid. The

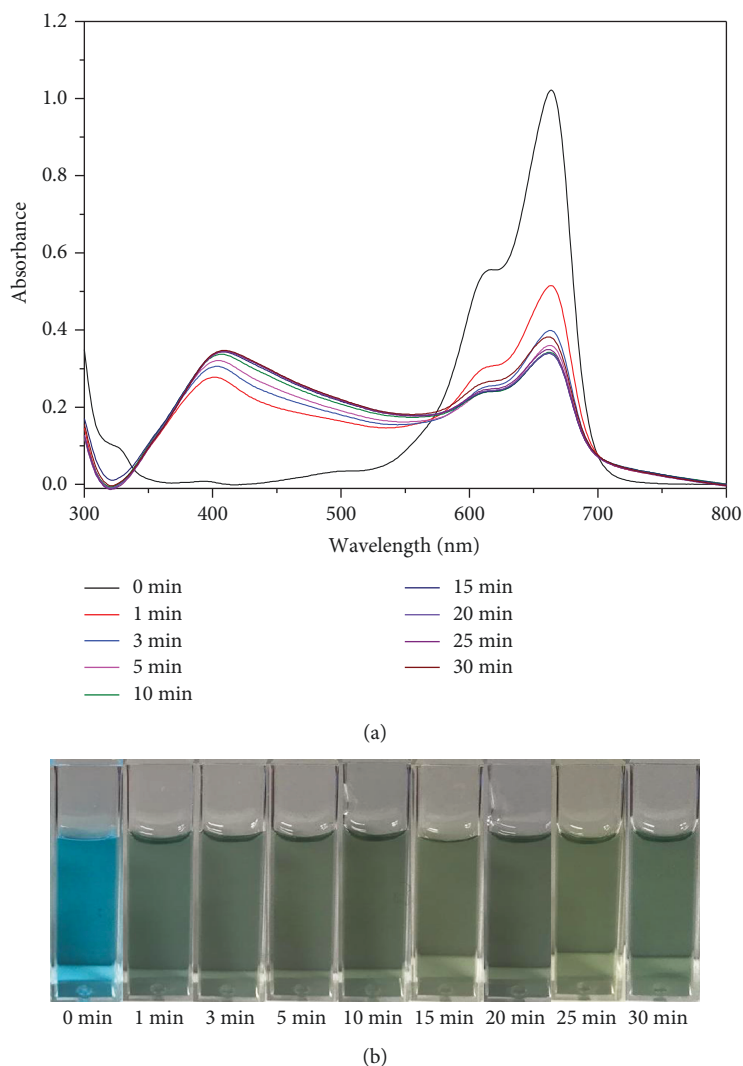


FIGURE 8: Catalytic activity of Ag NDs for MB according to reaction time: (a) UV-Vis spectra and (b) solution color.

crystalline structure of synthesized Ag NPs was confirmed by X-ray diffractometer patterns (XRD, Bruker AXS, D8 DISCOVER), and XRD patterns were measured at room temperature with a scan range of $2\theta = 10^\circ - 80^\circ$ and a scan rate of 0.5 second/step. After lyophilization, the dried Ag NPs were loaded into an attenuated total reflection infrared (ATR-IR) spectra (ALPHA, Bruker, Bremen, Germany), and the spectra were taken at wavenumbers from 600 to $4,000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . For comparison, the ATR-IR spectrum of a neat PVP sample was also recorded. The zeta potential and dynamic light scattering (DLS) data of the Ag NPs were measured using a Zetasizer ZS90 (Malvern, Worcestershire, UK).

3. Results and Discussion

3.1. Characterization of Ag NPs with Different Shapes. The synthesized Ag NPs with different shapes were analyzed by UV-Vis spectroscopy (Figure 1). The colors of Ag NP (Ag NSs, Ag NTs, and Ag NDs) solutions were yellow, blue, and red, respectively, and corresponding SPR peaks were observed

at 410, 820, and 510 nm, respectively. Ag NTs and Ag NDs also showed shoulder peaks at 330 nm originating from an out-of-plane quadruple plasmon [24]. Figure 2 shows the TEM images of Ag NPs with different shapes. The Ag NSs, Ag NTs, and Ag NDs had uniform shapes with relatively narrow distribution. Furthermore, nanotriangular plates and nanodisks were confirmed by the vertically stacked images of Ag NTs and Ag NDs, respectively (Figures 2(e) and 2(h)) [25]. The average particle size of Ag NSs was 20.4 nm, the mean length of one side of Ag NTs was 28.1 nm, and the average diameter of Ag NDs was 28.1 nm. In addition, the thicknesses of Ag NTs and Ag NDs were found to be 6.4 nm and 5.5 nm, respectively. In Table 1, the zeta potentials of Ag NSs, Ag NTs, and Ag NDs stabilized with PVP were -13.8 mV, -28.6 mV, and -29.2 mV, respectively. When the size of Ag NPs dispersed in aqueous solution was measured via DLS, the average particle sizes of Ag NSs, Ag NTs, and Ag NDs were 38.5 nm, 51.1 nm, and 50.6 nm, respectively. The particle size of Ag NPs from DLS was higher than from TEM images. In the TEM images, the physical size of the Ag NPs was measured, because the electron energy could be

transmitted into the PVP chain domain surrounding the Ag NPs. On the other hand, the DLS measured the hydrodynamic volume of the Ag NPs, because the DLS data contained the PVP chain domain surrounding the Ag NPs, resulting in the overestimated particle size [21].

From the ATR-IR analysis of Ag NPs stabilized with PVP, a strong absorption peak caused by the C=O stretching vibration of PVP was observed at $1,658\text{ cm}^{-1}$ (Figure 3) [26]. The Ag NPs with different shapes also showed this strong absorption, indicating that Ag NPs were stably surrounded by PVP. Figure 4 shows the XRD pattern of Ag NPs with different shapes. The crystalline peaks at about 38.0° , 44.2° , 64.5° , and 77.5° were assigned to the (111), (200), (220), and (311) planes, respectively, of a face-centered cubic (fcc) Ag crystal, indicating that Ag NPs with different shapes were composed of crystalline Ag [27].

3.2. Catalytic Activity of Ag NPs with Different Shapes. The catalytic activity of Ag NPs occurs when the electrons of released Ag ions are exchanged between a reducing agent (electron donor) and a dye (electron acceptor) (Figure 5). Therefore, two model dyes, MB and SO, were used to evaluate the catalytic activity of Ag NPs with different shapes. Model dyes with different absorption spectra were chosen to avoid overlapping with the SPR peaks of Ag NPs. The absorption maxima of MB and SO appeared at 664 nm and 510 nm, respectively. Therefore, Ag NSs and Ag NDs with SPR peaks at 410 nm and 510 nm, respectively, were used as catalyst for MB, whereas Ag NTs with an absorption peak at 820 nm were tested as a catalyst for SO. After the Ag NPs were added to each dye solution, the change in color and in UV-Vis spectra was observed with the reaction time. For Ag NSs shown in Figure 6, the rapid catalytic reaction was observed rather quickly, and the maximum peak at 664 nm corresponding to MB absorption almost disappeared after 30 min. The solution color was initially green, which was a mixture of yellow Ag NSs and blue MB. With reaction time, the color of the MB disappeared and the color of the NPs, yellow, became apparent (Figure 6(b)). In Figure 7, the absorption peak of MB showed an initially significant decrease in the catalytic reaction using Ag NDs.

On the other hand, the catalytic activity of Ag NTs toward SO was lower than that of MB, resulting in a slight decrease with time (Figure 8). The change in color was also not dramatic compared to that of Ag NSs. As a result, Ag NPs with different shapes were found to have catalytic activity for the model dyes, although their activity depended on dye-Ag NP interaction. Furthermore, the change in dye absorption peaks could be measured in real time without severe overlapping with the SPR peaks of the NPs.

4. Conclusions

In this study, Ag NPs with nanospherical, nanotriangular plate, and nanodisk shapes were synthesized by a simple method. The size and morphology of the synthesized Ag NPs were confirmed by the TEM images and XRD patterns. In addition, the catalytic activity of Ag NPs for two model dyes was examined. We found that for the catalytic reaction,

the synthesized Ag NPs with different shapes showed good catalytic activity, and the catalytic activity of the model dyes can also be evaluated without overlapping with the SPR peaks of the Ag NPs. Therefore, various types of Ag NPs can be a novel and easy catalyst that is applicable in real time without being removed by centrifugation in solution or incorporated into a matrix material.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

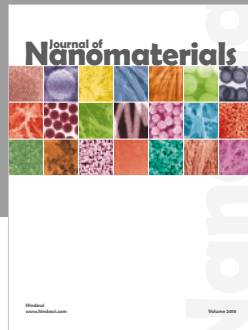
Acknowledgments

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References

- [1] A. Roucoux, J. Schulz, and H. Patin, "Reduced transition metal colloids: a novel family of reusable catalysts?," *Chemical Reviews*, vol. 102, no. 10, pp. 3757–3778, 2002.
- [2] A. Frattini, N. Pellegrini, D. Nicastro, and O. Sanctis, "Effect of amine groups in the synthesis of Ag nanoparticles using aminosilanes," *Materials Chemistry and Physics*, vol. 94, no. 1, pp. 148–152, 2005.
- [3] M. H. Rashid and T. K. Mandal, "Synthesis and catalytic application of nanostructured silver dendrites," *The Journal of Physical Chemistry C*, vol. 111, no. 45, pp. 16750–16760, 2007.
- [4] J. Tian, H. Li, W. Lu, Y. Luo, L. Wang, and X. Sun, "Preparation of Ag nanoparticle-decorated poly(m-phenylenediamine) microparticles and their application for hydrogen peroxide detection," *Analyst*, vol. 136, no. 9, pp. 1806–1809, 2011.
- [5] Y. Zhang, L. Wang, J. Tian, H. Li, Y. Luo, and X. Sun, "Ag@poly(m-phenylenediamine) core-shell nanoparticles for highly selective, multiplex nucleic acid detection," *Langmuir*, vol. 27, no. 6, pp. 2170–2175, 2011.
- [6] M. A. El-Sayed, "Some interesting properties of metals confined in time and nanometer space of different shapes," *Accounts of Chemical Research*, vol. 34, no. 4, pp. 257–264, 2001.
- [7] P. V. Kamat, "Photophysical, photochemical and photocatalytic aspects of metal nanoparticles," *The Journal of Physical Chemistry B*, vol. 106, no. 32, pp. 7729–7744, 2002.
- [8] R. Narayanan and M. A. El-Sayed, "Changing catalytic activity during colloidal platinum nanocatalysis due to shape changes: electron-transfer reaction," *Journal of the American Chemical Society*, vol. 126, no. 23, pp. 7194–7195, 2004.
- [9] M. H. Rashid, R. R. Bhattacherjee, A. Kotal, and T. K. Mandal, "Synthesis of spongy gold nanocrystals with pronounced catalytic activities," *Langmuir*, vol. 22, no. 17, pp. 7141–7143, 2006.
- [10] R. Xu, D. Wang, J. Zhang, and Y. Li, "Shape-dependent catalytic activity of silver nanoparticles for the oxidation of styrene," *Chemistry – An Asian Journal*, vol. 1, no. 6, pp. 888–893, 2006.

- [11] S. Schultz, D. R. Smith, J. J. Mock, and D. A. Schultz, "Single-target molecule detection with nonbleaching multicolor optical immunolabels," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 97, no. 3, pp. 996–1001, 2000.
- [12] Y. Xie, B. Yan, H. Xu et al., "Highly regenerable mussel-inspired Fe_3O_4 @polydopamine-Ag core-shell microspheres as catalyst and adsorbent for methylene blue removal," *ACS Applied Materials & Interfaces*, vol. 6, no. 11, pp. 8845–8852, 2014.
- [13] J. Helmlinger, C. Sengstock, C. Groß-Heitfeld et al., "Silver nanoparticles with different size and shape: equal cytotoxicity, but different antibacterial effects," *RSC Advances*, vol. 6, no. 22, pp. 18490–18501, 2016.
- [14] S. P. Mulvaney, M. D. Musick, C. D. Keating, and M. J. Natan, "Glass-coated, analyte-tagged nanoparticles: a new tagging system based on detection with surface-enhanced Raman scattering," *Langmuir*, vol. 19, no. 11, pp. 4784–4790, 2003.
- [15] J. Tominaga, C. Mihalcea, D. Büchel et al., "Local plasmon photonic transistor," *Applied Physics Letters*, vol. 78, no. 17, pp. 2417–2419, 2001.
- [16] Y. Yang, S. Matsubara, L. Xiong, T. Hayakawa, and M. Nogami, "Solvochemical synthesis of multiple shapes of silver nanoparticles and their SERS properties," *The Journal of Physical Chemistry C*, vol. 111, no. 26, pp. 9095–9104, 2007.
- [17] M. Zhang, Y. Q. Liu, and B. C. Ye, "Colorimetric assay for parallel detection of Cd^{2+} , Ni^{2+} and Co^{2+} using peptide-modified gold nanoparticles," *Analyst*, vol. 137, no. 3, pp. 601–607, 2012.
- [18] J. N. Tiwari, K. Mahesh, N. H. Le et al., "Reduced graphene oxide-based hydrogels for the efficient capture of dye pollutants from aqueous solutions," *Carbon*, vol. 56, pp. 173–182, 2013.
- [19] M.-Q. Yang, X. Pan, N. Zhang, and Y.-J. Xu, "A facile one-step way to anchor noble metal (Au, Ag, Pd) nanoparticles on a reduced graphene oxide mat with catalytic activity for selective reduction of nitroaromatic compounds," *CrystEngComm*, vol. 15, no. 34, pp. 6819–6828, 2013.
- [20] Y. Hao, Y. Chong, S. Li, and H. Yang, "Controlled synthesis of Au nanoparticles in the nanocages of SBA-16: improved activity and enhanced recyclability for the oxidative esterification of alcohols," *The Journal of Physical Chemistry C*, vol. 116, no. 11, pp. 6512–6519, 2012.
- [21] J. Y. Cheon, Y. O. Kang, and W. H. Park, "Formation of Ag nanoparticles in PVA solution and catalytic activity of their electrospun PVA nanofibers," *Fibers and Polymers*, vol. 16, no. 4, pp. 840–849, 2015.
- [22] M. Liang, R. Su, R. Huang et al., "Facile in situ synthesis of silver nanoparticles on procyanidin-grafted eggshell membrane and their catalytic properties," *ACS Applied Materials & Interfaces*, vol. 6, no. 7, pp. 4638–4649, 2014.
- [23] A. Shahzad, M. Chung, T. Yu, and W. S. Kim, "A simple and fast aqueous-phase synthesis of ultra-highly concentrated silver nanoparticles and their catalytic properties," *Chemistry - An Asian Journal*, vol. 10, no. 11, pp. 2512–2517, 2015.
- [24] T. Parnklang, C. Lertvachirapaiboon, P. Pienpinijtham, K. Wongravee, C. Thammacharoen, and S. Ekgasit, " H_2O_2 -triggered shape transformation of silver nanospheres to nanoprisms with controllable longitudinal LSPR wavelengths," *RSC Advances*, vol. 3, no. 31, pp. 12886–12894, 2013.
- [25] Q. Zhang, N. Li, J. Goebel, Z. Lu, and Y. Yin, "A systematic study of the synthesis of silver nanoplates: is citrate a "magic" reagent?," *Journal of the American Chemical Society*, vol. 133, no. 46, pp. 18931–18939, 2011.
- [26] E. K. Oikonomou, S. Karpati, S. Gassara et al., "Localization of antifouling surface additives in the pore structure of hollow fiber PVDF membranes," *Journal of Membrane Science*, vol. 538, pp. 77–85, 2017.
- [27] J. Cheon and W. Park, "Green synthesis of silver nanoparticles stabilized with mussel-inspired protein and colorimetric sensing of lead(II) and copper(II) ions," *International Journal of Molecular Sciences*, vol. 17, no. 12, p. 2006, 2016.



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