Fabrication and application of ZnO-Ag nanocomposite materials prepared by gas-phase methods

K Kusdianto, T D Sari, M A Laksono, S Madhania and S Winardi
Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Surabaya 60111, Indonesia

E-mail: swinardi@chem-eng.its.ac.id

Abstract. Zinc oxide nanoparticles have been used in various applications because of its unique physical and chemical properties. Unfortunately, the performance of pristine ZnO is inhibited by electron-hole recombination. The zinc oxide performance can be improved by metal doping to enhance its properties. This review paper provides summary of the synthesis and application of zinc oxide doped by silver (Ag) using different synthesis via gas-phase methods. From this review, synthesis parameters that will affect the ZnO-Ag nanoparticle and its application will be concluded. The gas-phase synthesis methods include flame spray pyrolysis, spray pyrolysis, sputtering, plasma enhanced chemical vapor deposition, electron beam evaporation, atomic layer deposition and electrospinning. It is clearly observed that the morphology, crystallinity, and performance of ZnO-Ag nanocomposite is significantly affected by the fabrication method. The precursors used, spray rate, deposition rate, precursor concentration, deposition time, morphology of the nanoparticle and deposition or annealing temperature affect the performance capability of ZnO-Ag. We believe that this review paper will provide valuable information and new insights into possible fabrication methods of ZnO-Ag nanocomposite materials in the gas-phase, which can be used for many applications as photocatalyst, anti-microbial applications, catalyst for hydrogen production as well as in dye-sensitized solar cells and gas sensors.

1. Introduction
Nanoparticles have earned a big reputation in recent decades due to their various applications, such as catalysts, semiconductors, and microelectronics. Nanoparticles are particles with at least one dimension and diameter in the range of 100 nanometers or less. Their properties are different from their bulk materials of the same composition, enabling them to perform extraordinary performance of conductivity, reactivity, and optical sensitivity. Nanoparticles are extensively used because of their exclusive properties and novel features [1]. With increased need for nanoparticles, different methods have been developed for their synthesis in various sectors. One of the commonly used nanoparticles is zinc oxide.

Zinc oxide is a semiconductor that has high binding energy (60 meV), wide band gap energy (3.37 eV), high mechanical and thermal stability at room temperature. So, zinc oxide offers attractive semiconductor properties and widely used as photocatalysts, electronic devices, solar cells, photoluminescence materials, and gas sensors [2]. One disadvantage of ZnO is the tendency of recombination of electron-hole pairs which can reduce the ability of photocatalysts [3]. In recent years,
many doping metals and metal oxides such as Au [4], Mn [5], Ag [6], TiO$_2$ [7] and Al [8] are used to improve ZnO performance. There are two methods of ZnO-Ag synthesis, gas-phase and liquid-phase. Schematic diagram of fabrication method and applications of ZnO-Ag is described in Fig. 1. In this review, however, we will focus on silver (Ag) as a dopant to improve ZnO performance and the gas-phase synthesis of ZnO-Ag. Ag has an ability to inhibit the electron-hole recombination because of its electron acceptor properties and plasmon resonance effect [8-11]. The gas-phase synthesis of ZnO-Ag is more effective at producing finer and smaller particles which can be more effective in its application.

Applications of zinc oxide in various sector are determined by the nanostructures of zinc oxide, which can be classified into one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D). One dimensional ZnO include nanorods, nanofibres, nanowires, nanotubes and nanoneedles. While, two-dimensional ZnO and three-dimensional ZnO are nanosheets and nanoflowers, respectively [2]. In this review, the synthesis method of ZnO-Ag nanoparticles and its application will be discussed. From this review, synthesis parameters affecting the ZnO-Ag nanoparticle and its application will be summarised. Different methods make it possible to get products with different shapes, sizes, and structures.

![Figure 1. A schematic diagram for fabrication method and application of ZnO-Ag nanocomposites](image)

2. **Synthesis of ZnO-Ag Nanocomposite Material**

2.1. **Flame spray pyrolysis method**

In flame spray pyrolysis, metal salt solution is sprayed through an atomizer producing micron-sized droplets. Then, the droplets are carried by carrier gas into the flame reactor. Inside the flame reactor, number of reaction occurs at high temperature, typically 450°C, such as pyrolysis, hydrolysis, oxidation and reduction. The reactions inside the flame reactor convert salt into metal oxide. The fuel that commonly used for the combustion inside the flame reactor are hydrocarbon, such as butane and propane, which is cost-effective, while air used as an oxidizer. Then, the metal oxide atoms aggregate into nanoparticles, which are then collected in the collection chamber. Flame spray pyrolysis is
conducted by dissolving 0.1 M zinc acetate in a water and then various concentrations of AgNO$_3$ are added. The precursors are then pumped into a nebulizer to form a droplet. A compressed air acting as a carrier gas then carries both the droplet and the LPG fuel into the flame reactor. Inside the flame reactor a flame will be produced to reduce all the precursors into ZnO-Ag and the particles will be captured inside an electrostatic precipitator [12].

Kusdianto et al [12] investigated the effect of Ag content in the photocatalytic activity of ZnO-Ag nanocomposites to degrade methylene blue. It was found that the particles produced have spherical morphology and aggregation was formed when Ag concentration exceeded its optimum value due to high concentration of particles present in the gas stream when passing through the flame reactor. By varying the Ag concentration (0.01-20 wt%), it was found that the crystallite size and pore diameter were not significantly changed. Crystallite size was found ranging from 2.4 to 9.1 nm. The best photocatalytic performance was achieved at 5 wt% Ag, with the maximum degradation efficiency of 63% after 80 minutes irradiation. Degradation decreased when Ag concentration exceeded 5 wt% because high amount of Ag nanoparticles blocking the light to the nanoparticles. The biggest specific surface area, which was 461.2 m$^2$/gram, was found when the concentration of Ag was 0.1 wt%.

![Figure 2. An illustration for photocatalytic performance with different Ag content.](image_url)

The same precursor, fuel and oxidizer were used by Kusdianto et al [5], but the difference from the research conducted by Kusdianto [12] is the absence of peristaltic pump to reduce the energy consumption. This research found that the addition of Ag reduced the agglomeration of particles. Increasing Ag concentration (0.01-20 wt%) led to a reduction in the particle size. The largest crystallite size was obtained at Ag concentration of 20 wt%. While the smallest crystallite size was obtained at Ag concentration of 0.2 wt%. The best photocatalytic performance was achieved 5 wt% Ag content, because the large amount of Ag blocked the light pathway into the nanoparticles. The degradation efficiency of ZnO-Ag under UV light irradiation was lower than sunlight irradiation.
because of localized surface plasmon resonance effect (LSPR) of silver (Ag). The maximum degradation efficiency of Methylene Blue reached 56% under UV light irradiation, while it was increased to 99% under sunlight after 80 minutes of irradiation. The degradation efficiency was lower than research that was conducted by Kusdianto [12] due to larger particles that were produced in this research (13.85 – 31.3 nm).

2.2. Spray pyrolysis technique
In spray pyrolysis technique, precursor solution is atomized into fine droplets. Then, the droplets undergo reactions at high temperature thus forming thin film or powder. There are several atomization techniques that are used to make thin film, some of them are ultrasonic nebulized atomization and nozzle atomizer [13]. Nozzle atomizer are neither effective enough to obtain micrometer or submicron size droplet nor to control their size distribution. In ultrasonic nebulized atomization, the droplets are formed in the size of micrometer and submicron [14,15]. In general, the precursor solutions are atomized using ultrasonic nebulizer which commonly operated at a frequency of 2.56 MHz. Then, the droplet formed are carried by the carrier gas, commonly air, through a pipe into the heated substrate. When the droplets approach the substrate, heterogeneous reaction occurs and the solvent vaporizes which formed thin film. While, to make particle in the form of powder, the droplets undergo reactions inside the furnace. Then, the particles are collected in the collection chamber, commonly electrostatic precipitator, using high voltage.

Shinde et al [16] studied the photocatalytic activity of acid orange 7 using Ag doped ZnO thin films under solar illumination. The effect of Ag doping (Ag/Zn ratio of 1, 2, 3, 4, and 5%) on ZnO on the photoelectrochemical, optical, luminescence, structural, morphological, electrical and thermal properties were also studied. Based on SEM test, the resulting film had a solid, uniform, and void-free surface characteristics. After the addition of Ag doping, the average grain size decreased. The average crystallite size decreased up to the doping of 3 at% and for the concentration above that, the size increased. Heat conductivity, thermal conductivity, electrical conductivity and electron mobility exhibits maximum value at 3 at% doping. The highest achieved value of conductivity and electron mobility of the AZO thin film was 33.36 $\Omega^{-1}$cm$^{-1}$ and 77.2 cm$^2$/Vs respectively. Single Ag doped ZnO electrode was able to degrade about 99.5% acid orange 7 after 120 min under sunlight illumination. The degradation of acid orange 7 followed first order reaction kinetics, in which the value of k was 6.06 x $10^{-4}$/s. The degradation rate constant increased with Ag doping concentration (1-5% [Ag]/[Zn] ratios).

In contrast to the study of Tarwal et al [17] in 2011 which aimed to see the effects of Ag doping on photoelectrochemical performance (PEC) of ZnO thin films, research conducted by Tarwal et al [18] in 2013 aimed to look at the effects of Ag doping (5, 10, 15, 20, 25 at%) on performance in ethanol gas sensors. Samples with different Ag doping had different optimal sensitivity and temperatures. Pure ZnO had a sensitivity of 51% at 250°C, while samples with 15% Ag had the highest sensitivity of 85% for 2000 ppm ethanol with an optimum operating temperature of 225°C. Samples with 15 at% Ag had the optimum value of sensitivity because more active adsorption centres will be formed if Ag doping is suitable. Excessive Ag concentrations reduced the particles’ sensitivity due to the changes in surface modification, e.g. aggregation, which reduced the ability of chemical adsorption and reaction. Furthermore, selectivity tests were also carried out to measure sensor's ability to respond to certain gases in the presence of other gases. Pure ZnO did not show selectivity to ethanol, and samples with Ag 15% showed the highest selectivity. Samples with 15% Ag showed the fastest response time and recovery time, which were 5 seconds and 27 seconds, respectively. Faster response and recovery were due to increased chemical adsorption and catalytic reactions on the surface with the appropriate amount of Ag. After conducting repeated experiments for 3 months, the material gave 97% performance from the initial performance, indicating the stability of the material.

Dermenci et al [19] used ultrasonic spray pyrolysis to see the photocatalytic activity of ZnO/Ag nanocomposite towards degradation of methylene blue under UV-A irradiation. Optimized synthesis conditions were also studied. It was found that the particle has spherical morphology and have
submicron sized. In addition, the particles became denser and crystallite size decreased with increasing precursor solution concentration (0.05-0.2 M). With increasing temperature (700-900°C), the primary particles became bigger and tended to form aggregate. Maximum degradation efficiency and degradation first-order rate coefficient achieved when the Ag concentration was 0.2 M and temperature 900°C. The maximum degradation efficiency reached 27% after 1 hour of UV-A irradiation. While, the maximum degradation first-order rate coefficient was found as 0.0052/min.

In contrast to previous studies which generally used Zn(CH$_3$COO)$_2$.2H$_2$O as a precursor solution. Hameed et al [20] in 2017 used zinc acetylacetone (ZnC$_{10}$H$_{18}$O$_5$) as a precursor solution. This paper aims to study the effects of Ag doping (0, 2, 4, 6, and 8 at%) on the structural, morphological, electrical and optical properties of the Ag: ZnO thin films. It was found that excessive Ag concentrations (8 at% Ag) damaged the crystallinity because of the pressure generated by the difference in ion sizes between Ag and Zn and the separation of dopants in grain boundaries. Crystallite size was reduced with the addition of Ag doping. At Ag 2 at%, grains are flower-shaped and uniform, with a dense, homogeneous surface. At Ag 4 at%, grains were flower-shaped and small in size with pores that were useful for solar cells. ZnO-Ag had a smaller grain size and a denser surface than pure ZnO. In ZnO-Ag, the growth orientation changed. The optical tests results showed that the average transmittance increased from 80% to 85% when the sample had an Ag concentration of 6 at%. At 8% Ag, there was a decrease in transmittance due to the increased scattering photons caused by crystal defects. The higher the transparency, the better it is for applications as photovoltaic devices. Thus, the sample with Ag 6 at% is suitable to be applied as gas sensors, optoelectronics, and solar cell coatings if it is coated on an indium tin oxide (ITO) glass plate.

2.3. Sputtering

Sputtering is a method of ejecting atoms or small clusters from the surface of the target materials by bombardment with high-velocity ions of an inert gas, which are then deposited on the substrate inside the vacuum chamber. Base pressure in the chamber usually in the range of 10$^{-3}$ to 10$^{-6}$ mbar, as a higher pressure interfere the transportation of the sputtered material. Two electrodes are used, one electrode is connected the target material and the other is connected the substrate, and in between are inert gas ions. Usually Argon is used as an inert gas because of its mass compatibility with materials of engineering interest and its relatively low cost. Commonly, the target material is connected to the high negative voltage, while positive or ground to the substrate. When the necessary vacuum level is reached, inert gas is introduced. Because of high electric field between the electrodes, ions are created. These ions then approach target material, causing the sputtering of nanoclusters, which subsequently deposited on the substrate.

Li et al [21] in 2012 made ZnO/Ag thin films on glass substrates using radio-frequency sputtering at room temperature. The effect of Ag doping on electrical properties was investigated. Argon was used as the inert gas. Silver dopings content used were 0.40%, 1.28%, and 2.14 at%. Pure ZnO showed n-type conductivity with a high electron concentration of 6.62 x 1018 cm$^{-3}$. The resistivity value of the ZnO:Ag film increased from 0.473 to 1007 Ω cm as the Ag doping increased. Ag doping increased resistivity and decreased electron concentration due to the substitution of Zn sites by Ag atoms that act as acceptor compensation centres. But, unfortunately, the nature of p-type is not observed. P-type of ZnO is optimal for many applications due to its high radiative stability [2]. Ag$_x$ donors increase with increasing Ag content. So, suppressing Ag$_x$ donors to form p-type ZnO:Ag films is important. O-rich conditions are preferred to suppress the formation of Ag$_x$ defects and increase AgZn defects, which are beneficial for getting p-type.

Zhang et al [22] used the combination of hydrothermal and plasma sputtering method to synthesize ZnO nanorods-Ag NPs hybrids as non-enzymatic H$_2$O$_2$ biosensor. Hexamethylenetetramine and Zn(CH$_3$COO)$_2$ were used as a precursor in hydrothermal method. While in plasma sputtering method, Ag was used as metal targets and Argon as an inert gas. SEM images showed that ZnO NRs has the rods morphology with good dispersion. The diameter of ZnO NRs is about 300 nm with the length of 1.5–2 μm. After being treated by plasma sputtering, particles of 20 nm were observed adhering on the
ZnO NRs. Introduction of Ag can improve the electrochemical property, which is the conductivity of the hybrids, and increase the electrode surface area. The ZnO NRs–Ag NPs is suitable as supporting component of the biosensor. It was found that the ZnO NRs-Ag NPs hybrids have a linear range from 0.2 to 12.8 mM, and the detection limit was estimated to be 7.8 μM. Compared to ZnO NRs–Ag NPs hybrids, the detection limit with ZnO NRs was 7.3 times lower.

2.4. **Electron beam evaporation**

In electron beam evaporation, a high current is passed through a wire filament that heats the filament up to a high temperature. The power to the filament can be either AC or DC. Compared with AC, DC e-beams tend to be tighter and more precise. Under high temperature, electrons are discharged from the surface. These electrons are focused and pointed to hit the source material. This high-energy bombardment heats up the source so it melts and evaporates (or sublimes). The source material can be kept in a crucible that can or cannot be cooled. Some materials operate best with a water-cooled metallic crucible and dependent on the thermal gradient between the crucible and the surface to allow a molten pool to form at the surface for evaporation, but for some of the material, in contact with the crucible, to stay solid. In this method, the material remain pure and is much less likely to react with the crucible than if it were molten where it might be possible to create an alloy or to diffuse into the molten pool. E-beam could be controlled by adjusting the power, the beam shape (diameter), the raster pattern, and the residence time.

Wei et al [23] used the combination of hydrothermal and electron beam evaporation method to cover ZnO nanorods with Ag film on polyethylene terephthalate (PET) flexible substrate and use them as the photoanode for water splitting. The effects of surface recombination inhibition, plasmonic enhanced absorption, and improved charge transport were studied by modifying the thickness of Ag (5-50 nm). The surface became smoother at the Ag film thickness of 30 nm. XRD analysis showed hexagonal ZnO and decreasing mean crystal size of Ag from 20 to 13 nm as Ag thickness decreases. Ag thickness of 10 nm exhibited the highest light absorption. At Ag thickness of 10 nm and substrate bending radius of 6 mm, the maximum short circuit current density (JSC at 0.616 mA/cm²) and photoelectron conversion efficiency (PCE at 0.81%) are obtained. The highest value of JSC and PCE are respectively seven times and ten times higher than those of the bare ZnO nanorods on flexible substrates without bending. This research can be useful for the application of flexible substrates in collecting light energy for the photoelectrochemical application.

2.5. **Plasma enhanced chemical vapour deposition**

Plasma enhanced chemical vapor deposition (PECVD) is the combination of chemical vapor deposition (CVD) and physical vapor deposition (PVD). PECVD uses electrical energy and activates the reaction by transferring the energy into the precursor and generates free radical formation accompanied by radical polymerization. Unlike CVD, PECVD uses variety of precursors, from inorganic to organic, and requires low temperature. This is because the reaction is activated using plasma gas. The use of plasma significantly reduces deposition temperature compared to other methods such as CVD. Deposition at room temperature can avoid thermal effects so that this method can be used to coat polymers or other materials with low melting temperatures (Pierson, 1999). Plasma production uses electrical energy 3 frequency variations which is audio frequency (10 or 20 kHz), radio frequency (13.56 MHz), and microwave frequency (2.54 GHz).

Simon et al [24] used PECVD and RF sputtering methods to synthesize Ag/ZnO nanocomposites on Si (100) and Al₂O₃ substrates. The product was then used as catalysts in producing hydrogen through the photo-reforming of alcoholic solutions. In addition, Ag/ZnO nanoparticles showed an excellent response in detecting hydrogen gas. Zn(II) bis(ketoiminate) and R = -(CH₂)₃OCH₃ used as the precursor. The structure of the ZnO did not change significantly with the increase in sputtering time (30-150 minutes). In addition, the Ag size changed from spherical to island-like aggregates. Upon annealing, spherical Ag aggregates was formed. This phenomenon was clearly observed when the sputtering time ≥ 90 minutes. Size of Ag increased significantly after annealing treatment. Without
annealing, the size of Ag is smaller and showed a higher content of Ag₂O than the annealed sample. The mechanism of ZnO-Ag nanoparticles as the catalyst for hydrogen production is as follows. Under UV irradiation, electrons are directly photoexcited from the valence to the conduction band of ZnO, and then the electrons are transferred to Ag nanoparticles. Afterwards, H⁺ reduction by the electrons on the silver particles results in H₂ generation, while alcohol oxidation is promoted by holes in ZnO valence band. The addition of Ag increases the production of H₂ because Ag improve the photocatalytic activity of ZnO. Best photocatalytic activity was observed in 30 minutes of annealing under UV-Vis illumination. While under sunlight illumination, the best photocatalytic activity was observed with annealing time of 90 minutes. Photocatalytic efficiency was better under solar light irradiation because of the surface plasmon resonance (SPR) of silver. Gas sensing test showed that the conductance improved with hydrogen exposure. Other than that, the sample had fast response and recovery times (∼ 3 min) due to high surface-to-volume ratio. This high surface-to-volume ratio was due to urchin-like structure of the sample. Therefore, the ZnO-Ag nanocomposite in this study can be used as the H₂ generation and sensing.

Previous researches have been conducted to fabricate Ag on transparent conducting oxides (TCOs). TCOs have widely as electrodes in various optoelectronic devices. However, because the nucleation of Ag layers, Ag thin film has high resistivity. Lei and Cheng [25] investigated the fabrication of Ag nanoparticles (NPs) on ZnO, which has a reasonably low resistivity and considerable optical transmittance. They used a combination of dual-plasma-enhanced metal-organic chemical vapor deposition (DPEMOCVD) and photoreduction methods to synthesis ZnO/Ag film that can be used as transparent electrodes in optoelectronic devices such as LEDs. High O₂ ionization rate is important to make high-quality and well-controlled stoichiometry of ZnO thin film, however conventional PEMCVD method has low ionization rate of O₂. Therefore to improve the concentration of oxygen free radicals and thus the ionization rate of O₂, DPEMOCVD was used. DPEMOCVD method uses dual plasma system, which is DV voltage and RF plasma. In this method, DV voltage ionizes oxygen free radicals, then in order to reduce the recombination of oxygen free radicals, the oxygen free radicals is diffused to the substrate that is surrounded by RF plasma. DPEMOCVD-grown ZnO thin film is etched in AgNO₃ and NaOH to adjust the pH. Then, photoreduction using UV irradiation takes place according to the following reaction:

\[
\begin{align*}
\text{ZnO} + \text{UV} & \rightarrow e^- + h^+ \\
\text{AgNO}_3 & \rightarrow \text{Ag}^+ + \text{NO}_3^- \\
\text{Ag}^+ + e^- & \rightarrow \text{Ag}
\end{align*}
\]

Then, after photoreduction, Ag NP/ZnO thin films were treated by rapid thermal annealing to reduce the resistivity. With increasing AgNO₃ concentration (0.09-0.15 M), Ag content increased and the Ag NPs on pure ZnO became denser. At 0.15 M AgNO₃, ZnO nanorods formed bundles and Ag NPs formed an aggregate. As annealing temperature increased (400-550°C), the distribution and grain sizes of Ag NPs became dense and large due to the aggregation. Average transmittance of Ag/ZnO thin films showed maximum value at 0.12 M concentration of AgNO₃ and annealing temperature of 400°C, which is 88%. Carrier concentration and carrier mobility showed the highest value at AgNO₃ concentration of 0.12 M, which were 2.8 × 10²⁰ cm⁻³ and 32 cm²/Vs, respectively. Ag NP/ZnO thin film at AgNO₃ concentration of 0.12 M and annealing temperature of 500°C had the lowest resistivity, 6.9 × 10⁴ Ω cm. Optimized Ag NP/ZnO TCOs were applied to InGaN/GaN LEDs as transparent conducting layers (TCLs). InGaN/GaN LEDs with optimal Ag NP/ZnO as TCLs had identical electrical and optical characteristics to those of commercial ITO devices.

2.6. Atomic layer deposition

Atomic layer deposition (ALD) can produce thin films of a wide variety of materials. ALD offers tunable film composition, thickness control at the Angstrom level and high aspect ratio structures, which are the advantages over CVD and PVD methods. ALD processes were developed from many types of CVD processes. ALD processes use alternative exposure of chemical precursors to react to create the desired material, usually at significantly lower temperature.
In ALD process, alternating pulses of gaseous chemical precursors undergo a reaction with the substrate. These individual gas-surface reactions are named ‘half-reactions’ and equip merely part of the material synthesis. Throughout each half-reaction, the precursor is pulsed into the vacuum chamber (<1 Torr) for a point of time to enable the precursor to fully react with the substrate surface thru a self-limiting process that leave one monolayer at the surface. Then, to clean the vacuum chamber, flow of inert carrier gas (commonly N₂ or Ar) enter the chamber to eliminate any unreacted precursor or by-products. After that, the flow of counter-reactant precursor and purge enter the reaction chamber and forming up to one layer of the desired material. Subsequently, this process is repeated until the appropriate film thickness is obtained.

Seong et al [26] used ALD method to synthesize ZnO-Ag core-shell nanoparticles with enhanced photocatalytic activity to degrade Rhodamine B. This process used diethylzinc and deionized water as the metal precursor and the reactant, respectively. One hundred cycles of ALD deposition were processed at 150 °C in a rotational ALD system. EDS analysis showed that the product has no impurities. ZnO able to coat Ag uniformly at thickness of 5 nm. Photoluminescence test showed that Ag-ZnO has high activity at UV emission. In addition, activity of ZnO-Ag was significantly higher than pure Ag. After 100 minutes sunlight irradiation showed that Ag-ZnO was able to degrade up to 99% of Rhodamine B. The ZnO-ZnO, ZnO, without ZnO and Ag were able to degrade RhB up to 83%, 59%, 1% and 0%, respectively. The highest pseudo-first-order rate constant k was 0.043/min. Based on FDTD analysis, the light enhancement factor of the Ag-ZnO NP increased as ZnO thickness increased (2.5-10 nm) and wavelength 633 nm. Maximal enhancement was observed at a ZnO shell thickness of 2.5 nm. But, a significant drop in the enhancement factor was obtained at ZnO shell thickness beyond 7.5 nm. Therefore, it can be concluded that the fabrication of NPs with metal core-semiconductor shell structures hold huge amount of potential for the utilization of solar light for environmental purposes.

2.7. Electrospinning

In electrospinning method, polymer solution is electrically driven by a high voltage and the flow rate of the feed is controlled by a capillary pump. When the electric field reaches a critical point where the repulsive electric force exceeds the surface limit of the polymer solution, the polymer solution is removed from the tip towards the collector. During the journey to the collector, the polymer solution solidifies due to rapid evaporation of the solution and then attaches to the collector [27-29]. With charge injection from a voltage source, the polymer solution has a different polarity than the collector. At present, the standard settings of electrospinning are vertical and horizontal positions. The electrospinning method is carried out at room temperature and atmospheric pressure. The electrospinning system consists of a high-voltage energy source, a spinneret (for example the tip of a pipette), and a collector's plate (a metal screen, plate, or rotating mandrel) [30, 31].

Chen et al [32] in 2014 produced polyacrylonitrile (PAN)-ZnO/Ag with a variety of ZnO morphologies, namely pineal, flower, and sea-urchin. The effects of various ZnO morphologies on photocatalytic efficiency, UV protection, antimicrobial activity, and mechanical properties were analyzed. This research combines single-capillary electrospinning, hydrothermal, and Ag reduction using UV light. Sea-urchin morphology had the highest BET surface area and degradation efficiency than any other sample. It could degrade up to 90% Methylene Blue for 30 minutes and 99% Methylene Blue for 120 minutes. This was because ZnO with sea-urchin morphology had the highest density thus providing a large surface area for contact with dyes. The degradation rate constant has the greatest value in sea-urchin morphology, which is 0.036/minute, which is 36 times greater than PAN fiber, 2 times greater than pineal morphology, and 1.3 times greater than flower morphology. Transmittance and antimicrobial activity against Staphylococcus aureus were best in ZnO samples with sea-urchin morphology. Light scattering from sea-urchin might contribute to the excellent UV-shielding property. ZnO/Ag increased tensile strength up to 1.5 times greater than pure PAN fiber. Also, it was very flexible that it can be used in water purification. We can conclude that fiber can be used for water purification, antimicrobial activity, and UV-shielding clothing.
Similar research was also conducted by Patel et al. [33] to make polyacrylonitrile (PAN) polymer nanofibers by electrosprinning method. But in research conducted by Patel, the manufacture of ZnO is not only done by the hydrothermal method but is made in three different ways namely reflux, blending, and hydrothermal. Besides, this study tested antimicrobial activity against gram-negative *Escherichia coli* and gram-positive *Micrococcus leuteus*. In the blending method, the formed samples undergo agglomeration whereas in the hydrothermal method, an uneven distribution occurred and an irregularly shaped composite was formed. PAN/ZnO-Ag nanofibers exhibit effective antibacterial agents compared to PAN-Ag or PAN-ZnO. This may be due to the synergetic effect of ZnO-Ag that adheres to the surface of the fiber. PAN/ZnO-Ag nanofibers produced by the reflux method are the best in the antibacterial activity against *M. luteus* and *E.coli* bacteria. This is due to the formation of ZnO-Ag composites that are very small on the surface of PAN nanofibers. PAN/ZnO-Ag composite nanofibers produced by the blending and hydrothermal method do not show sufficient antimicrobial activity due to the formation of aggregates and rod-shaped particles that are mostly formed in the PAN nanofiber membrane. It can be concluded that PAN/ZnO-Ag composite nanofibers are potential candidates in increasing antibacterial properties and can be applied as membranes, water filtration, and textiles.

Pascariu et al [34] in 2020 aims to investigate the effect of Ag doping (0.1, 0.5; 1 and 2 at%) on photocatalytic activity for degradation and antimicrobial activity. The photocatalytic activity was tested against Amaranth dyes. The addition of Ag causes morphological changes to be spherical and rod-like. The addition of Ag by 1% causes the morphology to change into urchin-like. The maximum efficiency of color removal is obtained at an Ag concentration of 1%, which is 95.9%, with a constant first-rate degradation rate of 9.517 x 10^{-3}/minute. Degradation efficiency is influenced by the shape and dimensions of the formed nanostructure. As the initial concentration of the color was increased (10.7-55 mg/L), the rate of degradation constant fell down. Photocatalytic activity with UV light and dye concentration of 10 mg/L shows that the maximum efficiency of color removal reaches 70.51% for pure ZnO, whereas for ZnO: Ag it reaches 98.4%. Samples with Ag concentration of 2% are the most efficient against Gram-positive (*S. aureus*) and Gram-negative (*E.coli*), while samples with Ag concentration of 0.1% are the most efficient against *C. albicans*. Increasing the concentration of Ag increases antimicrobial activity.

3. Conclusion

Based on the review above, it can be concluded that there are seven gas-phase methods of synthesizing ZnO-Ag, which is flame spray pyrolysis, spray pyrolysis, sputtering, electron beam evaporation, plasma enhanced chemical vapor deposition, atomic layer deposition and electrosprinning. ZnO-Ag can be used in degradation of textile waste, gas-sensor, antimicrobial agent, catalyst for hydrogen production and electronic devices (solar cells). Parameters affecting ZnO-Ag performance are the amount of Ag, the type of the precursors used, annealing temperature, precursor concentration, deposition temperature, deposition time, particle morphology, and spray rate (for spray pyrolysis method).

References

[1] Nel A, Xia T, Mädler L and Ning L Science 311 622-7
[2] Ong C B, Ng L Y and Mohammad A W 2018 *Renew. Sust. Energ. Rev.* 81 536-51
[3] Fageria P, Gangopadhyay and Pande S 2014 *RSC Advances* 4 24962-72
[4] Ashebir M E, Tesfamariam G M, Nigussie G Y and Gebreab T W 2018 *J. Nanomater.* 2018 1-9
[5] Kusdianto K, Widiyastuti W, Shimada M, Nartono T, Machmudah S and Winardi S 2019 *Int. J. Technol.* 10(3) 571-81
[6] Alshamsi H A H and Hussein B S 2018 *Orient. J. Chem.* 34 1898-1907
[7] Yun S, Lee J, Chung J and Lim S 2010 *J Phys Chem Solids* 71 1724–31
[8] Lee M S, Hong S S and Mohseni M 2005 *J. Molec. Catal. A Chem.* 242 135–40.
[9] Obalová L, Reli M, Lang J, Matějka V, Kukutschová J, Lacný Z and Kočí K 2013 *Catal.
Today 209 170–5

[10] Sellappan R, Nielsen M G, González-Posada F, Vesborg P C K, Chorkendorff I and Chakarov D 2013 J. Catal. 307 214–21.
[11] Zhang X, Zhou M and Lei L 2005 Mater. Chem. Phys. 91 73–9
[12] Kusdianto K, Kusuma T C, Hudandini M, Widiyastuti W, Madhania S, Machmudah S, Nurtono T and Winardi S 2019 Mater. Sci. Eng. 673 012012
[13] Sabnis S M, Bhadane P A and Kulkarni P G 2013 Journal of Applied Science 4(5) 07-11
[14] Jarzebski Z M and Marton J P 2002 J. Electrochem. Soc. 123 299C, 333C
[15] Badawy W, Decker F and Doblhof T 1993 Sol. Energy Mater. 363
[16] Shinde S S, Bhosale C H and Rajpure K Y 2012 J. Photochem. Photobiol. 117 262-8
[17] Tarwal N L and Patil P S 2011 Electrochimica Acta 56 6510-6
[18] Tarwal N L, Rajpure A V, Patil, J Y, Khandekar M S, Machmudah S, Kim J H and Jang J H 2013 J. Mater Sci 48 7274–82
[19] Dermenci K B, Gene B, Ebin B, Olmez-Hanci T and Gürmens S 2014 J. Alloys Compd. 586 267-73
[20] Hameed M S, Princice J J, Babu N R and Arunachalam A 2017 J. Mater. Sci.: Mater. Electron 28 8675–83
[21] Li W J, Kong C Y, Ruan H B, Qin G P, Huang G J, Yang T Y, Liang W W, Zhao Y H, Meng X D, Yu P, Cui Y T and Fang L 2012 Solid State Commun. 152 147-50
[22] Zhang D, Zhang Y, Yang C, Cunwang G, Wang Y, Wang H and Liu H 2015 Nanotechnology 26 335502
[23] Wei Y, Ke L, Kong J, Liu H, Jiao Z, Lu X, Du H and Sun X W 2012 Nanotechnology 23 235401 (8pp)
[24] Simon Q, Barreca D, Bekermann A, Gasparotto D, Marzotto C, Comini E, Gombac V, Fornasiero P, Lebedev O I, Turner S, Devi A, Fischer R A and Tendeloo G V 2011 Intl J. of Hydrogen Energy 36 15527-37
[25] Lei P and Cheng C 2017 Mater. Sci. Semicond. Process. 57 220-6
[26] Seong S, Park I, Jung Y, Lee T, Kim S Y, Park J S, Ko J and Ahn J 2019 Mater. Des. 177 107831
[27] Heikkila P and Harlin A 2008 Eur. Polym. J. 44 3067
[28] Huang Z M, Zhang Y Z, and Ramakrishna K S 2003 Compos. Sci. Technol. 63 2223
[29] Varesanor A, Carletto R A and Mazzucchetti G 2009 J. Mater. Process. Technol. 209 5178
[30] Liang D, Hsiao BS and Chu B 2007 Adv Drug Deliv Rev 59 1392–412
[31] Sill TJ and Recum HAV 2008 Biomaterials 29 1989-2006
[32] Chen Y, Kuo C, Chen B, Chiu P and Tsai P 2014 J. of Polym. Sci. 53 262-9
[33] Patel S, Konar M, Sahoo H and Hota G 2019 Nanotechnology 30 205704
[34] Pascariu P, Cojocaru C, Samoilca I, Airinei A, Olaru N, Rusu D, Rosca I and Suchea M 2020 J. of Alloys Compd.
[35] Madler L, Kammler H K, Pratsinis S E and Mueller R 2002 Chem. Eng. Sci. 33 369-89
[36] Kammler H K, Madler L and Pratsinis SE 2001 Chem. Eng. Technol. 24 583-59
[37] Tani T, Madler L and Pratsinis S E 2002 J. Nanopart. Res. 4 337-43
[38] Liu K, Yang B F, Yan H, Fu Z, Wen M, Chen Y and Zuo J 2008 Appl. Surf. Sci. 255 2052–6
[39] Liu K, Yang B F, Yan H, Fu Z, Wen M, Chen Y and Zuo J 2009 J. Lumin. 129 969–72
[40] Sapkal R T, Shinde S S, Babar A R, Moholkar A V, Rajpure K Y and Bhosale C H 2012 Mat. Express 2 64-70
[41] Pierson HO. Handbook of Chemical Vapor Deposition (CVD). 2nd Ed. Norwich, NY:William Andrew Publishing; 1999. p. iii.
Acknowledgments
The authors are grateful to the Direktorat Riset dan Pengabdian Masyarakat (DRPM) DIKTI for financially support this study under contract grant No. 1122/PKS/ITS/2020 with scheme “Penelitian Dasar”.