A synthesis of AgNP-rGO-PANI nanocomposite and its use in fabrication of chipless RFID sensor: current research progress

Junervin¹, T Djatna¹ and F Fahma¹

¹Graduate School Program of Agro-Industrial Engineering, IPB University, Bogor, Indonesia
e-mail: taufikdjatna@apps.ipb.ac.id

Abstract. Chipless RFID (Radio Frequency Identification) tag has attracted significant attention due to the low manufacturing cost. By eliminating the use of integrated circuit (IC), chipless RFID tag can offer competitive price in order to completely replace barcode systems. Besides, integration of physical parameter sensors with chipless RFID will open up a new domain for controlling and monitoring perishable items. It can also be fully printable by using inkjet-printed technology. The inkjet-printed technique is one of the most promising technological solutions for the realization of chipless RFID with low-cost advantage. Various types of conductive inks with different fillers such as metal nanoparticles, carbon nanotubes (CNT), and polymer have been developed for printed electronics. It needs deep investigation and study in designing low-cost but robust by using conductive ink on a low-cost substrate. The aim of this review is to claim research gap related to how AgNP-rGO-PANI (Silver Nanoparticle - Reduced Graphene Oxide - Polyaniline) nanocomposite has both scientific and economic advantages. The inkjet-printed method using conductive inks with nanocomposite fillers synthesized from semiconductor materials such as graphene, silver nanoparticles, and polyaniline on a thin sheet of low-cost substrate. This review provides an overview of synthesis methods of AgNP-rGO-PANI nanocomposite, structure and design of chipless RFID sensor, and chipless RFID sensor fabrication methods.

1. Introduction

During the past few years, chipless RFID tag has attracted significant attention due to the low manufacturing cost. The cost of an existing RFID tag is still much higher when compared to the price of the barcode. The main cost of an RFID tag comes from the chip embedded as a carrier for information and processing in the tag. Therefore, chipped RFID sensors are not suitable for low-cost applications such as warehouse goods management [1]. The aim of chipless RFID tags is to replace both barcode and chipped RFID used for item-level tagging. There have been some reported chipless RFID tag developments in recent years [3-6]. However, most are still reported as prototypes, and only a few are considered commercially viable. The primary goal of chipless RFID tags is to be printable on flexible substrates such as polymer, paper, cartons, and boxes. The inkjet-printed technique is one of the most promising technological solutions for the realization of chipless RFID with a low-cost advantage. Besides, the integration of physical parameter sensors with chipless RFID will open up a

¹ Corresponding author’s email: taufikdjatna@apps.ipb.ac.id
new domain for controlling and monitoring perishable items. Perishable products typically have several physical parameters (temperature [7], humidity [8], certain gas [9], etc.) to indicate spoilage. Therefore, to accurately detect expiry dates, it is desirable to have multiple parameters sensing in a single chipless RFID tag. The main difference between a chipless tag and a chipless sensor tag is that the resonance frequency of the chipless sensor tag can change according to the environment, but the chipless tag only contains an encoding unit and the resonance frequency always remains constant [2]. However, this is a fundamental challenge to find material that can impart electrical conductivity and responsiveness to physical parameters.

In recent years, numerous kinds of conductive materials have been developed for printed electronics. However, some inherent weaknesses limit their application. For example, polymer-based material has poor conductivity [10], pure metal materials like Au, Ag, Pt, Cu [11,12] have excellent conductivities but too expensive to be employed for mass production, oxidized, and poor sensitivities. Graphene-based material has caught a lot of attention as a new kind of printable flexible electronic material. Graphene is a one-atom-thick planar sheet of sp²-hybridized carbon atoms arranged in a hexagonal network [13]. It has unique properties such as their high surface area, high chemical stability rapid electron transfer kinetics and great electrocatalytic characteristics [14]. Due to these characteristics, graphene is being widely used in the synthesis of nanocomposite for sensing applications.

2. Materials for chipless RFID sensor
Most materials have been investigated for low-frequency applications. However, there is a major gap in the high-frequency characterization of sensing materials, synthesis, and sensitivity analysis [15]. Exploring the high-frequency characteristics of materials will provide new avenues in RFID sensor development.

![Figure 1](image-url)

**Figure 1.** Classification of materials depending on the conductivity scale [15].

Table 1. Classification of sensing materials.

| Physical parameters | Materials                              | References |
|---------------------|----------------------------------------|------------|
| Temperature         | Metallic oxide                         | [17]       |
| Humidity            | Polyvinyl Alcohol (PVA)                | [18]       |
| pH                  | Polyaniline (PANI)                     | [19]       |
| Strain              | Poly-3,4-ethylene-dioxythiophene (PEDOT)| [20]       |
| Gas sensing         | Single-walled carbon nanotubes (SWTs)  | [21]       |
Table 1 shows the classification of materials for sensing applications. These are classified according to particular physical parameters such as temperature, humidity, pH, strain, and gas. Bandgap energy changes with temperature on metallic oxide [17], polyvinyl alcohol (PVA) creates hydrogen bond with water molecules [18], pH change results in reduction or oxidation reaction and affects polyaniline (PANI) sheet resistance [19], and presence of ammonia gas changes electrical property of single-walled carbon nanotubes (SWTs) [21].

2.1 Temperature sensing materials
Metal oxide materials like zinc oxide (ZnO) and ITO are wide bandgap materials that show promise for sensing [17]. These materials are very responsive to external environmental changes, such as pressure, temperature, and electric field [22].

2.2 Humidity sensing materials
Polyvinyl alcohol (PVA) is hydrophilic material and can be used as a resistive sensor. The high-frequency characteristics of PVA have been reported [23]. The dielectric behavior of water is investigated as the temperature and PVA concentration are changed. The results show that permittivity decreases at any frequency (0.2–20 GHz) as the PVA concentration in water increases.

2.3 pH sensing materials
Most conductive polymers like PEDOT show sensitivity to pH variation. The conductivity of PEDOT depends apparently on the pH level, with the highest conductivities at low pH, but the change is not dramatic except for pH value exceeding 11. These changes are reversible over a wide pH range [24].

2.4 Gas sensing materials
Several nanostructures and organic materials show sensitivity to particular gases. Ammonia gas sensors based on single- and multiwalled carbon nanotube films [25] and ethylene gas detection by integrating tin oxide in a capacitive RF sensor has been reported [26].

2.5 Other potential sensing materials
Graphene has attracted scientific and technological interests in recent years. Graphene has unique properties such as their high surface area, high chemical stability rapid electron transfer kinetics and great electrocatalytic characteristics [14]. Due to these characteristics, graphene is being widely used in the synthesis of nanocomposite for sensing applications.

There are several methods by which we can synthesize rGO such as thermal reduction [27], and electrochemical reduction [28] and chemical reduction of GO [29]. However, the major drawback of the rGO is agglomeration and reverting to graphite. To overcome these problems, the research is focused on the preparation of the nanocomposite of rGO with conducting polymers as stabilizer material. Therefore, polyaniline (PANI) is considered as a perfect conducting polymer because of its low cost, lightweight, environmentally good, high energy density, controllable electrical conductivity, and faster loading/unloading rate during charge/discharge process [30]. However, the lower processing ability and weaker mechanical strength of PANI and its sensor could be enhanced by fabricating with metal nanoparticles (MNPs). Table 2 shows several nanocomposites containing MNPs, rGO, and PANI.

| Nanocomposite materials | Sensing Capabilities | References |
|-------------------------|----------------------|------------|
| CuNPs/graphene/PANI     | Electrochemical sensing of glucose | [31]       |
| ZnO/rGO/PANI            | Electrochemical sensing uric acid and dopamine | [32]       |
| AgNP/graphene/PANI      | Electrochemical sensing of hydrogen peroxide | [33]       |
Figure 2. Schematic representation of preparation of AgNPs–rGO–PANI nanocomposite [33].

Figure 2 shows schematic representation of preparation of AgNPs–rGO–PANI nanocomposite that reported in [33]. Firstly, the rGO–PANI nanocomposite was synthesized by using 1 : 100 mass ratio of graphene to aniline. For this 1.0 mg rGO and 100.0 mg aniline were taken and added to 20 mL HCl solution and sonicated for 30 min. After that, 10 mL aqueous APS solution was added slowly into the above mentioned solution. After this, the solution was followed by continued stirring for 5 h. After stirring, the rGO/PANI nanocomposite thus obtained was centrifuged at 10 000 rpm for 15 min and washed with distilled water. The above process was repeated four times for the removal of uncoordinated impurities and dried at 60°C.

The nanocomposite of three component (AgNPs–rGO–PANI) was prepared by a self-assembly method. For this, 0.01 g rGO–PANI nanocomposite was added into the 25 mL colloidal AgNP. Further, the reaction was stirred for next 10 h. After this, the final AgNPs–rGO–PANI nanocomposite was centrifuged at 10 000 rpm for 15 min and washed several times with distilled water and dried at 60°C.

3. Chipless RFID sensor system

Figure 3. Block diagram of Chipless RFID sensor system [22].

Figure 3 shows a block diagram of a chipless RFID sensor system. The tag sensor consists of multi-resonators which emit distinct frequency signatures when illuminated by an ultra-wideband (UWB)
signal. There are two types of resonators within the tag sensor [34]. The first resonator carry the data ID of the tag, and a second resonator carry the sensing information. The sensing mechanism is incorporated using materials which show RF sensitivity for environmental physical parameters such as temperature, humidity, gas, pH, etc [22].

Based on the open literature [1], it is possible to categorize chipless RFID tags in three main categories such as time domain reflectometry (TDR)-based chipless tags, spectral signature-based chipless tags, and amplitude/Phase backscatter modulation-based chipless tags. Table 3 shows the advantages and disadvantages of these categories.

3.1. Time domain reflectometry (TDR)-based chipless tags
TDR-based chipless RFID tags are interrogated by sending a signal from the reader in the form of a pulse and listening to the echoes of the pulse sent by the tag. A train of pulses is thereby created, which can be used to encode data.

3.2. Spectral signature-based chipless tags
Spectral signature-based chipless tags encode data into the spectrum using resonant structures. Each data bit is usually associated with the presence or absence of a resonant peak at a predetermined frequency in the spectrum.

3.3. Amplitude/phase backscatter modulation-based chipless tags
These tags require less bandwidth for operation than TDR-based and spectral signature-based chipless tags. Data encoding is performed by varying the amplitude or phase of the backscattered signal based on the loading of the chipless tag’s antenna.

| Categories                                | Advantages                                                                 | Disadvantages                                                                 |
|-------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Time Domain Reflectometry (TDR) -based Chipless Tags | Low cost, greater reading ranges, and their applicability in localization/positioning applications. | The number of bits that can be encoded and high-speed RFID reader RF front-ends required for generating and detecting short ultrawideband (UWB) pulses. |
| Spectral Signature-based Chipless Tags    | Fully printable, robust, have greater data storage capabilities than other chipless tags, and low cost | Large spectrum requirements for data encoding, chipless tag orientation requirements, size, and wideband dedicated RFID reader RF components. |
| Amplitude/Phase Backscatter Modulation-based Chipless Tags | Simple architecture and operation over narrow bandwidths | The number of bits that can be detected and that data encoding is performed by a lumped/chipped component which increases its cost. |

4. Chipless RFID sensor fabrication method
Printing technology is one of the foremost inventions for advanced manufacturing. Various printing techniques have been developed for the fabrication of flexible electronics. Printing technologies are revolutionizing the electronic field by providing cost-effective manufacturing. The PE technologies are commonly divided into screen printing, inkjet printing, and gravure printing [35].

4.1. Screen printing
Screen printing is fully adapted to roll-to-roll manufacturing by rotary screen printing [36]. Its principal design is composed of two opposite rotating cylinders, where the stencil is shaped as a hollow cylinder with a fixed internal squeegee and supported by a pressure roller [35].
4.2. **Inkjet printing**
The basic principle of inkjet printing is the accurate placement of ink droplets onto the desired spot (pixel), which is digitally controlled by a programmed computer [37]. For the accurate positioning of ink droplets, inkjet printing can be classified into two distinct modes, continuous mode and drops-on-demand [38].

4.3. **Gravure printing**
The gravure printing involves two opposite rolling cylinders, the first cylinder has an engraved pattern, which collects ink from the container, while the second roller supports the imprint. Meanwhile, the substrate slides between the two cylinders and allows for transferring of ink from the engraved cylinder onto its surface, resulting imprinted feature on the substrate [35].

| Printing techniques | Advantages | Disadvantages |
|--------------------|------------|---------------|
| Screen printing    | Due to its simplicity, reproducibility and high compatibility with various inks and substrates, making it a cost-effective approach for mass printing of flexible devices | It showed a relatively low resolution compared to digital printing, therefore inappropriate for the printing of miniaturized circuits with high precision |
| Inkjet printing    | Inkjet printing is utilized to attain uniform images with high resolution, and it allows for the deposition of very thin graphene patterns. | Its lower throughput compared to roll-to-roll conventional printing techniques |
| Gravure printing   | It offers a powerful approach for the fabrication of flexible electronics in high volume at very high speed | As gravure printing is a direct contact process, the pressure of the impression roller may create unexpected cracks and scratches on the surface layers of substrate |

**Table 5.** Required rheological properties for printing formulations (inks/pastes).

| Printing techniques | Viscosity (Pa s) | Surface tension (mN/m) |
|--------------------|-----------------|------------------------|
| Screen printing    | 0.5–5           | 38–47                  |
| Inkjet printing    | 0.01–0.5        | 14–23                  |
| Gravure printing   | 0.001–0.1       | 15–25                  |

Table 4 shows the advantages and disadvantages of printing techniques and table 5 shows the required rheological properties for printing formulations (inks/pastes).

5. **Conclusions**
Chipless RFID sensor is one of the most promising technological solutions for the replacement of barcode with low-cost advantage. The main classification of chipless tags is based on modulation techniques, which are time domain reflectometry (TDR)-based chipless tags, spectral signature-based chipless tags, and amplitude/phase backscatter modulation-based chipless tags. Printing technology can be effectively used to fabricate chipless RFID sensor with low-cost advantage. These technologies are commonly divided into screen printing, inkjet printing, and gravure printing. In recent years, most materials have been investigated for low-frequency applications. However, there is a major gap in the high-frequency characterization of sensing materials. The nanocomposite of three materials (AgNP–rGO–PANI) shows RF sensitivity for environmental physical parameters such as temperature, humidity, gas, pH, etc.
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