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Effect of Reducing Agents on The Performance of AgNPs and PANI Flexible Conductive Fabrics

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Abstract. Cotton fabric with the addition of silver nanoparticles (AgNPs) and polyaniline (PANI) was developed as a flexible electrode to measure muscle biopotential signals using Electromyography (EMG) in this study. AgNPs are synthesized using two reducing agents, Gum Acacia and Hydrazine Hydrate. The effect of the two different reducing agents will be studied by measuring the electrical conductivity of each sample and also by comparing flexible electrode performance during EMG measurements. The results obtained from this study are that the AgNP electrodes synthesized using the Gum Acacia have very high SNR and conductivity. The absence of an electrolyte gel during EMG measurement using the developed flexible electrode can provide comfort to the user without any risk of skin irritation due to electrolyte gel when the measurement process is carried out for a long duration. The AgNP fabric electrode with Gum Acacia as the reducing agent is expected to be used to replace commercial electrodes in the future.

Keywords: Conductivity; Flexible electrodes; Gum acacia; Hydrazine hydrate; Reducing agents

1. Introduction

The flexible electrode has a good conductivity value and high flexibility. The problem that is taken as the basis for developing this flexible electrode is that the electrodes commonly used to carry out biopotential measurements have their respective drawbacks. The dry electrode is fairly rigid and does not require an electrolyte gel during the measurement process, but the measures will produce a high noise signal (Saude & Morshed, 2016). The increased noise signal is created because of the trapped air cavity between the electrode surface and the skin and unwanted movement during measurement (Tseghai et al., 2020). Meanwhile, the wet electrode is an electrode that requires an electrolyte gel to measure the biopotential signal. Electrolyte gel added to the skin's surface could cause several skin disorders, such as irritation, inflammation, and allergies (Yokus & Jur, 2016). Therefore, a dry flexible electrode is needed because a dry flexible electrode can be used without additional gel (Penhaker, et al., 2017) and follows the shape of the skin surface to maintain good contact with the skin and provide good measurement results.

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Functionalization of fabrics with the addition of conductive materials could be performed to achieve a fabric-based dry flexible electrode. Conductive materials added to the fabrics should have good conductivity and maintain the fabrics' flexibility. The choice of conductive polymer material is because most polymers already have a high degree of flexibility and are elastic (Ahn, et al., 2020). Polyaniline is the most often used polymer because it has good electrical conductivity, is resistant to heat damage, and has a relatively easy synthesis process (Fu, et al., 2020). Conductive polyaniline can be synthesized using the COP (chemical oxidation polymerization) method (Wang, et al., 2020). The COP method is generally carried out by dissolving aniline in an acid medium. The type of polyaniline used in this electrode is emeraldine salt since emeraldine has high stability at room temperature and has the best electrical conductivity compared to leucomeraldin and pernigranilin (Gicevicius, et al., 2018). Emeraldine is polyaniline with reduced and oxidized conditions in balance. The base of emeraldine is blue, while the salt of emeraldine is green. Doping acid with emeraldine will cause emeraldine to form a compound in the form of an emeraldine salt.

AgNP with high purity and small size is necessary for medical applications (Khumaeni et al., 2019). The addition of AgNP to the fabric electrode increases the electrode conductivity. The small diameter size AgNP can get into crevices and stick to the surface of the fabric substrate. If the measurement conductivity increases, the noise reduction in the EMG will increase. Adding AgNP and polyaniline to cotton fabrics will produce a flexible electrode with good flexibility and conductivity that can be used for biopotential signal measurements such as Electroencephalography (EEG), Electrocardiography (ECG), and Electromyography (EMG) signals. The main advantage of this fabric-based flexible electrode is that the fabric electrode can follow the shape of the user's body curve when measuring the signals. Therefore, the skin-to-electrode contact could be improved, and the measurement results can be more accurate. In addition, the absence of an electrolyte gel can provide comfort to the user without giving symptoms of skin irritation when the measurement process is carried out for a long duration. Comfort in measurement is also very important because the biopotential signal can possibly change due to fatigue (Puspasari et al., 2017).

2. Materials and Methods

Plain white cotton fabric and aqua-dm were obtained from a local market in Indonesia. Aniline, Ammonium Persulfate (APS), NaOH, and HCl were purchased from Merck, Germany. Gum Acacia and Hydrazine Hydrate were obtained from a local chemical store in Indonesia. Silver nitrate ($AgNO_3$) was purchased from PT. Antam Indonesia.

2.1. Preparation of Fabric-Based Flexible Electrode with Addition of AgNP with Different Reducing Agents and PANI

At this stage, AgNP will be synthesized using two different reducing agents to compare the performance of the electrodes with each other. In this research, the dimensions of the white cotton fabric used are 4 cm x 2 cm. After the cotton fabric was prepared, the AgNP solution was designed using different reducing agents. AgNP reducing agents used were gum acacia and hydrazine hydrate. To increase the conductivity, the electrodes coated with AgNP are varied with an additional layer, namely PANI. Electrode performance will be seen based on the results of the SEM EDS characterization, conductivity, and EMG signal of each sample. Based on the characterization, variations of reducing agents that produce better performance will be selected for the next optimization stage. The procedure for preparing AgNP and PANI solutions is described in the following subsections.

2.1.1. Green synthesis of AgNPs with Gum Acacia

Gum Acacia is commonly used as a green synthesis-reducing agent to produce AgNP. Besides gum acacia, Rosman et al. (2021) has synthesized AgNP with another green synthesis-reducing agent, namely polychaete (Marphysa moribidii) (Rosman et al., 2021). However, gum Acacia has a low, reducing property; therefore, the AgNP synthesis process with Gum Acacia also requires a longer time. A total of 1%-wt (1 g) of Gum Acacia was added to 70 mL of distilled water in a flask. The solution is then stirred with a magnetic stirrer at the desired temperature (60-80°C) for about half an hour to obtain a homogeneous solution. At the same time, 0.1% by weight (0.1 g) of silver nitrate was dissolved in 30 mL of distilled water at room temperature and then rapidly injected into the above Gum Acacia solution with vigorous stirring (Dong et al., 2014). The solution was maintained at the desired temperature and allowed to react for 3 hours until a dark-colored solution was obtained. Then, the cotton fabric was dipped in the AgNP solution for 1 hour so that the solution was well absorbed into the cotton fabric. After soaking in AgNP solution, the sample will be dried in an oven at 60°C for 2 hours.

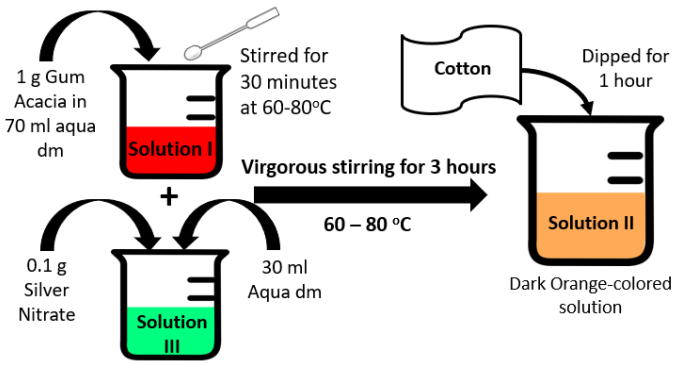


Figure 1 AgNP coating procedure on fabric with gum acacia (Dong et al., 2014)

2.1.2. Green synthesis of AgNPs with Hydrazine Hydrate

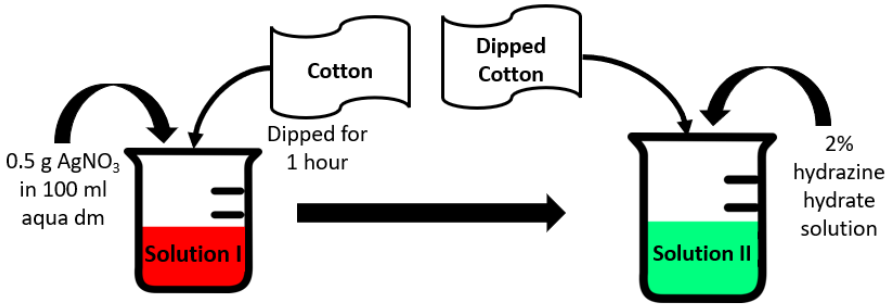


Figure 2 AgNP coating procedure on fabric with hydrazine hydrate

Hydrazine hydrate is one of the reducing agents which is quite strong in reducing Ag solution. However, hydrazine hydrate solution is a very toxic solution and can trigger cancer cells when in contact with body surfaces. The AgNP fabrication process using a reducing agent is carried out in a fumehood so that the gas from hydrazine hydrate is not inhaled. The fabrication begins with dissolving silver nitrate powder into aqua dm to produce a solution of $AgNO_3$ with a solubility of 5 g/l for 1 hour. Then, the cotton fabric is rapidly dipped in the 2% hydrazine hydrate solution. The sample was soaked until there were no bubbles resulting from reducing $AgNO_3$ to Ag on the fabric. After the sample is saturated, the sample will be dried in an oven at a temperature of 60°C for 2 hours. Fabric samples coated with AgNP with hydrazine hydrate will have a gray cotton fabric; the gray color indicates AgNP has adhered to the cotton fabric.

2.1.3. Synthesis of PANI

The synthesis procedure was started by preparing cotton fabric as a substrate, 0.5 mL of aniline monomer in 50 mL 1 M HCl (solution I), and 1.55 grams of APS in 50 mL HCl 1 M (solution II) (Abu-Thabit, 2016). The solutions I and II were mixed while stirring using a magnetic stirrer to keep the stirring rate constant so that the polymerization that occurred was evenly distributed. Next, the AgNP-treated fabric substrate was immersed in the solution during the polymerization process for approximately 30 minutes to obtain an average polymerization conversion of 90%. The success of the polymerization is indicated by a change in color to dark green, like the color of emerald salt. After the cotton fabric substrate is dark green, the cotton fabric is dried in an oven at 60°C to dry.

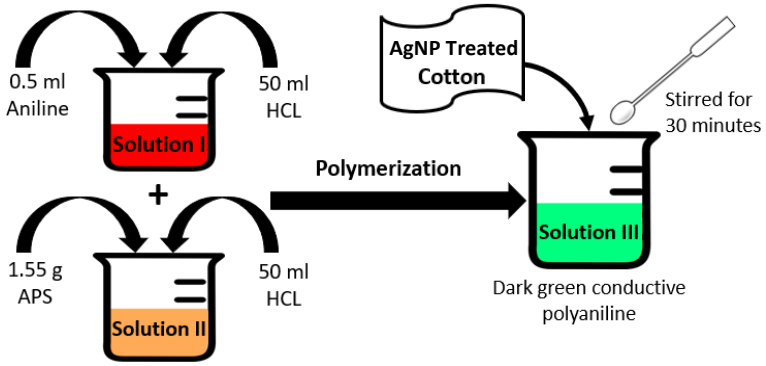


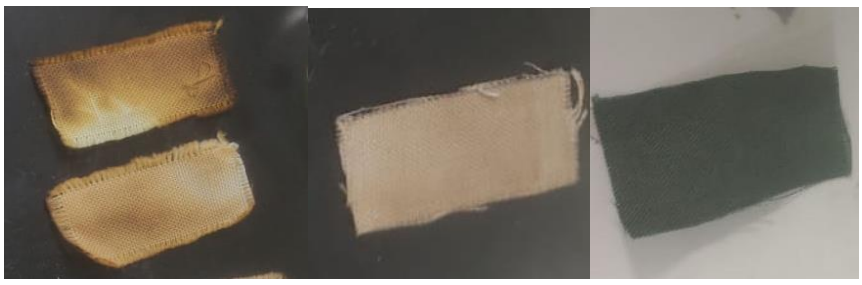
Figure 3 PANI coating procedure on fabric (Abu-Thabit, 2016)

Based on the synthesis procedure described previously, the electrode samples will be varied into four models the nomenclature of the samples obtained from the synthesis process can be seen in Table 1.

Table 1 Nomenclature of the sample

Sample	Composition		
A	Cotton	AgNP Gum Acacia	
B	Cotton	AgNP Hydrazine Hydrate	
C	Cotton	AgNP Gum Acacia	PANI
D	Cotton	AgNP Hydrazine Hydrate	PANI

The fabric-based flexible electrodes from each sample have different colors due to other treatments. The color change of white cotton fabric after being coated by AgNP solutions from other reducing agents and PANI can be seen in Figure 1.



(a) (b) (c)

Figure 4 Fabric substrate in (a) after being coated with AgNP acacia gum (b) after being coated with AgNP hydrazine hydrate (c) after PANI coating

2.2. Characterization of Fabric-Based Flexible Electrode

SEM (Hitachi SU3500) was used to analyze PANI-coated fabrics' morphology and composition. In addition, electrical conductivity characterization was carried out using a digital multimeter (Keithley DMM7510) and a DC source generator using the four-point probe (FPP) method (Figure 5). FPP is suitable for measuring the resistance of thin films or substrates in ohms per square by forcing a current through the two outer probes and reading the voltage across the two inner probes (Chlaihawi, et al., 2018). Using this FPP configuration can avoid errors in measurement due to contact resistance between the probe and sample. In this method, the value of the voltage generated by the electrode is measured, which is given an electric current with a constant value.

(a) (b)

Figure 5 (a) Keithley DMM7510 digital multimeter and (b) four-point probe

After the tool has been prepared, the DC source generator is turned on. The value of the input current source used is 0.5 mA, which is estimated because the source meter used has a maximum value limit of the measured voltage, which is 22 Volts. Measurements were repeated until 100 data were obtained for each electrode. The data obtained are then tabulated into a table in the form of the average voltage value, standard deviation, maximum voltage value, minimum voltage value, and peak-to-peak value of all electrode samples.

2.3. Biopotential EMG Measurement

Testing of the electrodes that have been generated in the EMG signal measurement instrument was carried out using the FlexComp Infiniti – 10 Channel System device, which was produced and displayed on the Infiniti BioGraph software.

(a) (b)

Figure 6 (a) Set-up of EMG signal measurement with FlexComp Infiniti – 10 Channel System device (b) the placement of the EMG measurement probe for the detection electrodes is placed on A and B while the reference electrode is placed on C

The placement of the EMG measurement probe can be observed in Figure 3 where two electrodes were attached to the biceps muscle, and one electrode was attached to the elbow, which served as a reference electrode. The three electrodes installed on the arm are then connected to the EMG test equipment, and the obtained measurement signals are displayed on a computer. The measurement signals were received by clenching the hands to get muscle signals when contracting and releasing fists to get muscle signals when relaxing for

5 seconds each. This process was repeated twice so that the total measurement was carried out for about 20 seconds. When the hand is relaxed, the biopotential signal shows a value close to zero, but when the hand contracts, the signal moves to a peak.

3. Results and Discussion

3.1. SEM EDS Observation

SEM-EDS is a tool for characterizing the morphology of the sample surface and calculating the composition of the material making up the sample. The design of each sample (A, B, C, and D) follows the composition in Table 1. Samples A and C were coated with silver nanoparticles synthesized using acacia gum, while samples B and D were synthesized with hydrazine hydrate. In addition, samples C and D were given an additional PANI layer. From the obtained SEM images in Figure 7, it can be seen that the variation of the electrode without the addition of PANI has flashes due to the charging effect. The charging product seen in the SEM image is due to the low conductivity of the observed sample. Qualitatively, the results of SEM A did not show a charging effect as large as the SEM results of sample B, so it can be concluded that the conductivity in sample A is higher than B. In addition, SEM samples C and D have better SEM results because no charging effect occurred. Absence of the charging effect indicates a higher conductivity on samples C and D than that of A and B due to the addition of PANI. Silver particles could be identified as small particles on the surface of the fabric on the SEM image.

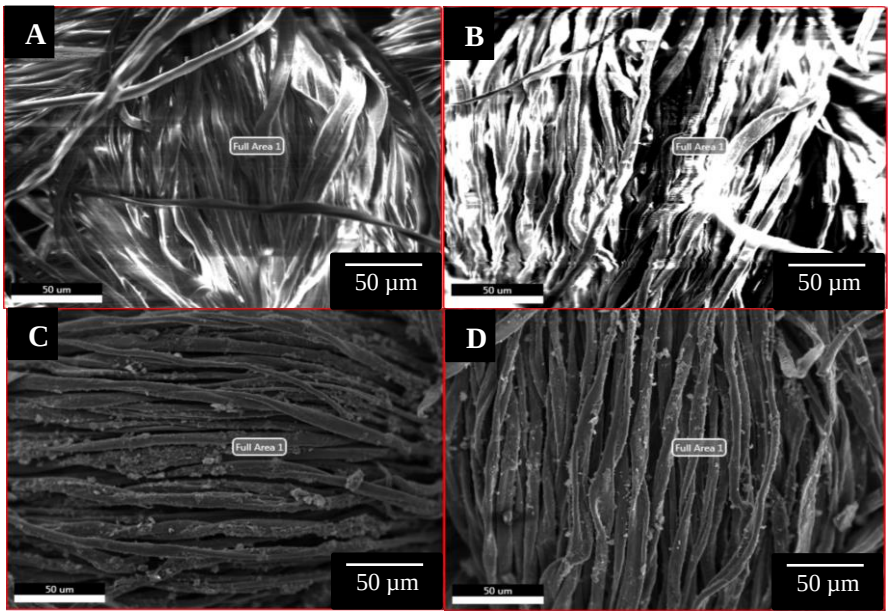


Figure 7 SEM characterizations of (a) sample A (b) sample B (c) sample C (d) sample D

The SEM results that have been obtained are then analyzed using EDS. Based on the results of the EDS analysis in Table 2, it was found that there was a decrease in silver content during the PANI coating process on AgNP electrodes. Samples A and C, which use gum acacia as the reducing agents, decreased about 0.8% silver particles during the PANI coating process. Otherwise, samples B and D decreased silver content by 0.7%. The silver content decreased due to the addition of C, O, N, S, and other PANI atoms and the possibility of silver particles being released during the PANI coating process . Samples A and B do not have N and S atomic compositions because samples A and B are only composed of AgNP and cotton fabric without PANI addition. According to Monier's research, cotton is only composed of C, H, and O atoms (Monier et al., 2014).

Table 2 EDS characterization of AgNP electrode with a variation of reducing agents and PANI addition

Sample	Atomic Composition (%)				
	C	N	O	S	Ag
A	47.2	-	51.7	-	1.1
B	46.9	-	52.1	-	1
C	46	3.9	42.7	7.1	0.3
D	41.5	8.5	39.2	10.5	0.3

3.2. Electrical Conductivity Measurements

The measured voltage data for the four samples amounted to 100, then averaged. The following is the result of the voltage data obtained from the measurement results, as listed in Table 3.

Table 3 Voltage measurement of flexible electrode sample (units in Volts)

Sample	A	B	C	D
n Data	100	100	100	100
Average	0.01036	0.00723	0.00143	0.00153
Standard Deviation	0.00147	0.00324	0.00007	0.00026

The dimensions of each tested sample were measured using a ruler to measure length and width and using the CHY-CA thickness measurement instrument to measure the thickness of the sample. The dimensions of the electrode samples can be seen in Table 4.

Table 4 Fabric electrode sample size dimension (units in meters)

Sample	A	B	C	D
Thickness	0.00018	0.00017	0.00017	0.00017
Length	0.04	0.04	0.04	0.041
Width	0.02	0.02	0.02	0.02

The electrode resistance could be calculated using the formula 1 below:

$$R = \frac{V}{I} \text{ x } CF1 \text{ x } CF2 \text{ x } CF3 \quad (1)$$

R is the sample resistance (Ω), V is the read voltage (Volt), and I is the electric current (0.5 mA). CF1, CF2, and CF3 were the correction factor values due to the influence of sample size, sample thickness, and temperature, respectively, when FPP measurement was performed. So that each has a value of CF1 = 3.2246; CF2 = 1,000; and CF3 = 1.0410. The sample's electrical conductivity value is obtained using equation 2 below.

$$\sigma = \frac{1}{\rho} = \frac{1}{R_S \text{ x } t} \quad (2)$$

Where σ is the electrical conductivity of the electrode, ρ is the resistivity of the electrode, Rs is the resistance of the electrode, and t is the thickness of the electrode. Each sample was tested for conductivity. The result is tabulated in Table 5.

Table 5 The flexible electrode's electricalconductivity (σ) and resistivity (ρ) table

Sample	A	B	C	D
Resistance (Ω)	48.5	69.6	9.6	10.2
Conductivity (S/m)	119.2	113.2	614.4	577.7

Based on the test results, sample C showed the highest conductivity value compared to other variations, which was 614.41 S/m. The number and uniform distribution of conductive molecules across the electrodes, such as polyaniline and silver nanoparticles, increased.

3.3. EMG Measurement of Flexible Electrode

Signal-to-Noise Ratio (SNR) can be calculated using formula 3:

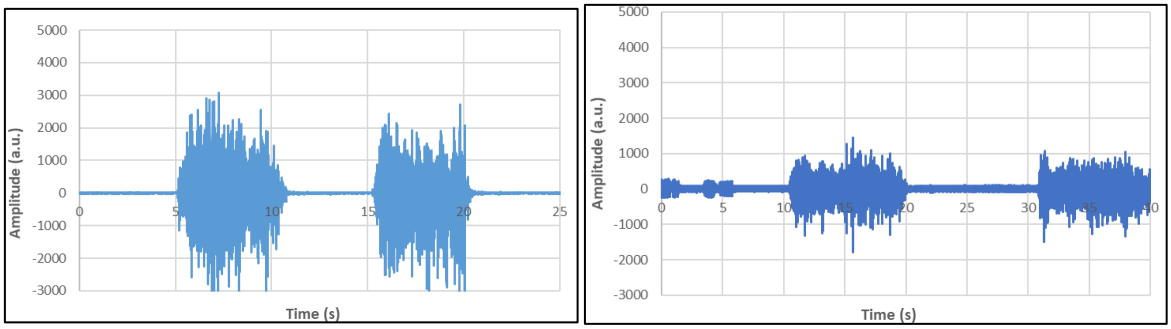
$$\text{SNR} = 20\log\left(\frac{S}{N}\right) \quad (3)$$

Where SNR is the signal-to-ratio, S is the RMS voltage of the measured EMG signal, and N is the RMS voltage of the measured noise signal. EMG measurements were carried out only on the electrode samples with the best conductivity. In this case, the electrodes added with PANI, samples C and D, gave the highest conductivity values. The EMG measurement of samples C and D are tabulated in Table 6.

Table 6 EMG measurement table of AgNP PANI electrode

Sample	C	D
SNR (dB)	24.4	15.8

The results of the EMG measurements show a correlation between the conductivity values of the electrodes and the obtained SNR values. The SNR value indicates that the noise signal does not interfere with the EMG measurement process. The higher the SNR value, the smaller the effect of the noise signal. Based on the results that have been processed, sample C shows the highest SNR value compared to the other sample. The SNR value obtained from sample C is 24.4 dB, while sample D shows 15.8 dB. The biopotential signal is shown in Figure 8.



(a) (b)

Figure 8 EMG measurement signal of (a) sample C [AgNP Gum Acacia + PANI] (b) sample D [AgNP Hydrazine Hydrate + PANI]

After getting the SNR results from fabric-based flexible electrode samples C and D, a comparative study of electrode performance was carried out to compare the performance of the electrodes produced by this research with the results of other researchers. The results of the comparative study can be seen in Table 7 below.

Based on the comparative study above, fabric-based flexible electrodes made of AgNP PANI with acacia gum as a reducing agent have a higher SNR value than commercial electrodes, which is 24.4 dB. While commercial electrodes have an SNR value of 21.2 dB Therefore, the performance of AgNP PANI is better than the common electrodes.

Table 7 Comparative electrode performance study for body biopotential signals measurement

No	Material	Substrate	Type	SNR (dB)	References
1	MWCNTs/PDMS composites on Ag	TPU on fabric	Dry	23.1	(Masihi, et al., 2021)
2	Laser Induced Graphene	PDMS	Dry	32	(Yang, et al., 2021)
3	Ag/AgCl	Parylene C	Dry	23.8	(Peng, et al., 2016)
4	Ag/AgCl	Commercial	Wet	21.2	(Masihi, et al., 2021)
5	AgNP PANI with Gum Acacia	Cotton fabric	Dry	24.4	This Study
6	AgNP PANI with Hydrazine Hydrate	Cotton fabric	Dry	15.8	This Study

4. Conclusions

The conclusion that can be drawn from this research is that the combination of AgNP and PANI in cotton flexible electrodes can perform quite well for measuring biopotential muscle signals. The flexible electrode has the advantage of good electrode flexibility and conductivity; therefore, it does not need to use an electrolyte gel to provide good skin-to-electrode contact. These advantages can solve problems that often occur when using common Ag/AgCl commercial electrodes, such, as high noise signals, uncomfortable usage, and skin allergies. AgNP PANI flexible electrode with Gum Acacia as a reducing agent has the highest conductivity and SNR value among other variations, which is 614.41 S/m, and an SNR value of 24.4 dB. Future work is focused on improving the attachment of AgNP and PANI to the cotton fabric and the sustainability of flexible electrodes.

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