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A Novel Brain-Computer Interface Flexible Electrode Material with Magnetorheological property

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Abstract: The electrode is the crucial component of the Brain-Computer Interface (BCI), and is the key for the development of the BCI technology. Compared with non-intrusive electrodes and intrusive electrodes, semi-invasive BCI electrodes could make a balance between the quality of the electroencephalogram (EEG) signal and security. However, the application of the compressed mesh electrodes, the typical semi-invasive electrode, has been restricted due to the folds and tangles of the electrode material during injection and the insufficient deployment after injection. To solve the problem, we develop a novel semi-invasive BCI flexible electrode material based on Fe₅O₇@GO/P(NIPAM-MAA) hydrogel with magnetic field controlled rheology. The rheology tests results indicate the hydrogel is injectable and its expansion during the transition from sol to gel at ~37°C can be actively controlled by applying a magnetic field. Its resistivity is less than 1200Ω, which makes it sensitive enough to transmit electrical signals between brains and computers. The signal waveform and amplitude recorded by Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode and wet electrode are basically the same, which proves that the prepared hydrogel electrode material can acquire and record effective EEG signals. Compared with the wet electrode, hydrogel electrodes show higher average peak-to-peak values and higher noise levels. Although the signal-to-noise ratio is similar between the Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode and the wet electrode, the hydrogel electrode is more stable, which proves that the Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode can accurately collect and record EEG signals with a stable signal-to-noise ratio.

Introduction

Brain-Computer Interface is the frontier of human brain engineering and a critical direction of man-machine interaction. Compared with other man-machine interaction systems, BCI doesn’t depend on the normal input and output ways of our brain. It's a new non-muscle channel that established between the human brain and computers or other electronic devices. Therefore, BCI is an alternative system built on artificial mechanisms and acts as a bridge between the brain and external devices, which can achieve direct information interaction and control of a real-time communication. It's a ground-breaking technology that produced on the basis of intersection of electronic information, bio-medicine, materials science, mechanics and other disciplines.

Although the signal-to-noise ratio is similar between the Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode and the wet electrode, hydrogel electrodes show higher average peak-to-peak values and higher noise levels. Although the signal-to-noise ratio is similar between the Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode and the wet electrode, the hydrogel electrode is more stable, which proves that the Fe₅O₇@GO/P(NIPAM-MAA) hydrogel electrode can accurately collect and record EEG signals with a stable signal-to-noise ratio.

The initial goal of BCI was the medical monitoring. BCI can monitor the neuron physiological activities of the brain by analyzing brain waves, providing important evidence for the diagnosis of brain diseases. As a new input and output manner, BCI also makes it possible for human brain signals to drive external devices directly. In 2014, at the opening ceremony of the Brazil World Cup, the paralyzed youth wore exoskeleton that was similar to the mechanical armor, kicking off the World Cup through BCI. The emergence and development of BCI technology has not only brought the gospel of functional recovery to the disabled, but also provided opportunities of functional enhancement to healthy people. In the field of aerospace, BCI technology can transform astronauts’ thinking activities into operating instructions, which will assist them in completing their space missions. It is worth mentioning that Elon Musk’s Neuralink company have implanted a flexible electrode with a diameter of 4~6 microns into the monkey brain and completed the preliminary testing and evaluation. In August 2020, Neuralink used live pigs to demonstrate BCI technology. The product is wireless transmission and wireless induction through minimally invasive surgery. In addition, the applications of BCI also involve intelligent transportation, identity verification, education and entertainment, among which the huge socioeconomic benefits and broad application prospects make BCI technology extremely competitive.

Electrode is a crucial component of the BCI and the key to the realization of BCI technology. According to the electrode
position, the BCI can be classified into two categories, including non-intrusive electrodes and invasive electrodes. Non-invasive, also known as wearable, doesn’t need to be implanted in the brain. This non-invasive method is less risky and can guarantee safety. At present, there are many researches in this area, such as claw electrodes\(^7\), bionic humidity-sensitivity electrode\(^8\), foam electrodes\(^9\), sponge electrodes\(^10\), textile electrodes\(^11\), Tattoo electrode\(^12\), etc. It can be seen that the wearable style is becoming more and more in the direction of flexibility, making it smaller, lighter, more comfortable, and non-stressful to meet the needs of long-term wear. Because of its scientific significance and potential economic benefits, the application of non-intrusive BCI has begun to take shape and is showing a tendency to rapid development, such as headband helmets, electronic tattoos, and so on. As we all know, the quality and intensity of the EEG signal is proportional to the distance between the electrode and the brain nerve.\(^13\) Therefore, although the wearable type is safe, convenient and fashionable, its shortcomings are also obvious. The collected EEG signal is weak, fuzzy, poor quality and unstable, that is, the signal-to-noise ratio is low. Compared with non-invasive, electrodes implanted in the skull can provide better spatial resolution, higher signal-to-noise ratio and wider frequency range. It can be used for a long time and is less susceptible to motion artifacts and external noise, which makes it a unique advantage in practical applications of BCI. There are many such studies, such as strip\(^14\), snake\(^15\), sinusoidal probe\(^16\), three-dimensional micro-needle electrode\(^17\), climbing twined electrode\(^18\), micro-wrinkled electrode\(^19\), micro-crack array\(^20\), flexible nerve clip\(^21\) and nerve tassel electrode\(^22\), etc. Although the intrusive BCI ensures the strength and quality of the collected EEG signals, anyway, whether the risk of surgical infections or the expensive and cumbersome procedures, security is still a major problem.

In terms of the shortcomings of the above two types of BCI, scholars have proposed the concept of semi-invasive technology\(^23\). Semi-invasive, also known as injectable, combines the advantages of non-invasive and invasive. Injecting through a syringe can accurately target and locate in specific brain regions, which could make a balance between the quality of EEG signals and security. At present, the research of semi-invasive BCI is still in its infancy. Among them, the most representative one is an ultra-flexible open mesh structure invented by Charles M Lieber’s team\(^24-26\). The compressed mesh electrode is injected into the skull through a syringe, and the mesh will stretch itself. It can fit on the brain tissue very softly, which can further blur the boundaries and bridge the gap between neural networks and electronic networks.

However, the existing semi-invasive BCI technologies are passive. During the injection, the potential wrinkles and tangles of the electrode material would affect the signal-to-noise ratio of the EEG signals. After injection, the electrode material can’t be fully deployed on the cerebral cortex, which also restricts the monitoring range of its EEG signal. In response to those problem, this study proposes a subversive idea of semi-invasive BCI technology that turns passive to active. Its core content is to control the deployment of the electrode material by applying an external magnetic field after the electrode material is injected.

![Image](Image)

**Figure 1.** The schematic diagram: (a) Injecting hydrogel precursor solution. (b) Under the physiological environment of 37°C, the hydrogel would change from solution to sol. (c) Applying an external magnetic field to achieve the purpose of expanding the sol area. (d) After removing the external magnetic field, the hydrogel would undergo a sol-to-gel transformation.

The ultimate goal is to develop a novel semi-invasive BCI electrode material with magnetic field-controlled rheology. The schematic diagram is shown in Figure 1. Compared with non-intrusive BCI electrodes, the novel semi-invasive BCI electrode would have a higher signal-to-noise ratio since it is placed directly on the surface of the brain, while compared with invasive BCI electrodes, it would be much safer because it avoids complicated craniotomy. With respect to the other semi-invasive BCI electrodes, it could control the unfolding of the material, and avoid the entanglement and wrinkles.

Hydrogels match the mechanical properties of brain tissues and have the unique rheological properties as injectable materials. Graphene oxide (GO) has excellent electrical conductivity, which is beneficial to the transmission of EEG signals. Fe\(_3\)O\(_4\) can be designed into nanometer size with paramagnetic, which would provide the hydrogels with reversible magnetorheological properties. Therefore, we synthesized a Fe\(_3\)O\(_4\)/GO/P(NIPAM-MAA) hydrogel and used it to prepare the novel semi-invasive BCI electrode. Furthermore, the Fe\(_3\)O\(_4\)/GO/P(NIPAM-MAA) hydrogel can be used not only as a semi-invasive electrode, but also as a substitute for a non-invasive electrode material. Since the intrusive EEG signal acquisition test requires comprehensive consideration of safety and ethical issues, this article only uses them to perform EEG acquisition experiments outside the scalp in a non-invasive manner.

**EXPERIMENTAL SECTION**

**Materials and Preparation Methods**

**Preparation of Fe\(_3\)O\(_4\)/GO**

The graphene oxide was prepared by the modified Hummers method\(^27\), and Fe\(_3\)O\(_4\)/GO nanoparticles were prepared by the chemical co-precipitation method. First, added 200mL of deionized water to the beaker and continued to bubbling with nitrogen for 30min. Added 50mg of GO and vibrated ultrasonically for 30min. Transferred the liquid in the beaker to a three-necked flask and heated it in a water bath at a constant temperature of 25°C. Then, added 2.35g FeCl\(_3\), 0.86g FeCl\(_2\) and stirred until fully dissolved. Turned on nitrogen and blew three
times. Added 30mL of ammonia and blew three times. Heated and stirred for 30 min at 25°C. Heated the water bath to 80°C.

![Figure 2](image)

**Preparation of FeOx@GO/P(NIPAM-MAA) Hydrogel**

First, placed 100mg N-isopropylacrylamide (NIPAM, 98% purity), 1.0% methacrylic acid (MAA), 15mg crosslinker N,N-methylenebisacrylamide (BIS), 15mg initiator ammonium persulfate (APS) and 2mL deionized water in a beaker to prepare a hydrogel precursor solution, and subjected to ultrasonic and magnetic stirring treatment. Then, weighed and added FeOx@GO solution evenly into a petri dish, and added 6μL of catalyst N,N,N,N-tetramethylethylenediamine (TMEDA). Finally, continued to sonicate and stir for 30min. After a few minutes of rest, FeOx@GO/P(NIPAM-MAA) hydrogel was obtained.

Characterization of FeOx@GO/P(NIPAM-MAA) Hydrogel

The morphology and structure of the P(NIPAM-MAA) hydrogel, FeOx@GO and FeOx@GO/P(NIPAM-MAA) hydrogel were analyzed by field emission scanning electron microscope (SEM), advanced Fourier transform infrared spectrophotometer (FTIR, IS50, USA). What’s more, physica MCR 301 rheometer (Anton Paar, Austria) was used to analyze the mechanical properties of the hydrogel.

Conductivity and Electrochemical Performance

The sheet resistance of FeOx@GO/P(NIPAM-MAA) hydrogel was tested by a four-probe tester (HP-504, China). This experiment randomly selected 15 points, and then took the average value. According to the formula, the resistivity could be calculated from the product of the average sheet resistance and the thickness of the hydrogel electrode.

Properties Testing

Temperature-sensitivity and Mechanical Properties

The temperature sensitivity of the hydrogel was tested by a differential scanning calorimeter (DSC, 2500, USA), and the temperature range was 25~45°C. In order to further verify the sensitivity of the hydrogel to temperature, the light transmittance was obtained by ultraviolet-visible light near infrared spectrophotometer (UV, Lambda950, USA). What’s more, physica MCR 301 rheometer (Anton Paar, Austria) was used to analyze the mechanical properties of the hydrogel.

Rheological Properties

The injectability of the hydrogel was macroscopically analyzed by the test tube inversion method. Initially, the hydrogel precursor solution was injected into the test tube with a sterile syringe. After observing and recording for a period of time, we turned the test tube upside down by 180°. If no liquid flows out, there is no doubt that the hydrogel has been formed. Then use a timer to record the time spent in this process. In order to quantitatively analyze the gelation time of the hydrogel, the rheometer was used to characterize the viscosity of the hydrogel over time. When the viscosity of the hydrogel no longer increases, the gelation process is complete.

The magnetorheological properties of FeOx@GO/P(NIPAM-MAA) hydrogel were determined using rheometer whose parallel-plate system (diameter 20mm, gap distance 1mm) was attached to the external magnetic field generator. The magnitude of the magnetic field strength can be changed by controlling the magnitude of the direct current emitted by the
parallel plate system. When the current is changed, a uniform magnetic field perpendicular to the sample would be formed between the upper and lower parallel plates of the rheometer. Table 1 shows the corresponding value of current intensity and magnetic field strength of rotating rheometer. At a constant frequency of 10 rad/s, the dependence of the storage modulus $G'$ and loss modulus $G''$ for Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel on shear strain (0.01%~100%) under different magnetic field strengths were tested. Under the constant strain amplitude (0.01%) and the frequency (10 rad/s), the dependence of the storage modulus and loss modulus for Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel on magnetic stress were tested. All tests were performed at 25°C.

| Name               | Corresponding value |
|--------------------|---------------------|
| Current intensity (A) | 0 1 2 3 4         |
| Magnetic field strength (mT) | 0 115 234 350 456 |

EEG Signal Acquisition Performance

The EEG signal is collected and recorded by a 32-lead EEG recorder (eegoTM mylab, ANT Neuro, Netherlands). As shown in Figure 3(a), after the subject puts on the electrode cap, the hydrogel electrode material is injected into 34 electrode sites. As shown in Figure 3(b), when all 34 channels are displayed in green on the computer interface, it means that the impedance of the electrode materials of all channels is below 20 kΩ, and then the next EEG signal acquisition test can be performed. Sampling frequency is 500 Hz. Among them, GND is a ground electrode, and CPz, M1, and M2 are reference electrodes. The EEG signal was collected for 3 h in a noise-reducing enclosed channel that was beneficial to signal transmission, but also provided a huge space for water molecules to increase the response rate of the hydrogel. However, compared with P(NIPAM-MAA) hydrogel, the surface of Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel was extremely rough due to the addition of Fe$_3$O$_4$@GO. Such rough surface morphology enabled the BCI electrode to maintain conformal contact with the brain more stable, which was of great significance for signal transmission. Figure 4(d) shows the FTIR spectra of Fe$_3$O$_4$@GO, P(NIPAM-MAA) and Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogels. From the FTIR spectra of P(NIPAM-MAA) hydrogel, the broad peak in the range of 3508~3284 cm$^{-1}$ was caused by the N-H absorption peak on the amide group of P(NIPAM) and the O-H vibration absorption peak in MAA. The absorption peak at 2973 cm$^{-1}$ was attributed to the C-H vibrational peak of methyl and methylene on the isopropyl. Two strong absorption peaks appeared at around 1720 cm$^{-1}$ and 1650 cm$^{-1}$, which were characteristic stretching vibration peaks of the C=O on the amide. The symmetric vibrational coupling splitting peaks of the dimethyl on the isopropyl was detected at 1417 cm$^{-1}$ and 1346 cm$^{-1}$. In the region of 1021~1271 cm$^{-1}$, the absorption peak was obviously enhanced, which was caused by the C=O stretching vibration absorption peak in MAA. It can be seen that MAA was successfully introduced into P(NIPAM), and P(NIPAM-MAA) hydrogel was successfully prepared. The FTIR of Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel was similar to that of P(NIPAM-MAA) hydrogel, but the absorption peak was obviously enhanced in the range of 3522~3251 cm$^{-1}$, which was caused by the -OH stretching vibration peak of Fe$_3$O$_4$@GO nanoparticles. It didn’t show the diffraction peak of Fe$_3$O$_4$@GO on the whole, indicating that Fe$_3$O$_4$@GO had been evenly dispersed in the hydrogel, which proved that an integrated Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel has been prepared.

RESULTS AND DISCUSSION

Morphological and Structural Characterization

Figure 4(a) indicates that the diameter of Fe$_3$O$_4$ particles is about 20~30 nm, and the fine particles are uniformly distributed. Fe$_3$O$_4$ was modified in situ on the surface of graphene oxide (GO), and the layered structure of GO was conducive to loading magnetic nanoparticles Fe$_3$O$_4$. Fe$_3$O$_4$ and GO were overlapped and compounded together. This structure can improve the synergistic effect of the two materials, indicating that Fe$_3$O$_4$@GO has been successfully prepared by chemical co-precipitation method.

As shown in Figure 4(b)(c), comparing the SEM images of the P(NIPAM-MAA) hydrogel and the Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel, it was found that the similarity of the two hydrogels is that the pores were relatively uniform, and the pore size was about 20 μm. They formed cross-linked three-dimensional porous network structures, which not only provided an access to the C-H vibrational peak of methyl and methylene on the isopropyl.
Figure 4. (a) SEM image of Fe₃O₄@GO. (b) SEM image of P(NIPAM-MAA) hydrogel. (c) SEM image of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel. (d) FTIR spectra of Fe₃O₄@GO (1), P(NIPAM-MAA) hydrogel (2) and Fe₃O₄@GO/P(NIPAM-MAA) hydrogel (3).

Characteristics of Nanoparticles

Figure 5(a) depicts the full XPS spectra of Fe₃O₄, Fe₂O₃@GO and the high-resolution narrow-area XPS image of Fe₂p, O1s, and C1s. In Figure 5(a1), there were no obvious peaks shift due to hybridization. In the XPS spectrum of Fe₃O₄@GO, it can be seen that some strong electron binding energy peaks appear at about 711.6eV, 532.6eV, 285.6eV, respectively corresponding to the characteristic peaks of Fe₂p, O1s, C1s, indicating that the prepared Fe₃O₄@GO sample contains at least Fe, O, C elements. In the XPS spectrum of Fe₂O₃, some strong electron binding energy peaks appear at 710.7eV and 724.3eV, respectively corresponding to Fe₂p₃/₂ and Fe₂p₁/₂ in Fe electron binding energy peaks appear at about 1350cm⁻¹ to 1323cm⁻¹, the peak intensity became weaker, and the peak shape became wider, indicating that the introduction of Fe₃O₄ nanoparticles made GO exhibit higher disorder and more defects. The G peak moved from 1592cm⁻¹ to 1598cm⁻¹. The Raman shift of the G peak confirmed the charge transfer between GO and Fe₃O₄ in the chemical co-precipitation reaction, indicating that a strong interaction force was formed between GO and Fe₃O₄. The intensity ratio of peak D to peak G (I_D/I_G) is an important parameter that characterizes the disorder of the surface structure of carbon-based materials. Compared with GO, the I_D/I_G of Fe₃O₄@GO increased from 0.96 to 1.45, indicating that GO had formed defects in the two-dimensional crystal structure of carbon atoms after magnetic functional modification. Figure 5(d) describes the TGA curves of GO and Fe₃O₄@GO samples. In the TGA curve of GO, when the temperature is below 200°C, there would be a slight weight loss, which is mainly caused by the removal of physically adsorbed water molecules on the surface of the GO sample. In the temperature range of 200°C~400°C, it had a severe weight loss because of the thermal decomposition of the oxygen-containing functional groups in GO. In the temperature range of 400°C~700°C, GO had a slow and stable weight loss, which was caused by the removal of more stable oxygen-containing functional groups in GO and the thermal decomposition of the carbon skeleton. However, Fe₃O₄@GO had less weight loss in the whole temperature range, and the thermal weight loss curve only slightly dropped when the temperature was above 200°C. The reason is that a strong interfacial bonding force is formed between Fe₃O₄ and GO, indicating that the thermal stability of Fe₃O₄@GO is higher than that of GO. BET surface areas of GO before and after modification with Fe₃O₄ were 479.676 m²/g and 153.678 m²/g, respectively.

Temperature-sensitivity and Mechanical Property

Isopropylacrylamide (NIPAM) is currently the most representative temperature-sensitive hydrogel. From the perspective of structure, the monomer NIPAM contains C=C, which is easy to open for radical polymerization. NIPAM contains both a hydrophilic amide and a hydrophobic isopropyl, which exhibits temperature sensitivity by adjusting the ratio of amide and isopropyl. Since the lower critical solution temperature (LCST) of NIPAM is close to the human...
temperature (32°C), the LCST of the hydrogel can be adjusted according to the hydrophilicity and hydrophobicity of another functional monomer-methacrylic acid (MAA). The influence of different MAA content on LCST of P(NIPAM-MAA) thermosensitive hydrogel is shown in Table 2. When the temperature is below LCST, a strong hydrogen bond is formed between the amide and the water molecule, which presents macroscopically hydrophilic and volume expansion. When the temperature is above the LCST, the hydrophobicity of the isopropyl is dominant, and the hydrogel macroscopically exhibits volume shrinkage.

Figure 6(a) denotes the DSC curve of the hydrogel, that is, the endothermic and exothermic reaction as a function of temperature. When the hydrogel undergoes a phase transition, there would be a downward endothermic peak on the DSC curve. The LCST of pure PNIPAM hydrogel was around 32°C. With the increase of MAA content, the LCST increased accordingly, and the endothermic peak on the corresponding DSC curve would gradually move to the right. Under the condition that the content of MAA is 1%, the LCST of the hydrogel is 37°C. Figure 6(b) shows the dependence of the light transmittance for the hydrogel on temperature. When the temperature is below LCST, the light transmittance of the hydrogel was higher and the change was relatively small. When the temperature rose to LCST, the light transmittance dropped sharply, and the endothermic peak on the corresponding DSC curve would gradually move to the right. Under the condition that the content of MAA is 1%, the LCST of the hydrogel is 37°C, which demonstrates that the prepared hydrogel has a good temperature sensitivity property.

Figure 6(c) indicates the dependence of the shear modulus for the hydrogels yield on temperature. When the temperature was below LCST, the shear modulus of hydrogel was smaller and tended to be stable. When the temperature reached LCST, the shear modulus of the hydrogel changed sharply. As the temperature continued to increase above the LCST, the shear modulus of the hydrogel rose to the maximum and no longer changes. The shear modulus values of P(NIPAM-MAA) hydrogels with MAA content of 0.0%, 0.6%, 1.0% are about 3500Pa, 4400Pa, 5000Pa, respectively, indicating that with the increase of MAA content, the mechanical property of P(NIPAM-MAA) hydrogel is improved, and is on the same order of magnitude as that of brain tissues (Pa~kPa).

### Resistivity and Electrochemical Performance

Figure 7(a) illustrates the sheet resistance of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel. The thickness of the hydrogel sample is 4mm, so according to the formula, the resistivity of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel is 119.48Ω·m. The hydrogel material exhibits excellent electrical conductivity, which is sufficient to support the signal transmission.

Figure 7(b) shows the cyclic voltammetry curve (CV) of the hydrogels when the test voltage window is -0.8~0.8V at a scan rate of 10mV/s. It can be seen that when the Fe₃O₄@GO dispersed phase is not added, the CV pattern of the P(NIPAM-MAA) hydrogel is a straight line parallel to the X axis, indicating that it does not have electrical conductivity. Compared with P(NIPAM-MAA) hydrogel, the CV pattern of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel is close to a rectangle, and the area enclosed by the CV curve is larger, indicating that the prepared hydrogel electrode has a larger charge storage capacity, which proves that the prepared Fe₃O₄@GO/P(NIPAM-MAA) hydrogel electrode material has better electrochemical performance. The electrode material exhibits a good charge injection capability, which mainly depends on the huge and effective contact area provided by the Fe₃O₄@GO/P(NIPAM-MAA) hydrogel. When the scanning voltage is reversed, the corresponding current would also be reversed, which indicates that the electrode material has good redox reversibility and is suitable for use as a flexible electrode material for Brain-Computer Interface. In addition, the shape of the CV pattern after 30 scanning cycles is approximately the same, showing that it has good electrochemical stability. This is of great significance to the BCI electrode, which can make the collection of EEG signals more stable, and is also conducive to the recording and transmission of EEG signals.

The polarization curve represents the curve of the relationship between the electrode potential (V) and the current density (I) on the electrode. The steeper the polarization curve, the greater the degree of potential deviation, the stronger the polarization, that is, the greater the obstruction of the electrode process. As shown in the Figure 8, the curve of the Fe₃O₄@GO/P(NIPAM-MAA) hydrogel with the bio-potential electrode is gentle, indicating that the degree of polarization is small and the electrode process is relatively successful.
Figure 7. (a) Sheet resistance of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel. (b) Cyclic voltammetry curve of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel.

Figure 8. Electrode polarization curve of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel.

Figure 9. (a) Magnetic hysteresis curves of Fe₃O₄, Fe₃O₄@GO, Fe₃O₄@GO/P(NIPAM-MAA) hydrogels. (b) Detail view of the magnetic hysteresis curves.

Magnetic property of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel

Figure 9(a) indicates the magnetic hysteresis curves Fe₃O₄, Fe₃O₄@GO, Fe₃O₄@GO/P(NIPAM-MAA) hydrogels. Their saturation magnetization values were 60, 58, 10emu/g respectively. GO and hydrogel are non-magnetic materials, their introduction would decline the magnetic properties of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel. Therefore, the magnetic properties of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel mainly depend on the content of Fe₃O₄ nanoparticles. As shown in Figure 9(b), they had no hysteresis loop at room temperature, and the remanence and coercivity were both 0, which proved that they have superparamagnetism at room temperature. Superparamagnetism is of great significance to magnetic nanoparticles. It can neglect the interaction between nanoparticles, making them uniformly dispersed in aqueous solution without serious agglomeration. More importantly, the materials can be reused without being influenced by “history.” In other words, when no magnetic field is applied, the material is completely restored to its previous state.

Rheological Properties of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel

The test tube inversion method was used to macroscopically analyze the injectable property of P(NIPAM-MAA) hydrogel. Initially, the hydrogel precursor solution is injected into the test tube with a sterile syringe. After observing and recording for a period of time, turn the test tube upside down by 180°. Figure 10(a) describes the viscous liquid state before injection, and Figure 10(b) shows the final gel state. It took 132s to record this process according to the stopwatch timer. In order to further quantitatively analyze the gelation time of the hydrogel, we used a rheometer to test the viscosity of the hydrogel. As shown in Figure 10(c), it was a liquid at the beginning, and hydrogel had a lower viscosity. As time goes by, the viscosity of the hydrogel would increase. When the viscosity of the hydrogel no longer continued to increase, the hydrogel had been solidified and formed. The viscosity of the hydrogel was below 500Pa·s at the beginning of injection, which can ensure the spread ability of the electrode material, indicating that the prepared hydrogel has good injectability. And the gelation time was about 120s, ensuring a sufficient and security magnetization time.

Figure 10(d) indicates the dependence of the storage modulus (G') and loss modulus (G'') for Fe₃O₄@GO/P(NIPAM-MAA) hydrogel on shear strain amplitude under different magnetic field strengths. Without applying an external magnetic field, neither the storage modulus nor the loss modulus of the magnetic hydrogel has an obvious plateau stage. When an external magnetic field is applied, the G' of hydrogel remains unchanged at a low strain amplitude, and a small plateau appears. When the critical strain amplitude is reached, the G' decrease with the increase of strain amplitude, and the G'' increase firstly and then decrease with the increase of strain amplitude. In the case of low shear strain amplitude, the G’’ is higher than the G‘, which is in a viscoelastic state. When the strain amplitude exceeds a certain critical value, the G’ is lower than the G‘’, which is in a flowing state. Below the critical strain amplitude, the region in which the modulus value remains constant is called the linear viscoelastic region. While after the critical strain amplitude is exceeded, the G’ and the G’” decrease rapidly, which is called the nonlinear viscoelastic zone. With the increase of the magnetic field strength, the linear viscoelastic region of the hydrogel gradually decreases, and the nonlinear viscoelastic region gradually increases. The intersection points of the G’ and the G’” curves gradually shifts to left, in other words, the hydrogel would reach a flowing state under lower shear strain, exhibiting significant magnetorheological effect.

Figure 10(e) shows the dependence of the storage modulus and loss modulus for Fe₃O₄@GO/P(NIPAM-MAA) hydrogel on magnetic field strength. It can be seen that the G’ and the G’” of Fe₃O₄@GO/P(NIPAM-MAA) hydrogel both increase with the increase of magnetic field strength. Under the same strain amplitude, with the increase of the magnetic field strength, due to the polarization, the mutual attraction between the magnetic particles in the hydrogel increases, making the internal network...
structure more stable and exhibiting higher storage modulus. At the same time, in order to be able to change this network structure, the greater the energy required, that is, the loss modulus also increases.

**Demonstration of magnetic controlled spreading**

The magnetic control deformation simulation experiment was conducted on a plastic brain model (Figure 11) at 37°C. First, Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel solution was injected on the surface model (Figure 11a). During its transition from sol to gel, we applied an external magnetic field by two magnets, and then the hydrogel underwent significant deformation (Figure 11b). As the position of the applied magnetic field changes, the hydrogel continues to deform in all directions. After 120s, the sol-gel transition process was finished, and the morphology of the hydrogel was fixed (Figure 11c). It can be seen from the demonstration results that the deformation of the hydrogel can be actively controlled by applying an external magnetic field, indicating that the Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel has good magnetorheological properties.

**EEG Signals Acquisition Performance of the Hydrogel Electrode**

In order to verify the feasibility of the EEG signals acquisition test, a preliminary experiment was first carried out. Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel was injected into the CP5 and CP6 channels of the electrode cap. As a comparison, the wet electrode conductive paste was injected into the Pz channel, which main component was the conductive polymer carboxymethyl cellulose. When the electrode material was injected, the contact resistance of the two materials was within the allowable range (less than 20kΩ). Figure 12(a) illustrates the change curve of the voltage amplitude of the EEG signals collected by the hydrogel electrode and the wet electrode in the time interval of 20s. (b) Randomly selected 11-12s EEG signal recording. (c) Randomly selected 11-12s EEG signal recording.

The human brain has about 6.66×10$^4$ nerves per cubic millimeter, and the EEG signal has the characteristics of weak amplitude, strong randomness, and susceptibility to interference. Therefore, it is usually necessary to collect multi-channel signals at the same time when collecting EEG signals. In order to rule out chance, Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel was injected into 34 channels of the electrode cap to collect EEG signals in the whole brain. Taking FC1 channel as an example, Figure 13 shows the selected segment records of this channel every 0.5h during the whole test. It can be seen that the EEG data collected by the FC1 channel is relatively stable, and the voltage amplitude of the EEG signal is within 80μV. The average voltage amplitudes of the recorded EEG signals in the six time periods were 11.29, 11.71, 14.73, 23.28, 14.53, 17.35μV, and the signal basically did not attenuate. It shows that with the passage of time, the hydrogel can maintain good contact with the scalp, and the intrinsic impedance of the electrode and the quality of the recorded EEG signals have not changed significantly. However, the quality of the EEG signals recorded in the second half of the time is obviously not as good as the first half of the time, which may be due to the subject’s mental state of fatigue and restlessness during the long test process. Based on the change trend of EEG signals intensity recorded by FC1 channel over time, Fe$_3$O$_4$@GO/P(NIPAM-MAA) hydrogel can be used as an ideal BCI electrode material, which can meet the normal monitoring activities of brain-computer interconnection equipment.
The Signal-to-Noise Ratio (SNR) is used to characterize the quality and intensity of the collected EEG signals, and the SNR is defined by the ratio of the signal level to the noise level. Generally speaking, the larger the SNR, the better the quality of the collected and recorded EEG signals and the higher the intensity. For signals, calculate the peak-to-peak amplitude of the average waveform, and then take the average peak amplitude and record it as the signal level (A). For noise, the peak-to-peak amplitude of the average waveform is subtracted from the peak-to-peak amplitude of all waveforms, and the standard deviation is calculated from the result value. Two times the average standard deviation is recorded as the noise level (C). Figure 14(a)(b)(c) indicates the average peak amplitude, average noise amplitude and signal-to-noise ratio of the EEG signals during the entire recording period. Compared with wet electrodes, hydrogel electrodes have a higher average peak-to-peak value, but also exhibit higher noise levels. According to statistical calculations, during the entire recording period, although the average signal-to-noise ratio of the hydrogel electrode and the wet electrode are similar, at 1.21 and 1.20, respectively, the signal-to-noise ratio of the hydrogel electrode material is more stable. This indicates that the signal-to-noise ratio of the EEG signals recorded by the two electrode materials are similar. If the hydrogel electrode is used as a semi-invasive electrode, it would have a much higher signal-to-noise ratio, because the electrode is directly placed on the surface of cerebral cortex without the barrier of skull.

![Figure 13](image1.png)

Figure 13. FC1 channel selection record every 0.5h during the test. (a) Record at 0.5h. (b) Record at 1.0h. (c) Record at 1.5h. (d) Record at 2.0h. (e) Record at 2.5h. (f) Record at 3.0h.

![Figure 14](image2.png)

Figure 14. (a) Mean peak to peak amplitude over the entire recording period. (b) Mean noise amplitude over the entire recording period. (c) Signal-to-Noise Ratio over the entire recording period.

Conclusions

In this work, we demonstrated fabrication, characterization, and performance of a novel semi-invasive Brain-Computer Interface flexible electrode composite made from Fe₃O₄@GO and P(NIPAM-MAA) hydrogels. We found that the composite can transform from sol to gel at body temperature within 120s. The composite has significant magnetorheological property, enable us to control its expansion by applying a remote magnetic field during the gelation process. The gelled composite has interpenetrating three-dimensional porous network structure and low resistivity, which makes it provide an access channel for signal transmission. Compared with the non-invasive BCI electrodes, the electrode based on this composite is injectable and could actively expand on the surface of cerebral cortex, which makes it have higher signal-to-noise ratio and avoid the potential wrinkles and tangles of the electrode. While compared with the invasive electrodes, it would have greater security. The novel composite seems to be an ideal material for developing the next generation semi-invasive BCI electrodes with a good balance between the signal-to-noise ratio and security. To be sure, for non-invasive BCI electrodes, hydrogel electrodes could exhibit a higher signal-to-noise ratio. Obviously, the resolution of the hydrogel electrode is lower than that of the invasive BCI electrode. In any case, semi-invasive BCI hydrogel electrodes still have research prospects in some special applications. Semi-invasive electrodes have attracted widespread attention in the academic world due to their unique advantages such as low material cost, simple and efficient preparation, no irritation or sensitization and soon. However, concerning the semi-invasive electrodes, we need continue to explore the problems of precise positioning, smooth injection and intelligent controlled release. In addition, on the basis of full consideration of safety and ethical issues, we should continue to explore the semi-invasive way of collecting and recording EEG in the scalp using hydrogel electrode materials. In a nutshell, the research on semi-invasive flexible electrodes in various countries is still in its infancy and there are relatively few related reports. Anyway, with the increasing demands of BCI around the world, the development of such electrodes would make break through progress.

Author Contributions

Guangwei He; Methodology; Writing- Original draft preparation; Yu Tong: Rheology Analysis; Chi Zhang: EEG signals acquisition; BeiBei Xue: Testing; Xufeng Dong: Supervision, Conceptualization, Writing- Reviewing and Editing; Shouhu Xuan: Suggestions; Peixin Sun: Visualization, EEG signals acquisition; Min Qi: Validation, Supervision

Conflicts of interest

There are no conflicts to declare.

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