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Translation of a chemical reaction to electrical signal generation: An organic-inorganic complexation strategy

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A complexation strategy has been reported here by the addition of cysteine to the Cu(I)-polyaniline composite system, where cysteine was performed the role of a ligand. The in-situ electrical measurement of the complexation process exhibited a resistive switching behaviour with the ON-to-OFF ratio of $5 \times 10^2$ and followed the Ohmic and Poole-Frenkel emission mechanism for the low-conductance state and Ohmic behaviour for the high-conductance state, with the volatile resistive switching property. Further, the polyaniline stabilized copper sulfide nanoparticles, cysteine as sulphur source, based device exhibited the bipolar resistive switching behaviour where low conductance state was followed the Poole-Frenkel emission mechanism and the Ohmic mechanism was noticed for high conductance state. The device exhibited excellent endurance and retention capacity for $2 \times 10^3$ cycles with an average ON-OFF ratio of $10^4$, with a non-volatile resistive switching behaviour.

The interfacing of electronics with biology is significantly important as the soft nature of the biologically relevant organic molecules offer a range benefits including mechanical flexibility and compatibility with the physiological system.\textsuperscript{1} Substantial amount of research works have been reported where biomolecules are proposed as computing elements.\textsuperscript{2, 3} Some particular types of redox proteins demonstrated as electronic materials and performed as electron-transport junctions.\textsuperscript{4, 5}

Protein detection and quantification technique is applied for therapeutics, clinical diagnosis and treatment as well as research on cell signalling technology. There are different methods are available in the literature to detect protein molecules in different organisms. Enzyme-free colorimetric detection of α-fetoprotein has been reported by organic molecule modified quantum dots or metal-organic framework through signal generation and amplification technique.\textsuperscript{6, 7} Ferritin-based redox protein has been displayed memristive behaviour where hysteretic resistive switching effect was reported due to the electrochemical processes
occurring in the active centre of ferritin, Fe(II)/Fe(III). In the field of biomolecular electronics, Azurin, a bacterial blue copper protein, stands out as one of the most widely studied protein, where Cu-ion performed the key function as an electron transfer agent. Copper ion plays a crucial role in a physiological system and the interactions study between copper and organic ligands, with biological relevance, is considered as one of the most fertile pitches in multidisciplinary research platform. Copper, a redox-active element, in the form of zero-valent, uni-valent and bi-valent, serves the role as a catalyst and also act as structural co-factor of a wide range of biomolecules. Among the various biomolecules, proteins molecules are attracted tremendous attention for the integration in multi-functional molecular devices. On the other hand, amino acid, such as, cysteine with thiol-side chain often participates in enzymatic reactions, as a nucleophilic agent.

The cysteine-copper complexes perform a variety of functions in the biological, environmental, and medical fields. The formation constants of Cu-complexes with cysteine, based on thermodynamic model, confirmed that univalent copper-ion is predominant in blood plasma, aqueous humour and cornea of the human eye. The Cu(I)-cysteine complex also acted as a hole scavenging co-catalyst that influences the activity of CdSe for hydrogen production in the presence of visible light and also minimize the electron-hole pair recombination due to photo-excitation.

Translation from the chemical reaction to electrical signal generation is a well-established method in electrochemical sensing applications. In this communication, we report a typical complexation reaction between Cu(I) and cysteine, and the chemical reaction was in-situ translated in the form of electrical signal that exhibited a resistive switching effect. We have extrapolated the conventional sensing method by fabricating a metal-(active material)-metal type of device and studied the transport mechanism of the reaction between Cu(I) and cysteine. The reactant Cu(I) was synthesized using a previously reported method in the form of Cu(I)-polyaniline (CuP).

We have studied the electrical property of cysteine (Cys) and Cu(I) complexation reaction in the form of a device and the detail fabrication method is available in the experimental section. Figure 1A, inset, exhibits the graphical representation (semi-log) of current-voltage (I-V) behaviour of Cu(I)-polyaniline (Au-CuP-Au), D (I) and cysteine (Au-Cys-Au), D (II), based device when the voltage sweep were applied from 0 to +5 V, +5 to -5 V and -5 to 0 V directions. Figure 1A, main panel, shows the I-V characteristics, under the above-mentioned sweep conditions, when 5 µL of cysteine solution, with the concentration of 10, 30 and 60 mM, was
added individually to the three sets of devices D (I), in the form of droplets at the boundary position of the top electrodes, represented by D (Ia), D (Ib) and D (Ic), respectively.

The change of I-V behaviour indicates the complexation process took place between Cu(I) and cysteine. The formation of Cu(I) complexes with cysteine is well documented in the literature. In the case of D (Ia), the I-V characteristic exhibited a deviation from D (I) but without proper resistive switching, while the devices D (Ib) and D (Ic) exhibited the resistive switching with the ON-OFF ratio of $5 \times 10^2$ and $\sim 10^1$, respectively. For the devices, D (Ia) and D (Ic), the conductivity values are close to the devices made with CuP, D (I), and cysteine, D (II), respectively, due to the incorporation of low and high concentration of cysteine to the device, D (I). For the rest of our study, we will consider the current-voltage characteristic of the device, D (Ib), where the maximum ON-OFF ratio ($5 \times 10^2$) was achieved.

The device, D (Ib), exhibited two SET processes (the process of transferring the device from the low conductance to high conductance state) at 2.2 and 3.0 V, during the sweep direction from 0 to +5 V and the RESET process (the process of transferring the device from the high conductance to low conductance state) was noticed at 0.9 V, during the sweep direction from +5 to -5 V. Similarly, the device exhibited two SET processes at -2.3 and -4.0 V and RESET process at -1.1 V on the other side of the I-V plot. The entire I-V plot demonstrate a unipolar behaviour with symmetric ‘S’ type in nature.

During the voltage sweep from 0 V to 5 V, steady improvement of the current value has been observed within the voltage range from 0 to 2.2 V. At 2.2 V, a sudden improvement of current value can be explained in terms of an establishment of a transition state that results the increase of reduction potential value of Cu(I). Further increase of voltage, influences the reduction of Cu(I) with the formation of atomic copper and at the potential value of 3.0 V, when sufficient numbers of atomic copper were formed, the device exhibited a complete SET process. For the voltage sweep from +5 V to -5 V, a steady decrease of the current value has been observed within the voltage range from +5 to 0.9V, presumably due to slow oxidation of copper atom. A subsequent sharp current fall (RESET) at 0.9V indicate the majority of copper atoms were oxidized and converted to Cu(I). The left-hand side of the I-V plot also validities a similar mechanism. The current-voltage characteristics of the device, D (Ib), followed the ohmic mechanism within the range from 0 to 2.2 V (OFF-state), figure 1B. Initially, small number of electrons were generated at the electrode-[Cu(I)-CYS] interface and under the influence of potential the mobility of the electrons attributed to the Ohmic conduction, where the current is proportional to the electric field with the slope value of 0.99. As already mentioned, further
increase of voltage (from 2.2 to 3.0 V) influences the reduction of Cu(I) with the formation of atomic copper followed by the copper nanoparticles. The voltage ranges from 2.2 to 3.0 V (OFF-state), figure 1B (inset), the electrons can move slowly through the matrix and trapped on copper nanoparticles. With increase of electric field, the electrons migrate from its localized state, and move to the conduction band and the transport behaviour was followed by Poole-Frenkel emission mechanism, \( \ln \left( \frac{I}{V} \right)^\alpha \propto V^{0.5} \). The presence of such type of two conduction mechanisms dominating at different bias voltage regions have been reported earlier at low conductance state. Highly oriented ZnO thin film exhibited the Ohmic behaviour and Poole-Frenkel emission at low- and high field region for low conductance state. In a similar fashion, thin film of Gd:SiO\(_2\)-based device under illumination condition exhibited the Ohmic behaviour at low-field region and Poole-Frenkel emission at the high electric field region for the low conductance state.

The formation of two SET-type characteristics at 2.2 and -2.4 V (figure 1A, within the box) in both sides of the current-voltage graph presumably due to the initialization process of atomic copper formation. For the ON-state, within the potential range from +5 to 0.9 V, the transport mechanism was influenced by Ohmic behaviour with the slope value of 1.10.

The memory behaviour of a device mainly depends on the endurance, and re-writable properties. For the endurance study, -2 V pulse train (50% duty cycle) was employed to the device D (Ib), as shown in the figure 2A (inset). The device exhibited a stable OFF-state within the experiment cycle number of \( 2 \times 10^3 \), whereas the ON-state demonstrated a dilapidation after \( 10^3 \) cycles, and the device behaved like volatile in nature. To investigate the ability of the device for differentiating low conductance state \( (R_0) \) from the high conductance state \( (R_1) \) after erasing and writing process, respectively, the Write-Read (1)-Erase-Read (0) \( (WR_1ER_0) \) cycle was designed (supporting information, figure S1). The device D(I) was subjected to the \( WR_1ER_0 \) cycle and not showed any difference between the \( R_1 \) and \( R_0 \) states in terms of current value, figure 2B, zone (a). On addition of cysteine (5 µL of 30 mM), after certain amount of buffer period (figure 2B, buffer zone), the device demonstrated the difference in current between \( R_1 \) and \( R_0 \) with the value of 6 µA, figure 2B, zone (b), which indicate that the complex system has the ability to identify Read (1) and Read (0)-states, noticeably.

In a separate experiment, we have synthesized polyaniline stabilized copper sulfide nanoparticles (PACS) using cysteine as sulphur source (detail synthesis protocol is available in the experimental section). The fabrication of polyaniline stabilized copper sulfide nanoparticles is a two-step process. The first step involved with the formation of CuP between...
the reaction with copper sulphate and aniline, and the second step is the complexation between Cu(I)-polyaniline and cysteine. The second step is a slow process, involved with complexation and formation of transition state that ultimately forms copper sulfide nanoparticles, encapsulated within the polyaniline matrix. Synthesis of metal sulfide using cysteine as a sulphur source is well documented in the literature. The PACS based organic-inorganic hybrid system was used as an active material for resistive random-access memory application. The detail device fabrication method is available in the experimental section. The device made with PACS (Au-PACS-Au) was subjected to the voltage sweep from 0 to +5 V, +5 to -5 V and -5 to 0 V direction and the current response was plotted in the figure (3A). During the voltage sweep from 0 to +5 V the device exhibited the SET process at 3.8 V, whereas the RESET phenomena was noticed at -3.3 V during the voltage sweep from +5 to -5 V direction. The device showed a stable OFF-state behaviour during the voltage sweep from -5 to 0 V. The current-voltage characteristics of the device exhibited the bipolar resistive switching behaviour with an asymmetric ‘S’ type character. To realize the transport property of the device, the current-voltage graph was fitted with different theoretical models for both low conducting (OFF) and high conducting (ON) states. Figure 3B exhibited the I-V characteristics, where the low conductance state was followed the Poole-Frenkel (PF) emission mechanism, \( \ln \left( \frac{I}{V} \right) \propto \sqrt{V} \) and the high conductance state was fitted with Ohmic conduction mechanism, \( \ln (I) \propto \ln (V) \), with a slope of 1.14. Initially, the electrons were trapped and localized on polyaniline matrix and under suitable potential the trapped electrons were released and passed through various density of states of the valence band (OFF-state). Under suitable potential, the valence band electron jumped to the conduction band of copper sulfide and the transport property of the conduction band electrons was followed by ohmic mechanism (ON-state). Figure 3B, inset, represents the TEM image of the polyaniline stabilized copper sulfide nanoparticles, where the dark spots are the copper sulfide (Cu₂S) nanoparticles within the range of 5-10 nm, dispersed in the polymer matrix.

To determine the endurance property of the device, a pulse train was applied, as mentioned in figure 2A, inset, and the device exhibited excellent endurance property for \( 2 \times 10^3 \) cycles with an average ON-OFF ratio of \( \sim 10^4 \) (figure 3C). To extract the retention behaviour (ability of the device to retain its state in absence of refreshing power supply) of the device, a pulse train consisting of -2 V for 0.1 sec with the time interval of 60 sec (supporting information, figure S2) was applied and the device exhibited excellent retention capacity for \( 2 \times 10^3 \) sec, figure 3C,
inset, with an average ON-OFF ratio of $10^4$. To study the electrical rewritable property of the device (Au-PACS-Au), WR$_1$ER$_0$ cycle was designed, as shown in the supporting information, figure S3. The graphical representation (figure 3D) of the electrical rewritable property displayed the difference of current value (78 µA) between $R_1$ and $R_0$. The above study demonstrated that the nonvolatile type of memory has been achieved when the stable form of PACS type of organic-inorganic hybrid system was applied as an active material for the metal-insulator-metal type of device.

In summary, we have decoded a chemical complexation process in the language of electrical signal using an example of Cu(I)-cysteine system. For the in-situ experiment, due to the dynamic nature of the complexation process the resistive switching performance of the device showed volatile behaviour, whereas in a stable system (formation of the copper sulfide nanoparticles after completion of the reaction between Cu(I) and cysteine) the device displayed a nonvolatile performance with higher ON-OFF ratio. The proposition of the transport mechanism of a chemical reaction is the main emphasis of this kind of study.

**Experimental section:**

**Device fabrication and electrical characterization:**

Glass slide supported flexible paper was used for the device fabrication, where the role of the slide was to provide the mechanical strength. The active material, Cu(I)-polyaniline / cysteine / PACS, was dispersed in the form of a thin film with the thickness of ~5 µm on the previously deposited bottom electrodes (gold) on the flexible paper. After proper drying, the top gold electrodes were deposited in a crossbar fashion and a sandwich structured device was fabricated, Au-CuP-Au, D (I) / Au-Cys-Au, D (II) / Au-PACS-Au. The bottom electrode was connected to the high voltage terminal whereas the top electrode was connected to the ground terminal of the electrical characterization unit. The current-voltage (I-V) measurement was performed with 0.17V/s scan rate and 0.1V step size. Keithley 2401 and 2612B source meter was used for the electrical characterization.

**Synthesis of polyaniline stabilized copper sulfide nanoparticles (PACS):** In a typical experiment, 0.093 g of aniline ($10^{-2}$ mol dm$^{-3}$) was dissolved in 10 mL methanol. To this solution, 0.250 g of CuSO$_4$. 5H$_2$O in 10 mL of water ($10^{-2}$ mol dm$^{-3}$) was added slowly under continuous stirring conditions. During the addition, the solution took on a green colour, while at the end, a greenish precipitation was formed, indicates the formation of Cu (I)-polyaniline composite at the bottom of the conical flask. To this reaction mixture 5 mL of cysteine ($10^{-1}$
mol dm$^{-3}$) was added and allowed to stir for 12 h. Entire reaction was performed under ambient condition. The dark brown precipitate material was allowed to settle for 30 min and collected through filtration technique. The solid mass was dried under vacuum and applied as an active material for the device (Au-PACS-Au). The X-Ray diffraction and X-ray photoelectron spectroscopy characterizations are supplied in the supporting information, figure S4 and S5, respectively.

**Conflicts of interest**

There are no conflicts to declare.

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Figure Caption:

Figure 1: (A) The current-voltage (semi-log) behaviour of the devices, D (Ia), D (Ib) and D (Ic), after the addition of 5 µL of cysteine solution with the concentration of 10, 30 and 60 mM, respectively. Inset figure represents the I-V behaviour of D (I) and D (II). (B) The transport mechanism of the D (Ib) was fitted with the ohmic and PF for the OFF-state and ohmic for the ON-state (inset: The graphical representation of the PF region).

Figure 2: (A) The endurance study of the device D (Ib) for $2 \times 10^3$ cycles. Inset figure shows the pulse train condition for the endurance study. (B) The electrical rewritable property of the device D (I), before and after addition of cysteine.

Figure 3: (A) The current-voltage characteristics of the device Au-PACS-Au, in semi-log form. (B) The transport behaviour was fitted with Poole-Frenkel (PF) emission and Ohmic conduction mechanism for low and high conductance state, respectively. The inset figure shows the transmission electron microscopic image of polyaniline stabilized copper sulfide nanoparticles, where the dark spots are the copper sulfide nanoparticles. (C) The endurance study of the device (Au-PACS-Au) for $2 \times 10^3$ cycles. Inset figure shows the retention (nonvolatile) study of Au-PACS-Au device for $2 \times 10^3$ sec. (D) The electrical rewritable property of the Au-PACS-Au based device.
Figure: 3

A. Voltage (V) vs. Current (A)

B. In(V) vs. In(I)

C. ON-OFF ratio vs. Time (s)

D. Current (A) vs. Pulse Number

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