



Review Article

# Review on Structure, Properties and Appli-ance of Essential Conjugated Polymers

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## Abstract

One of the important classes of polymers is conductive polymers. These polymers mainly comprise of aromatic and aliphatic backbone. Polyaniline is one of most important type of conjugated polymers due to its excellent conductivity and other essential physical properties. Consequently, main focus of this review is structure, properties and application of technically important conjugated polymer. The conducting polymers such as polyaniline, polythiophene, polypyrrole, polyacetylene and pol(*p*-phenylene) have been discussed. Conductive polymer offers significant conductivity values similar to that of metal and semiconductors. Finally, the uses of polymers in different technical fields such as sensors, rechargeable batteries, photovoltaics, and fuel cells have been conversed.

**Keywords:** Conducting polymer; Polyaniline; Conductivity; Sensor

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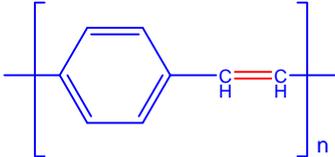
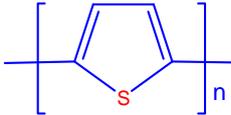
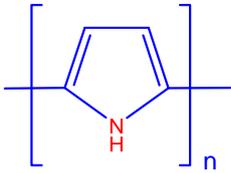
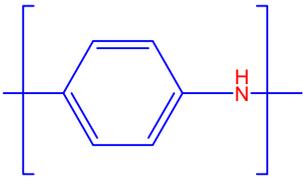
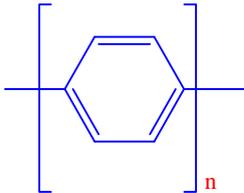
## 1. Introduction

During the past decade, nanotechnology has become an active field of research because of tremendous potential for a variety of applications [1]. There are mainly four types of nanostructures i.e. zero-, one-, two- and three-dimensional structures. Among them, one-dimensional (1D-) nanostructures have been the focus owing to their unique physical, chemical, and electronic properties in nanoscale systems. The second characteristic of 1D-nanostructure is its device function, which can be exploited as device elements in many kinds of nano-devices [2, 3]. Conducting polymer discovery is remarkable in its completion as possible substitute for semiconductors and metallic conductors. The struggle for having tailor-made polymer with reference to its mechanical, electrical, thermal, and optical features have been followed by numerous research groups [4]. Consequently, recent understanding and state of art of conducting polymer (based on aromatic system) would be highly necessary and thus inspired dedicated researchers in this field [5]. The progress in conducting polymers with conductivity equal to that of metals and semiconductors are shown in Table 1. Conductive polymers related to polyaromatics or polyenes mainly polythiophene, polythiophene, polypyrrole, poly(p-phenylene), poly (phenylene vinylene) class have been widely studied [6]. Polyaniline is of main interest among family of conjugated polymers due to its outstanding conduction mechanism and good environmental stability in the presence of water and oxygen. Polyaniline is also one of most conductive polymer. The decade of 70s witnessed evolution of various conductive polymers. However, these polymers show poor solubility in most of common solvent. They also have low thermos-plasticity, which reduced processing of conductive polymers research for preparation of soluble forms of conductive polymer [7].

## 2. Conjugated Polymer

Conducting polymer discovery and doping capability over full range of insulator to metals resulted in generation of new category of material with combined electrical, optical, and electronic properties, and mechanical features [8]. Furthermore, the capability to control electronegativity and electronic features by molecular design has made conducting polymer considerable. Conductive polymers are plastics that have ability to conduct electricity just as semiconductors and metals [9]. The prolonged  $\pi$ -orbital of conjugated polymer result in quasi-one dimensional electronic structure with related new non-linear excitations (polarons, solitons, bipolarons). The excellent combination of electrical, electronic, mechanical and electrochemical features of these semiconductors and synthetic metals have made them excellent candidates. The capability to control their features with rational chemical synthesis have made conjugated polymers a potential field of interdisciplinary research [10]. A new class of materials which demonstrate highly reversible redox behavior and strange deal of properties of metal and plastics are conductive polymers. Conducting polymers was first synthesized in 1960s as they are the most current invention in polymers. Conducting polymers have both optical and electrical properties related to those of metals and inorganic semiconductors. The potential benefit of conductive polymers with effective relevance in number of growing technologies (telecommunication, biomolecular electronics, display devices, and electrochemical storage systems) have been considered [11]. Polymers with freely held electrons in their backbones are frequently recognized as conducting polymers. Each atom beside the backbone has  $\pi$  bond, which is much weaker than  $\sigma$  bonds holding atoms in polymer chain together. First formed several decades ago, there are more than 25 conductive polymers known today [12].

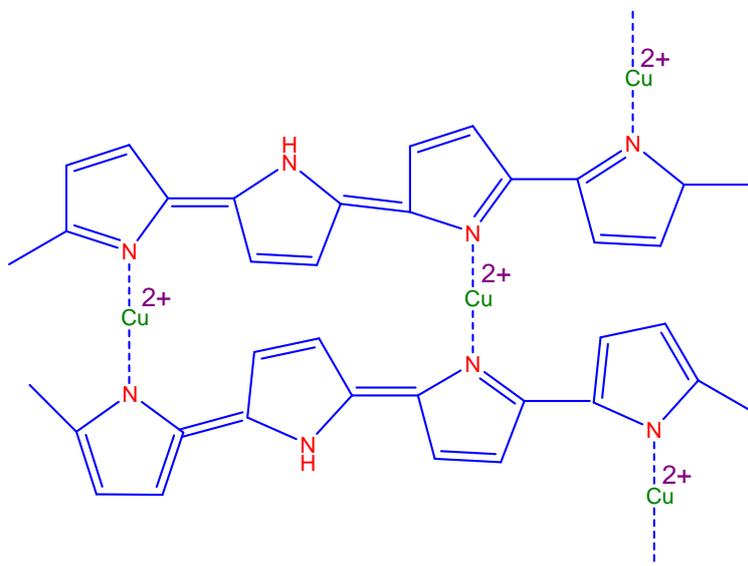
**Table 1** Conductivity of some conjugated polymer.

| Conducting polymer        | Conductivity (S/cm) | Structural formula   |
|---------------------------|---------------------|--|
| Poly(phenylene vinylene)  | 1                   |    |
| Polythiophene             | 200                 |    |
| Polypyrrole               | 600                 |    |
| Polyaniline               | 10                  |  |
| Polyacetylene             | 5                   |  |
| Poly( <i>p</i> -henylene) | 500                 |  |

### 3. Structure and Properties of Conjugated Polymer

The superior values of the electrical conductivity achieved in such organic polymers have led to the name 'synthetic metals'. Various applications of conducting polymers comprising biosensing devices and analytical chemistry have been developed [13]. Conducting polymers exhibit  $\pi$ -electron backbone which have strange electronic features such as low energy optical transitions, electrical conductivity, low ionization potential, and high electron affinity. This comprehensive  $\pi$ -conjugated system of the conducting polymers has irregular single and double bonds all along the polymer chain and their conductivities and structures [14]. In 1977, the discovery that polyacetylene could be easily oxidized

(by electron acceptors) or reduced (by donors) was a breakthrough in the area of conductive polymers. Nowadays, conductive polymers are promising basis of number of new technologies comprising plastic electronics. These polymers are important in determining device performance [15]. The surface modification of conventional electrodes provide new and fascinating features. They are useful in membrane separations, electro catalysis and chromatography. They also generate new technological potentials in design of biochemical and chemical sensors [16]. Polyaniline (PANI) is an essential member in the family of inherently conductive polymers (ICPs). PANI has been considered due to ease of synthesis, good environmental stability, and comparatively good processability. Due to its electronic, chemical and optical features, it has gained enormous interest. Thus it signify well-organized class of conductive polymers in materials science [17]. The electrochemical oxidation of aromatic benzenoid, heterocyclic, or non-benzenoid molecules habitually lead to the development of electrically conducting organic polymer film at the electrode surface. These films usually have excellent electrical contact and adhesion to electrode surface. Thin films, when supported by an electrode surface, can be electrochemically cycled between the conducting state, oxidized, neutral, and insulating state. Thicker films can be produced in the conducting state oxidized, and can be peeled off from the surface of electrode to give free-standing, electrically conducting films [18]. Because these films are in the oxidized state, they signify polymeric cations, whereas their whole charge balance is obtained by integration of oppose anions from electroplating solution [19]. According to this approach, conducting films have now been formed from broad range of organic molecules. These comprise heterocyclic compounds such as thiophene, pyrrole, indole, furan, carbazole, and thianaphthene. Conducting polymeric films have also been generated from polycyclic nonbenzenoid and benzenoid hydrocarbons such as fluorene, azulene, fluoranthene, pyrene, and tri-phenylene [20].



**Fig. 1** Ion exchange mechanism by coordination chemistry.

### 3.1. Polyaniline

Polyaniline (PANI) is one of most extensively studied conducting polymers due to its strong bimolecular interaction, superficial synthesis, existing electrochemical, electrical and optical features. Due to outstanding tuneable conductivity either by charge transfer doping and protonation, it holds great potential in comparison to other conducting polymers [21]. Due to its low synthetic cost, and outstanding thermal and environmental stability, it is most extensively studied conducting polymer.

There are three main forms of PANI, namely the fully oxidized (pernigraniline) state, fully reduce (leucoemeraldine) and the more conducting emeraldine base (half oxidized). Thus by doping to form emeraldine salt, emeraldine is most conductive form. Polyaniline can be easily synthesized either electrochemically or chemically from acidic aqueous solutions. The chemical route has great importance because it is sensible route for PANI mass production. Thus, the most common synthesis route is the oxidative polymerization with ammonium peroxodisulfate as oxidant [22]. Polyaniline is ranked among the most studied conducting polymers. Besides its electrical features, catalytic, optical, electrochemical, and surface features have been considered. However, in the typical approaches, PANI is synthesized from aniline, oxidant, and small molecule. It has very poor solubility in common solvents such as ethanol, methanol, and acetone. PANI nanostructures with large interfacial areas between PANI and their surroundings can have an enhanced dispersibility in the hosting matrixes [23]. Ion exchange mechanism in polyaniline is shown in Fig. 1.

### 3.2. Polythiophene

Polythiophene (PTh) is of growing interest among conducting polyheterocycles prepared from five-membered heterocycles because of excellent stability to moisture and oxygen [24]. Polythiophene has been synthesized by both chemical and electrical polymerizations. By electrochemical polymerization route, highly conductive PTh with conductivity ranges between 10-100 S/cm, have been achieved. Although, the chemical polymerization route generates less conductive black powder. It has significances mainly simple procedure, short reaction time, and easy processing. The most extensively used chemical oxidative polymerization is Grignard coupling of 2,2' -diiodothiophene, 2,2' -dibromothiophene or three methyl thiophene in presence of initiator and consequent doping of obtained polymer with suitable oxidant [25]. The polymer conductivities thus achieved ranges between 0.1-1 S/cm. A one step chemical polymerization and thiophene doping have been achieved by employing AsF<sub>5</sub> as oxidants. The conductivity of the polymer was  $2 \times 10^{-2}$  S/cm which is three order of magnitude smaller than those of electrochemically prepared PTh. The reaction of 2,2' -bithiophene (BT) with copper percholate or iron percholate give both doping and oxidative polymerization [26]. The obtained PTh have outstanding conductivity in the range of 3-17 S/cm.

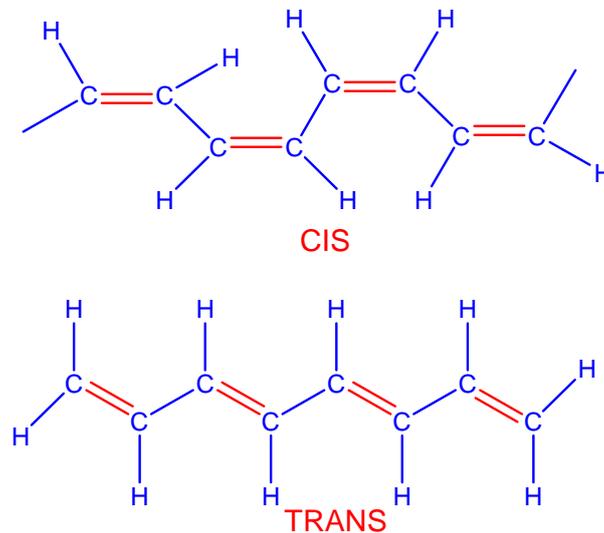
### 3.3. Polypyrrole

One of the most widely used polymer is conductive polymeric view of bioanalytical sensors. Due to easy synthesis and processing of polypyrrole (PPy), good conductivity and better cyto-compatibility are seen. For biomedical applications, doped PPy have been explored for biomedical applications mainly biosensors, and tissue engineering applications. PPy can be synthesized by electrochemical or chemical method by varying advantages. The electrical conductivity of PPy can be improved from  $10^{-12}$  to  $\sim 10^2$  S/cm depending on extent and type of doping [27]. The electrons in monomers are attracted to nuclei in neighboring monomers to generate mobility between the chain and along chain, generating conductivity in PPy. Its conductivity can be enhanced with doping ratio and percentage vary with preparation route and dopant [28, 29].

### 3.4. Polyacetylene

The simplest conjugated polymer is polyacetylene. It comprises weakly coupled chain of CH monomers forming pseudo-one-dimensional lattice. Three out of four valence electrons are in  $sp^2$

hybridized orbitals. Two  $\sigma$ -type bond forms 1-d lattice while with hydrogen side group forms three  $\sigma$ -bond. The bond angle of  $120^\circ$  between the three electrons can be fulfilled through two possible arrangements of carbons trans  $-(CH)_x$  and cis  $-(CH)_x$  with two and four CH monomers per unit cell (Fig. 2). The remaining valence electrons in either isomer have symmetry of  $2p_z$  orbital with charge density of lobes perpendicular to planes defined by other three. In terms of energy band description, the  $\sigma$ -bonds form low lying completely filled bands, while  $\pi$  bond led to partially filled energy band structure responsible for significant electronic features. The bond length of all are equal.



**Fig. 2** Polymer chain structure of cis and trans  $-(CH)_x$ .

Thus quasi-1-d metal is obtained from pure trans  $-(CH)_x$  with half-filled band. Such system is unstable with reference to dimerization alteration (Peirls instability) [30, 31]. The movement of neighboring CH group occur towards each other forming alternatively long (for single) and short bond (for double). Thus, energy of system is lowering. Generally, one could interchange single and double bond by symmetry disagreement without effecting in energy. Thus there are two lowest energy states, L and R having two perspective bonding structures. This two-fold degeneracy lead to presence of nonlinear topological excitation bond-alternation domain walls or solitons, which appear to be responsible for several remarkable properties of  $(CH)_x$  [32].

### 3.5. Poly(*p*-phenylene vinylene)

The first conjugated polymer displayed to exhibit electroluminescence is poly(*p*-phenylene vinylene) (PPV). It has excellent temperature stability and is intractable. PPV is thermally stable above  $400^\circ\text{C}$  (up to its decomposition temperature) in absence of chemical species mainly oxygen [33, 34]. The presence of (poly-electrolyte) precursor route permits solution processing at high solution viscosity at low solid content. Techniques mainly blade or spin coating of precursor polymer utilized to achieve thin films which results in thick and pin hole free films of PPV [35]. Light emitting polymer (LEP) are formed by precursor coating on substrate such as indium-tin-oxide (ITO) coated glass monitored by thermal conversion to PPV and final cathodic deposition. The layers of polymer thickness ranges in order of 100 nm in such LEP devices. Thus, PPV polyelectrolyte precursor was developed that comprises of random copolymer with side groups containing acetate and tetrahydrothiophenium

groups with bromide counter ions and mixture of methanol/water as solvent [36, 37].

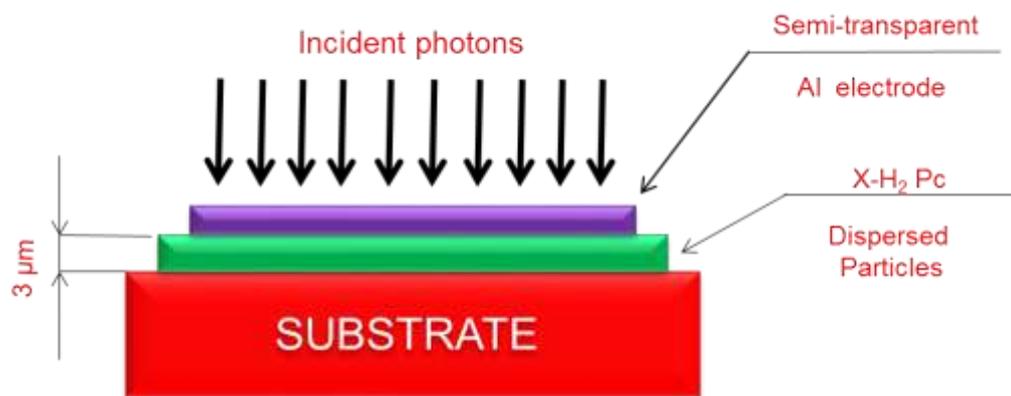
## 4. Application of Conjugated Polymer

In last couple of years, polymer-based electronics has become one of fascinating field with applications comprising of polymer light-emitting diodes (PLEDs), photodiodes, and transistors (Table 2). Although, polymer is employed as active layer in most cases or as thin buffer layers on inorganic conductor mainly indium tin oxide (ITO) and metal electrodes [38]. The aim is to develop large area, low cost, and flexible electronic devices based on polymer processing and deposition route. A basic example of application for such technology would be found in energy conversion of photovoltaic based on solar energy. Here, the chief attraction of polymer photovoltaic cell has been found in low cost and easy processing [39, 40].

**Table 2** Applications of conducting polymer in device.

| Conductive Polymers  | Device Applications  |
|--|--|
| Polythiophene and substituted polythiophene                  | (i) Electrochemical capacitors<br>(ii) Microlithography<br>(iii) Electroluminescence<br>(iv) Corrosion inhibitors<br>(v) Cathode material for battery            |
| Polyaniline and substituted polyaniline                      | (i) Rechargeable battery<br>(ii) Sensors<br>(iii) Photolithography<br>(iv) Corrosion inhibitors<br>(v) Electrochemical capacitors<br>(vi) Electrochromic display |
| Poly(p-phenylene) (PPP)<br><i>p</i> -phenylenevinylene (PPV) | (i) Photoconductors<br>(ii) Laser material<br>(iii) Electroluminescence<br>(iv) Solar energy cells   |
| Polypyrrole and substituted polypyrrole                      | (i) Photolithography<br>(ii) Electroluminescence<br>(iii) Electrochromic display<br>(iv) Rechargeable battery<br>(v) Sensors<br>(vi) Corrosion inhibitors        |

Solar cell composed of polymer film containing sensitizer is shown in Fig. 3. Polyaniline is one of capable conducting polymer for sensors. It is highly sensitive to vapors because of its conductivity. A common platform of device for construction of such sensors is chemiresistor. In characteristic polyaniline chemiresistor, thin film of polyaniline is usually coated by drop casting or spin coating on electrodes as sensitive layer for chemical vapors. On introduction to chemical vapors, a change in film resistance can be readily recorded by computer controlled circuit. The potential of such chemiresistor is determined by interaction between polymer and chemical vapors [41]. Polypyrrole with band gap of about 2.0 eV in its neutral state appeared to be good photoconducting candidate, since comprises strong intrinsic absorption in visible range. Generally, no severe influence has been made in observing/attempting of photoconductivity of polythiophene. Although, it has been reported that such films are quite insensitive to moisture and air, which is the most serious problem influencing the performance of photoconductor. Electrochemically produced polypyrrole films with band gap of 3.2 eV, after sensitization with one of above mentioned route, can be expected to exhibit excellent photoconductivity. The doping influence of on photoconductive device made up of poly p-vinylene (PPV) has been studied [42]. In electrographic applications, electrochemical polymerization route can be found to have significant in the sense that photoconducting polymer can be mold on metallic object of any shape. The grouping of liquid toner and photoconductor comprising charged particle suspended in an organic medium together with counter electrode gives a display device and electrophoretic image storage.



**Fig. 3** Solar cell composed of polymer film conducting sensitizer.

It was found that the arrangement is very similar to electronic setup defined with only difference in suspended charge particle. Such applications for electrochemically polymerized semiconducting films appear to be relatively feasible. Since, one of the most heterocyclic polymers have an intrinsic band gap in visible range [43]. On background of present day energy problems, solar cells have gained much of interest as alternative energy source because of its abundance and non-depleting/non-polluting nature. Photovoltaic conversion has gained extensive interest among several methods of solar energy conversion because of its potential capability to provide cheap electricity in non-transporting units. The recent development in electroactive polymers, as new class of semiconducting materials, has generated remarkable interest in fabrication of polymer-based solar cells. Photovoltaic devices based on conjugated polymer/ $C_{60}$  heterojunctions have been investigated by utilizing polymers such as poly 3-alkyl thiophene ( $P_3AT$ ), MEH-PPV [44]. Conducting polymers because of their electronic abilities are excellent candidate as cathode in rechargeable batteries. They

have various significance such as processability, ease of manufacture, low cost and light weight. In 1981, research finding on polyacetylene lithium battery was reported [45]. Solid-state batteries are also possible to make employing  $(CH)_x$ . Some of these type of batteries has been fabricated. Conductive polymers have long life, rechargeability, current density up to  $50 \text{ mA/cm}^2$ , and energy density of  $10 \text{ Watt-h/kg}$ . Lithium ion batteries are especially important among all the batteries since they have high discharging voltage [46-51]. General setup for electrochemical polymerization is shown in Fig. 4. Moreover, polymer composite electrolyte having fine electrical and mechanical characteristics has been utilized in rechargeable polymer lithium ion batteries because of stability towards environmental factors [52-58].

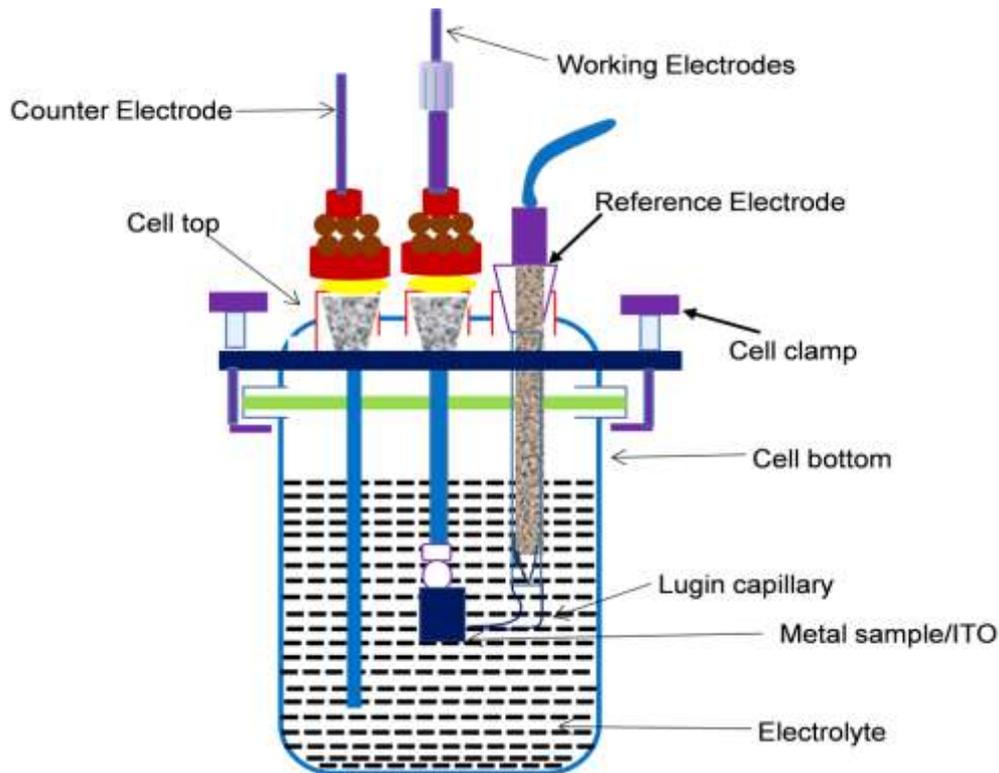


Fig. 4 General setup for electrochemical polymerization.

## 5. Conclusion

In this review, different types of conducting polymers have been discussed. Polyaniline is one of most studied and employed conducting polymer. The type of conducting polymers discussed are polypyrrole, polyaniline, polythiophene, poly (*p*-phenylene), and polyacetylene. Consequently, they have structure similar to that of metals and semiconductors. Due to superior electrical conductivity, organic polymers are also named as synthetic metals. The conducting polymers have extensive applications in numerous technical fields such as fuel cells, rechargeable batteries, sensors, and photo-electrodes.

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