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Review

Molecules, semiconductors, light and information: Towards future sensing and computing paradigms

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ABSTRACT

Over the last few years we have witnessed a great progress in the research devoted to unconventional computing – an unorthodox approach to information handling. It includes both novel algorithms and computing paradigms as well as completely new elements of circuitry: whole organisms (e.g., *Physarum* species), DNA, enzymes, various biomolecules, molecular and nanoparticulate materials. One of the biggest challenges in this field is the realisation of *in-materio* computing – i.e., the utilisation of properties of pristine materials, instead of high-tech structures – for advanced information processing. In this review we present recent achievements in the design of logic devices (binary, ternary and fuzzy) implemented in molecular and nanoscale components, photoelectrochemical chemosensing, photoactive memristive devices and reservoir computing systems. A common denominator for all these devices is the involvement of molecular species, semiconducting nanoparticles and light in information processing.

Contents

1. Introduction

In the 21st century information is one of the most valued goods. It is being collected, transmitted, stored, and encrypted using the most sophisticated techniques. Information is a notion that defies simple definitions. In the most general terms it was described by Norbert Wiener "Information is information, not matter or energy" [1]. It has been agreed, however, that information cannot exist without a carrier (matter or energy) [2]. In this review we will focus on various information carriers in the nano-world: ions, molecules, nanostructures, and their participation in simple acts of information processing, which utilise energy in the form of light and electric potential. This field, at least in the area of the binary

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logic, is highly advanced [3–7], however other logical systems are underrepresented in at molecular scale [8–14]. Information can be processed at different abstraction levels: syntactic, semantic and pragmatic. The syntactic level describes the formal relations between elements of the language and is necessary for automated information processing (e.g., as a stream of zeros and ones). At this level of complexity any meaning of transmitted or processed information is neglected. At the semantic level the stream of symbols becomes a message. Still, it can be handled and stored without any context and irrespectively of its pragmatic value. At the pragmatic level the context is introduced, which gives information its practical value (of economical, psychological or political character) that depends also on time. Usually delayed information is less valuable and correct predictions of near future are of the high value [15].

The classical approach to information processing is based on the Boolean logic [16]. All information to be transmitted, stored or processed is encoded as a stream of '0' and '1' characters. Due to its simplicity the technology is very efficient and noise resistant. At the same time its use poses severe conceptual problems and requires additional steps of conversion into a digital signal. In many cases it is seamless, but there are numerous problems that can be easily solved with the use of multi-valued logic systems. One of the examples is the SQL (structural query language) which uses the ternary logic for processing of incomplete sets of data [17].

The fuzzy logic may be perceived as a generalisation of any discrete logic system. The principal objective of the fuzzy logic is the formalisation of typical human information processing capabilities: (i) reasoning in imprecise environment on the basis of incomplete or uncertain information and (ii) performing complex physical and mental tasks (walking, driving, playing musical instruments and writing review papers) without any numerical measurements and computation [18]. This is beneficial for any systems which include a user/machine interface.

The neuromorphic computation has emerged as a relatively well-defined paradigm for the type of computation described above. A natural candidate for the realisation of the neuromorphic computation is an artificial neural network. The reservoir computing branched off from these developments, and matured into a subset of techniques for neuromorphic computation [19–23]. A reservoir computer consists of two components, a dynamical system that serves as a reservoir of states, and a readout layer. In very simplistic terms, the reservoir computer can be seen as a finite state automaton that accepts time series data as an input, and makes transitions between the internal states of the reservoir, accordingly. The readout layer is used only to access the results of computation. The key idea behind this construct is that one never tries to carefully engineer the reservoir part, only the readout layer. The reservoir computing technique has been used for plethora of applications in health [24], bridge monitoring [25], optical pattern recognition [26], or other types of control systems that exploit machine learning techniques [26–28]. The method has also found an extensive use in the area of sensing [29–39], as will be discussed later. A generic theory of using reservoir computing for sensing, the SWEET sensing algorithm, has been recently developed [40].

2. Photoelectrochemical sensors

The first phase of the sensing process gives us merely syntactic knowledge about the sensor response to the state of environment, without any significance (semantics) or value (pragmatics). In order to determine the value of the information obtained, it is necessary to place it in the previously established semantic frame – in the case of photoelectrochemical (PEC) sensor devices our framework takes the form of a calibration curve with specified precision of obtained photocurrent amplitudes in regard to analyte concentrations [41,42].

In most cases, PEC sensors are implemented in a three-electrode system, and the mechanism of operation is based on the internal photoelectric effect of a semiconductor-based working electrode (assembled on a conducting substrate), coupled with a reference electrode (e.g., saturated silver chloride or saturated calomel electrodes) and a counter electrode (e.g., platinum wire), all in the presence of electrolyte containing donor D/D^+ and acceptor A/A^- species. Photogenerated charge carriers from the semiconductor can move to the conducting substrate or to the counter electrode (with corresponding oxidation/reduction of donor (D/D^+)/ acceptor (A/A^-) species in the electrolyte), resulting in anodic or cathodic photocurrents, respectively. By controlling the applied potential, the photoelectrochemical photocurrent switching (PEPS) effect can be observed [43–45].

In general, the PEC sensing strategy can be classified as dependent on: electron transfer, energy transfer, ion exchange or reactant determinant mechanisms (Fig. 1) [46]. *Electron transfer* strategies can be regulated through the applied potential [47,48], the promotion of competitive electron processes [47,49,50] or the use of hybrid systems with energy levels matched to enhance the photocurrent response [51,52]. The latter approach provides an important advantages such as possible photosensitization and higher energy conversion efficiency due to more efficient charge separation [53]. *Energy transfer* strategies can be divided into three types: surface plasmon resonance (SPR), resonant energy transfer and chemiluminescence-based energy transfer. The SPR phenomenon is based on collective surface oscillations of electrons induced by incident light. Surface plasmons which undergo dumping may induce excitation within adjacent semiconductor, which, in the presence of a proper electron donor, results in the signal amplification [54]. In the case of resonant energy transfer, competitive processes of interparticle interactions in the form of nonradiative or radiative electron-hole recombination take place. It allows either the exciton energy transfer from semiconductor

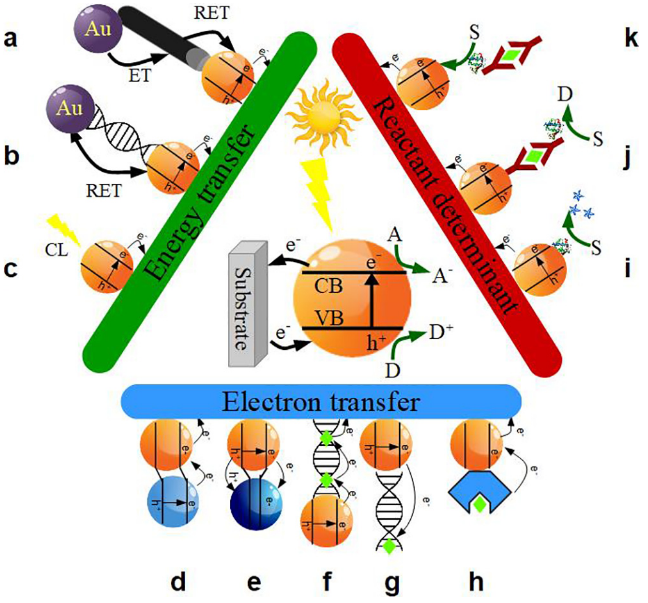

Fig. 1. A schematic illustration of various strategies for creating PEC sensors: surface plasmon resonance (a), resonant energy transfer (b), chemiluminescence-based energy transfer (c), charge separation (d), electron trapping (e), competitive electron transfer (f, g), conditional, analyte-induced photosensitization (h), introduction/release of photoactive species (i), consumption/generation of electron donor/acceptor (j) and effect of steric hindrance (k). Adapted from Ref. [46].