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## Review

## Coordination chemistry for information acquisition and processing

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## Contents

1. Introduction .....	1
2. Semiconductors, molecules, and light .....	1
3. PET and optical electron transfer (OET) processes in semiconductor-based systems and molecules .....	5
4. Information gathering with molecular "fluorophore-spacer-receptor" systems .....	9
5. Boolean logic devices based on the PEPs effect and other molecular phenomena .....	11
6. Towards multi-valued logic systems .....	14
7. First steps into fuzzy logic .....	17
8. Other types of human-level computing .....	20
Acknowledgements .....	24
References .....	24

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## ABSTRACT

In the 21st century, information has become the most valuable resource that is available to modern societies. Thus, great efforts have been made to develop new information processing and storage techniques. Chemistry can offer a wide variety of computing paradigms that are closely related to the natural processes found in living organisms (e.g., in the nervous systems of animals). Moreover, these phenomena cannot be reproduced easily by solely using silicon-based technology. Other great advantages of molecular-scale systems include their simplicity and the diversity of interactions that occur among them. Thus, devices constructed using chemical entities may be programmed to deal with different information carriers (photons, electrons, ions, and molecules), possibly surpassing the capabilities of classic electronic circuits.

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## 1. Introduction

This review describes the development of research on chemical information acquisition and processing in Krakow and Belfast. The common platforms for all of the devices considered are photoinduced electron transfer (PET) processes in molecular and semiconducting materials. Although they start from different positions and materials, there are conceptual parallels that allow the discussion of systems with gradually increasing complexity, which operate on the basis of Boolean logic [1], fuzzy logic [2], and other

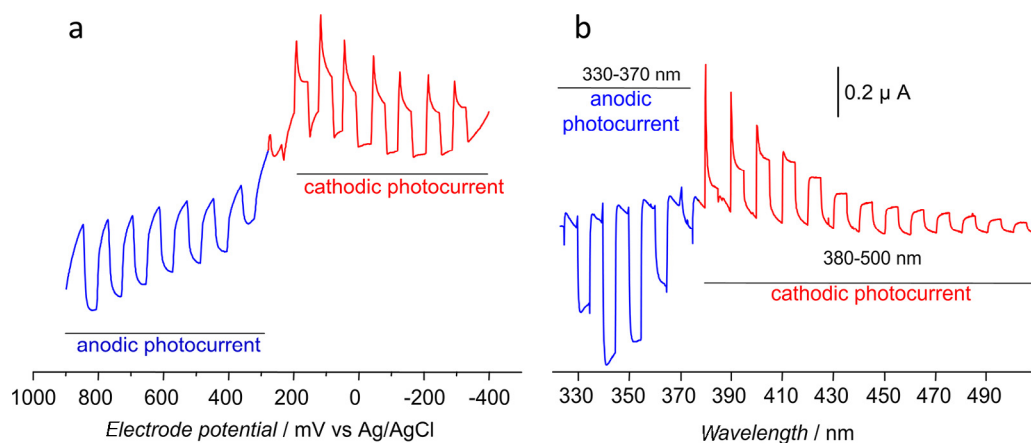
paradigms at higher levels of complexity [3]. Indeed, two books have emerged from these studies in Kraków [4] and Belfast [5], which summarise chemical information gathering and processing research around the world. This review develops the concepts presented in those books and in a chapter of a book that is soon to be published titled "Advances in Unconventional Computing".

## 2. Semiconductors, molecules, and light

Information processing is based on changes. Thus, if everything stays the same, we do not receive a message. The crucial factors that cause some changes in semiconductors and molecules are light, potentials, and/or the binding of atomic/molecular species. One of the most important characteristics of semiconductors and molecules is their ability to alter after appropriate stimulation. Furthermore, many of these changes are reversible. Light is the most

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**Fig. 1.** Linear sweep voltammetry performed for an *n*-type semiconductor ( $\text{TiO}_2$  modified with  $[\text{Fe}(\text{CN})_6]^{4-}$ ) under pulsed illumination at 350 nm (a) and the photocurrent action spectrum of the same material recorded at 200 mV vs an Ag/AgCl reference electrode with varying wavelength of the incident light (b).

powerful carrier of information, so it is natural that photochemical and photophysical processes are recognised as the most suitable for information processing at the molecular scale. Semiconductors separate electron–hole pairs when illuminated within an appropriate wavelength range. This property is applied widely in photovoltaics, photocatalysis, and general photochemistry. It also allows the use of materials in semiconductor laser technology and optoelectronics, as well as in molecular photochemical industry. In terms of information processing, charge separation within molecularly-modified or unmodified semiconductors is embodied in the photoelectrochemical effect of photocurrent switching (PEPS), which can be applied in the construction of switches, logic gates, and other basic elements used in computing systems. When molecules are considered alone, similar switches, sensors, and logic gates can also be constructed by modulating the competition between fluorescence and PET.

In classical situations, an anodic photocurrent is generated after the illumination of *n*-type semiconductors, whereas a cathodic photocurrent will be observed in the case of *p*-type semiconductors. However, in some special situations, under appropriate polarisation with external potential, a switching between anodic and cathodic photocurrents can be observed (Fig. 1) [6–9]. This effect was described for the first time in 2006 [10] and it has since been investigated extensively. This phenomenon is defined as a change in the photocurrent polarity due to a change in either the semiconducting electrode potential and/or the wavelength of incident light [10], which is known as the PEPS effect.

The PEPS effect has only been observed in several groups of semiconducting materials, where we can distinguish unmodified and surface-modified semiconductors. In the first group, the photocurrent switching effect has been observed mainly in unmodified oxide semiconductors, such as  $\text{Bi}_x\text{La}_{1-x}\text{VO}_4$  solid solutions ( $x$  between 0.23 and 0.93) [11], lead molybdate [12], and V–VI–VII semiconductors: bismuth oxyiodide [9,13], bismuth oxynitrate [14], and antimony sulfoiodide [15], as well as cadmium sulphide [16,17] and lead sulphide [18]. In unmodified semiconductors, the observation of the switching effect is possible only with sufficiently low potential barrier  $E_{bi}$  at the solid–liquid junction, which may be achieved by reducing the grain size of the semiconductor and decreasing the doping level [19], or when appropriate surface states are present.

More interesting examples are hybrid materials, where the surface of the semiconductor is modified with organic or inorganic species. Some of the most important examples of these materials are shown in Table 1.

Considering the examples presented in Table 1, we may formulate some general principles that must be satisfied in order to observe

the PEPS effect. The most obvious is the illumination of a semiconducting system within its absorption range in order to generate an electron–hole pair (excluding the scenario where sensitisation of a semiconductor occurs). The second rule is the presence of efficient electron donors/acceptors dissolved in an electrolyte (e.g.,  $\text{I}^-/\text{I}_3^-$  [13],  $\text{Ce}^{4+}/\text{Ce}^{3+}$  [12,15], and sacrificial electron donors such as EDTA [35]), which influences both the thermodynamics and kinetics of the system, and this should be considered during the design step for each device. The process is thermodynamically allowed when the redox potential of an electron donor/acceptor is located between the conduction and valence band edges. In this case only,  $\Delta G$  is negative for the reduction of oxidised species from the electrolyte with an electron from the conduction band as well as the oxidation of reduced species with a hole from the valence band. We assume that the reduction process is associated with the conduction band, whereas the oxidation relies on the valence band [36]. Our assumption is usually valid when the band gap of a semiconductor is not excessively wide and for a relatively high reorganisation energy value.

Considering the cases described above, it should also be noted that the PEPS effect can be observed in redox-innocent supporting electrolytes (e.g., aqueous solution of  $\text{KNO}_3$ ) if the band gap of a semiconductor is sufficiently wide (more than ca. 2 eV) [11]. In this case, two redox couples can be distinguished in the equilibrium with air:  $\text{OH}^+/\text{OH}^-$  and  $\text{O}_2/\text{O}_2^-$ , where their formal potentials are 1.9 V [37] and  $-0.16$  V vs. standard hydrogen electrode (SHE), respectively [38]. When the electrolyte is purged with oxygen, its reduction potential shifts anodically, thereby facilitating a cathodic photocurrent flow, which leads to a switching effect at a sufficiently negative electrode potential.

The kinetic features of these processes are also crucial. The electron donor/acceptor system present in the electrolyte should ensure that the charge is transferred through the semiconductor–liquid junction at a sufficiently rapid speed to avoid recombination events. From the viewpoint of thermodynamics, appropriate reduction potential values for the redox couples vs. the conduction and valence band edges will ensure the electrochemical stability of the material under investigation. Thus, with sufficient cathodic polarisation of the electrode and in the absence of an efficient electron acceptor, the reduction of metal ions from the crystal lattice may occur, whereas holes photogenerated under irradiation in the valence band may oxidise metal ions from the lattice. This is usually not the case for oxide semiconductors, but this problem must be considered for sulphides and iodides [36].

Finally, the third factor that has a significant impact on the occurrence of the PEPS effect and its mechanism is the characteristic of the potential barrier at the semiconductor–electrolyte

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