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Photoelectrochemical detection of metal ions

Wei-Wei Zhao,* Jing-Juan Xu and Hong-Yuan Chen

Depending on the situation, metal ions may either play beneficial roles or be harmful to human health and ecosystems. Sensitive and accurate detection of metal ions is thus a critical issue in the field of analytical sciences and great efforts have been devoted to the development of various metal ion sensors. Photoelectrochemical (PEC) detection is an emerging technique for the bio/chemical detection of metal ions, and features a fast response, low cost and high sensitivity. Using representative examples, this review will first introduce the fundamentals and summarize recent progress in the PEC detection of metal ions. In addition, interesting strategies for the design of particular PEC metal ion sensors are discussed. Challenges and opportunities in this field are also presented.

1. Introduction

Metal ions are ubiquitous in nature and the human body. Depending on their concentration ranges, these ions could have beneficial or deleterious effects on human health and ecosystems.[1] In most cases, trace levels of metal ions are essential for both the cellular functions such as transportation/cell signaling and the healthy development of natural systems. However, when they go beyond certain limits, they will become toxic and cause dysfunctional cytological/physiological effects. Among various metals, heavy metals, with atomic weights between 63.5 and 200.6 g mol^{-1} and a specific gravity greater than 5 g cm^{-3}, are recognized to be low density chemical components with high toxicity.[2] Among the heavy metals, copper (Cu), iron (Fe), manganese (Mn), cobalt (Co), zinc (Zn) *etc.* are required to support biological activities at low concentrations but become toxic when in excess,[3] whereas lead (Pb), mercury

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Wei-Wei Zhao

Wei-Wei Zhao was educated at Nanjing University of Aeronautics and Astronautics and received his B.S. and M.E. in 2005 and 2008, respectively. Then he moved to Nanjing University (NJU) and received his PhD in 2012. Currently, he works at NJU as an associate professor and his research focuses on biomolecular detection via various advanced electrochemical techniques. He is the coauthor of more than 40 international papers, and most of them are related to DNA and protein assay.

Jing-Juan Xu

Jing-Juan Xu, born in 1968, graduated from Wuhan University in 1990 and earned her M.Sc. and PhD from Nanjing University in 1997 and 2000, respectively. Currently she is full professor in the Department of Chemistry at NJU and has published more than 200 scientific papers. She received funding from the National Outstanding Youth Foundation of China (2010) and won the "10th Chinese Young Women Scientists Award" (2013). She was selected as a "RSC Fellow" (2014) and approved as the Chang Jiang Professor (2014). Her research interest focuses on the development of various electrochemical, electrochemiluminescent and photoelectrochemical sensors based on nanostructured materials with enhanced sensitivity and selectivity, and the fabrication of lab-on-chip detectors for biological analysis.

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(Hg), chromium (Cr), cadmium (Cd), arsenic (As) *etc.* are considered hazardous even at low concentrations.[4] These heavy metals are non-biodegradable and get accumulated in the biosphere, leading to enduring bioaccumulation in ecosystems.[5] When they enter living organisms through the alimentary chain, these metal ions could cause enzyme inhibition, oxidative stress and impaired antioxidant metabolism, leading to the generation of free radicals that cause DNA damage, lipid peroxidation and depletion of protein sulfhydryl and hence several diseases such as neurodegenerative diseases and cancer.[6,7] Therefore, the sensitive and selective detection of metal ions is an indispensable task for analysts. Traditional techniques for the detection of metal ions include atomic absorption/emission spectrometry, inductively coupled plasma mass spectrometry and cold vapor atomic fluorescence spectrometry.[8–11] However, these techniques generally suffer from their limitations such as expensive instrumentation, specialized personnel, laborious sample pretreatment processes, and inadaptability for in site measurement. Obviously, the development of new techniques capable of simple, inexpensive and in site detection of metal ions is highly desirable for environmental, biological, and industrial applications.

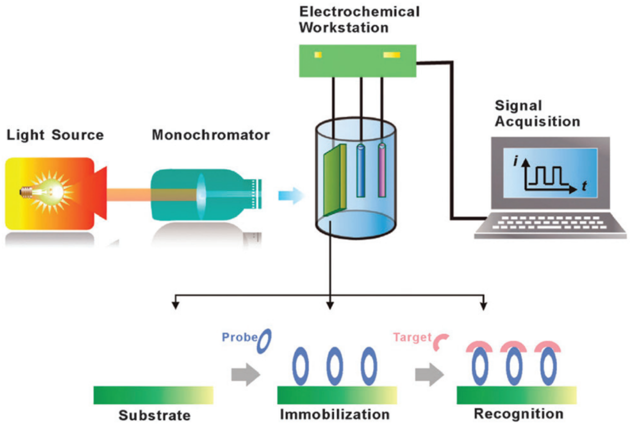

Fig. 1 Schematic of the general instrumentation and working principle of PEC (bio)detection. (Reprinted with permission from ref. 13. Copyright 2015, Royal Society of Chemistry.)

Photoelectrochemical (PEC) detection represents a newly developed approach for chemical and biomolecular detection.[12–25] The ideal fusion of electrochemical detection and photoelectrochemistry has provided such opportunities for the elegant analysis of numerous targets of interest. As shown in Fig. 1, inherently, PEC detection is principally conducted with a three-electrode system containing a working electrode (WE), a reference electrode (RE) and a counter electrode (CE). Due to the involvement of photoelectrochemistry, the WE necessitates the existence of specific semiconductor materials such as quantum dots (QDs) to allow for the PEC reactions that are intimately related to the recognition events and/or concentration of the targets. Upon illumination, the presence of the analytes could cause changes of a specific physicochemical factor associated with the semiconductors and thereby the variation of electrical signals for detection. Essentially, the basic principle of PEC detection is the photo-to-electric conversion of the semiconductor species, in which charge carriers are photoexcited and then heterogeneously transferred to convert the studied biochemical information of an analyte concentration. Such a process is related closely to the analyte-based recognition, surface/materials chemistry, and dynamic processes at the semiconductor/electrolyte interface *e.g.* photochemistry, electrochemistry as well as interfacial charge transfer/storage/recombination. For analytical and bioanalytical applications, PEC detection has been exploited for the specific and sensitive detection of manifold biochemical species of clinical and environmental significance, especially DNA analysis, immunoassay, enzymatic sensing and metal ion detection.[26–40] Compared to conventional electrochemical detection, PEC detection of metal ions shares its advantages but permits more sensitive detection and hence has rapidly become a hot topic in analytical chemistry. Fig. 2 displays the basic concept of PEC detection of metal ions. The interactions between the metal ions and the recognition probes or photo-

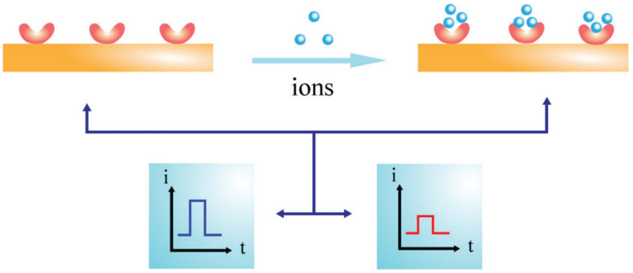

Fig. 2 Basic concept of PEC detection of metal ions.

Hong-Yuan Chen

Hong-Yuan Chen was born in 1937 in Sanmen of Zhejiang Province in China. After graduation from Nanjing University in 1961, he has been working in the Department of Chemistry at NJU. From 1981 to 1984, he worked at Mainz University as a visiting scholar. During 1986–1999, he worked as a guest professor or visiting professor in Germany four times. In 2001, he was elected as the academician of Chinese Academy of Science. He is a member of several scientific societies and several advisory boards of scientific journals. He has authored and co-authored over 750 papers and several chapters and books. His research interests include electrochemical biosensing, bioelectrochemistry, ultramicroelectrodes and biomolecular-electronic devices and the Micro-Total Analysis System.

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active species would be detected *via* the increased or decreased electrical signal.

To date, there have been many reviews of metal ion analysis using different detection modalities such as fluorescent, colorimetric and electrochemical,[1,41–50] whereas no effort has been put on summarizing the PEC one. This review is the first paper to cover the field of PEC detection of metal ions. Fundamentals and recent progress in this field will be introduced, and the analytical applications are summarized on the basis of different ion species. Interesting transduction mechanisms for the design of particular PEC metal ion sensors are discussed. Besides, the trends are also presented. Overall we would like to present a general overview of the development and application of PEC detection of metal ions with high sensitivity and selectivity.

2. PEC detection of metal ions

As stated before, metal ions in the toxicity range could deteriorate human health and pose greater risks to the environment. Pb, Hg, Cd, Cr, As *etc*. ions are considered to be highly toxic even at low concentrations. These species bind the thiol groups of proteins and alter the biochemical lifecycle when entering the cells, impairing the human brain, the nervous system, the endocrine system *etc.*, thus causing most of the heavy metal-related diseases. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have strictly defined the concentration limits of these metal ions that are allowed in drinking water. PEC detection offers a convenient avenue for these metal ion analyses due to its simplicity and low detection limit. During the past few years, considerable efforts have been devoted to the development of various PEC protocols for novel detection of metal ions. This section will systematically survey the PEC detection of common metal ions.

2.1 Detection of lead (Pb) ions

Pb is one of the most abundant and poisonous heavy metals, and affects almost every organ and system (the main target for lead toxicity is the nervous system) in the body. Pb pollution is a global persisting issue as its mining/smelting is common in many countries, and 300 million tons of mined Pb is still circulating in the environment. Exposure to Pb and its chemicals can occur through inhalation, ingestion and dermal contact. In the human body, lower levels of Pb act as a Ca analog, interfering with ion channels during nerve conduction, which is one of the mechanisms that affect cognition. In addition, Pb has affinity to sulfhydryl groups and binds to enzymes and inhibits porphobilinogen synthase and ferrochelatase, preventing both porphobilinogen formation and the incorporation of iron into protoporphyrin IX, thereby decreasing the heme production. Besides, Pb ions, like many other heavy metal ions, also induce the generation of reactive oxygen species (ROS) that damages lipids and DNA.

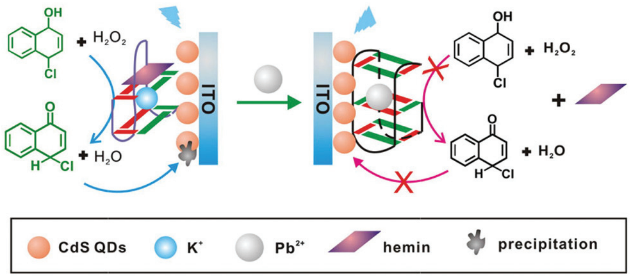

Fig. 3 Schematic diagram of the process to fabricate a BCP amplified PEC biosensor. (Reproduced with permission from ref. 51. Copyright 2013, Elsevier Publishing.)

Based on the coupling of allosteric transition of G-quadruplex DNAzyme and the biocatalytic precipitation (BCP), as shown in Fig. 3, our group has developed a sensitive PEC approach for Pb^{2+} detection on a CdS quantum dot electrode. Pb^{2+} could induce the conformational change of K^+-stabilized G-quadruplex-based DNAzyme, leading to the decrease of the catalytic activity to H_2O_2-mediated 4-chloro-1-naphthol oxidation for PEC signaling. From the respective BCP reaction that monitors the event of DNAzyme deactivation, a novel PEC Pb^{2+} sensor could be realized with a detection limit of 1.0×10^{-8} M.[51] Lei *et al.* then reported an interesting "signal-on" PEC detection of Pb^{2+} based on target-dependent aptamer conformational conversion, the amplified effect of reduced graphene oxide (RGO) and resonance energy transfer between CdS QDs and Au NPs. In the absence of Pb^{2+}, the Au NP-labeled DNA could hybridize with an aptamer probe on the electrode surface and quench the photocurrent of QDs through an energy transfer process. In the presence of Pb^{2+}, the aptamer is induced into a G-quadruplex structure that releases the Au NP-labeled DNA due to the competitive occupation of binding sites, thus leading to the recovery of photocurrent. Under optimized conditions, this PEC biosensor could detect Pb^{2+} with a linear range of 0.1–50 nM and a detection limit of 0.05 nM.[52] Using a Pb^{2+}-dependent DNAzyme as the recognition unit and a dsDNA intercalator $Ru(bpy)_2(dppz)^{2+}$ as the PEC signal reporter, Zhang *et al.* reported a novel ZnO nanoflower-based PEC DNAzyme sensor for the detection of Pb^{2+}. In the presence of Pb^{2+}, RNA-cleavage activity of the DNAzyme was activated and its substrate strand was cleaved, causing the release of $Ru(bpy)_2(dppz)^{2+}$ from the DNA film and the corresponding photocurrent decrease. Under the optimized conditions, a linear detection range of 0.5–20 nM with a detection limit of 0.1 nM has been obtained.[53] Wang *et al.* then proposed a PEC aptasensing of Pb^{2+} based on the *in situ* generation of a photosensitizer of a self-operating photocathode. The presence of Pb^{2+} would induce the allosteric transition of K^+-stabilized hemin/G-quadruplex, which would release the hemin to sensitize the p-type NiO electrode, forming the self-operating photocathode. The cathodic photocurrent linearly increases with the Pb^{2+} concentration in the range of 20 to 1500 nM with a detection limit of 4.0 nM.[54] Li and Tian *et al.* exploited the electrodeposition of PbS NPs onto TiO_2 nanotubes for PEC detection of Pb^{2+}. This sensor shows a linear range from 10^{-8} to 10^{-5} M, and a low detection limit of

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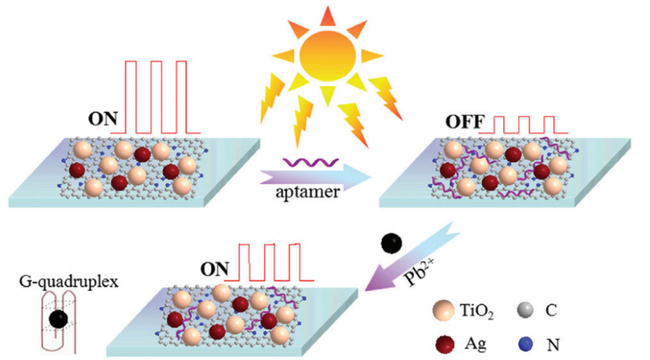

Fig. 4 Schematic diagram of the preparation of the as-fabricated "on–off–on" switch system based PEC aptasensor. (Reproduced with permission from ref. 56. Copyright 2016, Elsevier Publishing.)

0.39 nM (~0.08 ppb).[55] Recently, as shown in Fig. 4, Wang's group reported the Pb^{2+}-induced formation of a G-quadruplex/Pb^{2+} complex on photoactive films, and varied signals were recorded for the PEC detection of Pb^{2+}. Using this method, a wide linear response for Pb^{2+} detection was obtained from 1 pM to 5 nM with a detection limit down to 0.3 pM.[56]

2.2 Detection of mercury (Hg) ions

Hg, widespread in air, water and soil, is extremely toxic to human health and the ecosystem. The human-generated Hg pollution is mainly originating from stationary combustion, gold and non-ferrous metal production, cement and caustic soda production, waste disposal *etc*. Acute exposure or chronic exposure to Hg vapor even at low concentrations can damage the brain, the central nervous system and the immune system and cause various cognitive and motion disorders. Hg vapor can also be easily oxidized to water-soluble ions and thereby generate more toxic organic forms that can accumulate *via* the food chain. Hg poisoning can thus arise from inhalation of Hg vapor, exposure to water-soluble forms of Hg, or consumption of contaminated food. In the human body, numerous thiol containing biomolecules could be affected due to the greater affinity of Hg to sulfur, leading to the inhibition of various enzymes, nephrotoxicity and neurotoxicity. Hg exposure would also affect the function of mitochondria in cells.

Crouch *et al.* reported PEC determination of Hg^{2+} in aqueous solutions by the use of the rhodamine 6G derivative and polyaniline immobilized on ITO glass plates that were subjected to photovoltage measurements in the absence and presence of Hg^{2+}. The optical responses of the coated electrode were used to determine the sensitivity and selectivity of the Hg^{2+} sensor in the presence of background ions. The reported sensor responded linearly in the range 10–150 μg L^{-1} with a detection limit of 6 μg L^{-1}.[57] With a TiO_2-modified composite photoelectrode, they further developed the improved PEC detection of Hg^{2+} and the photoresponse increased linearly in the range from 10 to 200 μgL^{-1} with a detection limit of 4 μg L^{-1}.[58] Significantly, many PEC detection methods of Hg^{2+} have been developed on the basis of thymine–Hg^{2+}–thymine interactions.[59–67] For example, with the aid of the dsDNA intercalator $Ru(bpy)_2(dppz)^{2+}$, as shown in Fig. 5, Guo *et al.* reported a sensitive and selective PEC DNA sensor for Hg^{2+} detection. The presence of Hg^{2+} would induce the formation of a dsDNA structure which binds $Ru(bpy)_2(dppz)^{2+}$ for signaling. Under the optimized conditions, a linear relationship in the range of 0.1–10 nM with a detection limit of 20 pM was obtained.[59] Still on the basis of thymine–Hg^{2+}–thymine interaction, Li *et al.* proposed two PEC biosensors against Hg^{2+}; one is achieved by the *in situ*-generated nanogold for the plasmonic near-field absorption enhancement effect with a linear detection range of 5–500 pmol L^{-1} and a detection limit of 2 pmol L^{-1},[60] while the other one is realized by the Hg^{2+} induced dehybridization of the original poly(dT)–poly(dA) duplexes and then the release of the intercalator quercetin–copper(II) complex with a linear detection range of 0.01 to 1.00 pmol L^{-1} with a detection limit of 3.33 fmol L^{-1}.[61] As shown in Fig. 6, using CdS QD-tagged Hg^{2+}-specific oligonucleotides, we reported a folding-based PEC sensor for reagentless and highly sensitive Hg^{2+} detection; the linear dependence was observed in the range of 5–500 pM with a detection limit of 1 pM.[62] Based on dual signal amplification by exciton energy transfer coupled with the sensitization effect, Zhu *et al.* further reported a highly sensitive and selective PEC biosensor for

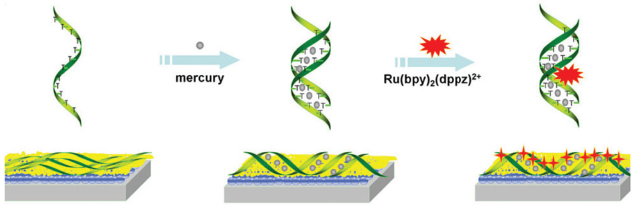

Fig. 5 Schematic diagram of a T–Hg^{2+}–T based PEC aptasensor. (Reprinted with permission from ref. 59. Copyright 2012, Elsevier Publishing.)

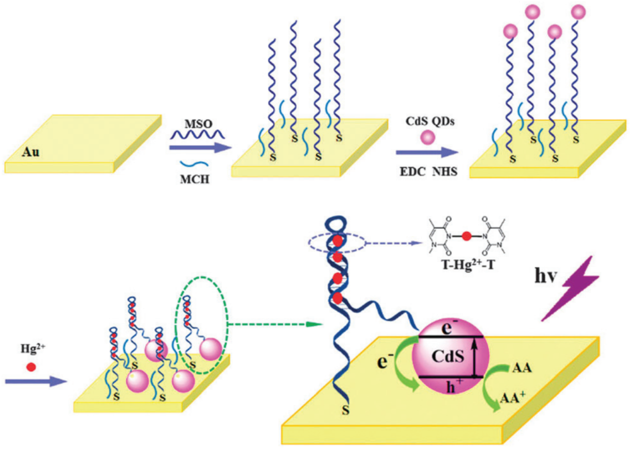

Fig. 6 Schematic illustration of the fabrication of a PEC Hg^{2+} biosensor. (Reprinted with permission from ref. 62. Copyright 2014, Royal Society of Chemistry.)

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Hg^{2+} detection with a linear range of 10 fM to 200 nM and a detection limit of 3.3 fM.[63] Besides, Wang *et al.* developed a novel PEC detection of Hg^{2+} based on the Hg^{2+}-induced *in situ* formation of the p–n junction with a linear concentration range of 0.01–10.0 mM and a detection limit of 4.6×10^{-9} mol L^{-1}.[64] Shuang *et al.* reported a method based on the Hg^{2+}-induced exciton trapping effect with a linear range of 1.0×10^{-9}–1.0×10^{-3} M and a detection limit of 0.3×10^{-9} M.[65] Zhang *et al.* reported a Hg^{2+}-induced inhibition effect upon the plasmonic photoelectrode for PEC detection of Hg^{2+} with a linear range of 0.01–10 nM and a detection limit of 2.5 pM.[66]

2.3 Detection of chromium (Cr) ions

Cr occurs abundantly in Earth's crust. As Cr compounds have been extensively used in various industrial processes and products such as dyes, paints and leather tanning, widespread Cr contamination in the environment has resulted. Cr exhibits many possible oxidation states, among which the Cr(III) state is most stable energetically; the Cr(III) and Cr(VI) states are the two prominent stable species in the environment, whereas the (I), (II), (V) and (IV) states are rare. The relationship between Cr(III) and Cr(VI) strongly depends on the pH and oxidative properties of the location, but Cr(III) is the dominating species in most cases while Cr(VI) compounds are powerful oxidants at low or neutral pH. It is well known that the toxicological and biological properties of the element depend strongly on its chemical form. For the Cr element, although it remains in debate, Cr(III) is possibly required as an essential micronutrient for human health. However, Cr(III) and Cr metals are not considered to be health hazards, whereas Cr(VI) is certainly toxic and carcinogenic for humans. Exposure to Cr(VI) could inhibit many enzymes, producing ROS that leads to the changed metabolic pathway and lipid peroxidation.

Hu *et al.* proposed an indirect subnanomole level PEC sensing platform for Cr(VI) based on its selective inhibition of quercetin oxidation. Specifically, the LUMO of quercetin is well matched with the conduction band of TiO_2 and it was thus used to act as both the sensitizer to extend the absorption light range of TiO_2 and the electron donor to enhance the separation of photogenerated carriers. Upon addition of Cr(VI), as shown in Fig. 7, quercetin could be at least partially oxidized by Cr(VI). So the enhanced photocurrent generated by quercetin would be decreased quantitatively and selectively, and the electrode displayed a linear decrease in response as the Cr(VI) concentration increased from 1 to 10 nmol L^{-1} and from 20 to 140 nmol L^{-1} with a detection limit of 0.24 nmol L^{-1}.[68]

2.4 Detection of cadmium (Cd) ions

Cd is also an extremely toxic and carcinogenic metal that prefers the oxidation state +2 in most of its compounds. Human exposures to environmental Cd are primarily from fossil fuel combustion, phosphate fertilizers, iron and steel production, cement production and related activities, as well as contaminated foods, *etc.* In the human body, Cd could act as a carcinogen that inhibits important enzymes and the mismatch repair of DNA, and also induces the generation of free radicals and oxidative stress. That is why high level exposure of Cd is related closely to damage to the liver and kidneys and increased risk of cardiovascular diseases and cancer mortality.

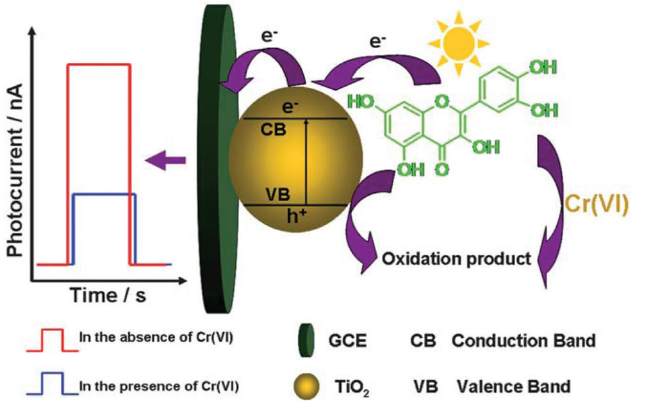

Fig. 7 The proposed PEC sensing mechanism for Cr(VI) at the TiO_2 modified electrode. (Reprinted with permission from ref. 68. Copyright 2013, Royal Society of Chemistry.)

Tian *et al.* reported a facile and efficient PEC approach to the determination of Cd^{2+} ions with high selectivity and sensitivity. The working principle is based on *in situ* electrodeposition of CdSe clusters on TiO_2 nanotubes, as illustrated in Fig. 8. Almost no absorption in the visible region can be observed on the bare TiO_2 film due to its wide band gap (3.2 eV), while negligible photocurrent was observed on the TiO_2 nanotube film under visible light illumination. By electrochemical scanning with the gradual addition of Cd^{2+} to H_2SO_4 solution containing SeO_2 added in advance, CdSe clusters with a narrow band gap could be generated on TiO_2 nanotubes ($CdSe/TiO_2$), producing photocurrent under visible light irradiation. Since the photocurrent increases with increasing amount of electrodeposited CdSe clusters on TiO_2 nanotubes, the protocol enables the quantitative analysis of Cd^{2+} concentration in the solution with a linear range from 1×10^{-9} to 1×10^{-2} M and a detection limit of 0.35 nM.[69]

2.5 Detection of copper (Cu) ions

After Zn and Fe, Cu is the third most abundant trace metal element, and it is essential to all living organisms as a trace dietary mineral in the human body. It plays an important role in various biological processes such as catalyzing the processes in heme synthesis/iron absorption and serving as a structural and catalytic cofactor for many proteins and enzymes. However, superfluous ingestion of Cu can be highly toxic to cellular homeostasis, causing many neurodegenerative diseases and damage to the liver/kidney. Besides, it is also considered to be a carcinogen because it has also shown an inhibition effect on various enzymes, and could increase the intracellular ROS production that eventually leads to DNA damage. In addition, a high concentration of Cu ions would depress the self-purification ability of natural waters since they can kill the biological retreatment systems in water.

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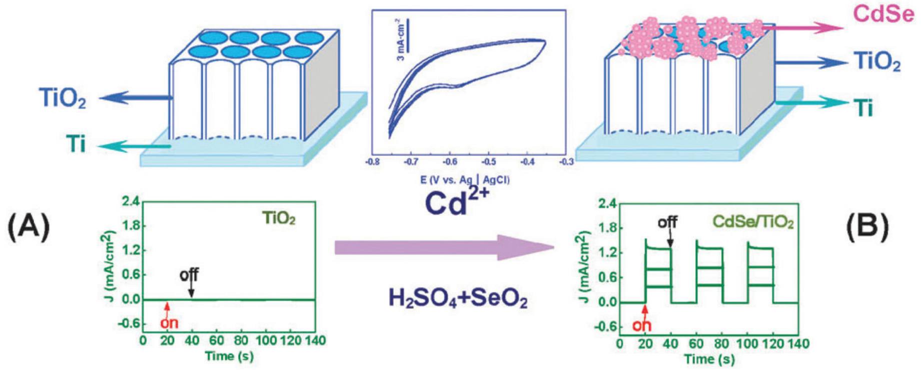

Fig. 8 Schematic illustration of the photoelectrochemical detection of Cd^{2+} based on *in situ* electrodeposition of CdSe clusters on TiO_2 nanotubes. The lower figures: short-circuit photocurrents obtained at (A) TiO_2 nanotubes and (B) $CdSe/TiO_2$ film in 1 M NaOH solution containing 1 M Na_2S and S under visible light illumination. (Reprinted with permission from ref. 69. Copyright 2012, Royal Society of Chemistry.)

Based on the selective interaction between CdS QDs and Cu^{2+}, as shown in Fig. 9, we have previously demonstrated that the formation of Cu_xS-doped CdS QDs could disrupt the electron transfer from the conduction band of CdS to ITO and result in a decrease of photocurrent for the sensitive and selective PEC detection of trace amounts of Cu^{2+}, with a linear detection range from 0.02 to 20.0 mM and a detection limit of 1.0×10^{-8} M. This work provides the first example of QDs for the PEC sensing of metal ions.[70] Using this strategy, Zhu *et al.* reported the use of ZnO/CdS hierarchical nanospheres for Cu^{2+} detection, and the detection range is 0.02–40.0 μM with a detection limit of 0.01 μM.[71] Ju *et al.* reported the use of CdTe QDs for Cu^{2+} detection, and the detection range is 8.0×10^{-8} to 1.0×10^{-4} M with a detection limit of 5.9×10^{-9} M.[72] Li *et al.* reported the use of SnO_2/CdS for Cu^{2+} detection, and the detection range is 1.00–38.0 μM with a detection limit of 0.55 μM.[73] Zheng *et al.* reported the use of mesoporous Fe_2O_3–CdS nanopyramid heterostructures for Cu^{2+} detection, and the detection range is 50 nM–600 μM with a detection limit of 0.5 nM. More significantly, they further investigated the detection of Cu^{2+} released from living cells. HeLa cells were directly cultured on top of the mesoporous Fe_2O_3–CdS arrays to reach the growth confluence, preserving well-conditioned morphologies and tight contact to the mesoporous Fe_2O_3–CdS interfaces. During the digestion and apoptosis processes of cells generated by trypsin, the Cu^{2+} ions (in both free and complex forms) are released from the living cells, and real-time monitoring shows that discrete photocurrent increases are repeatedly observed upon the corresponding addition of trypsin to the HeLa cell culture, indicating the excellent capability of direct culturing and PEC detection of the important cellular molecules.[74] Foo *et al.* then reported the use of reduced graphene oxide/CdS-modified carbon cloth for Cu^{2+} detection, and the photocurrent response was concentration-dependent over the linear ranges of 0.1–1.0 μM and 1.0–40.0 μM with a detection limit of 0.05 μM.[75] Using other mechanisms, as shown in Fig. 10, Han *et al.* used the click chemistry for PEC Cu^{2+} detection, and the detection range is 1.0×10^{-9} to 1.0×10^{-6} M with a detection limit of 2.0×10^{-10} M.[76] Li *et al.* used *in situ* electrodeposition of cuprous oxide for PEC Cu^{2+} detection, and the detection range is 1×10^{-11}–1×10^{-3} mol L^{-1} with a detection limit of 3.33 pmol L^{-1}.[77] PEC reduction of Cu^{2+} to metal Cu

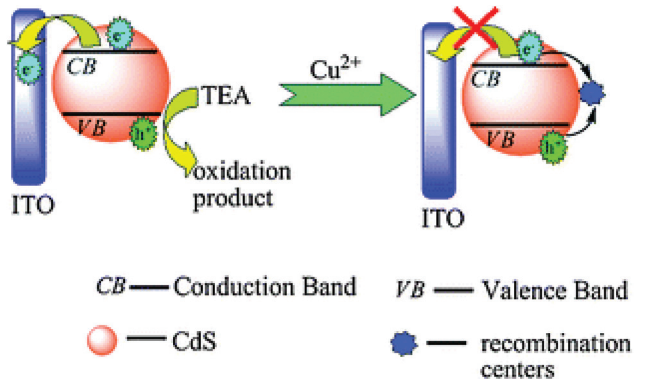

Fig. 9 The photophysics of CdS QDs in the absence and presence of Cu^{2+}. (Reprinted with permission from ref. 70. Copyright 2010, Royal Society of Chemistry.)

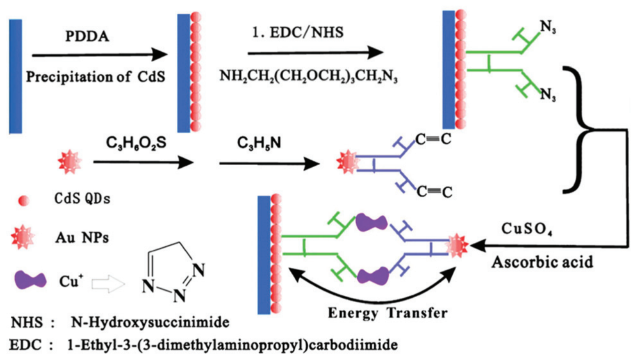

Fig. 10 The principle of Cu^{2+} detection based on the click reaction by the PEC method. (Reprinted with permission from ref. 76. Copyright 2015, Elsevier Publishing.)

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has also been studied for its detection; however, the selectivity of this method seems unconvincing.[78–81]

2.6 Detection of silver (Ag) ions

Ag plays no known natural biological role in humans, and Ag itself is not toxic to humans while most silver salts are. In daily life, Ag is being used in numerous commercial products such as costumes, jewelry and silverware, and in food storage, air conditioning and water purification. However, overexposure to silver may lead to its absorption into the circulatory system and deposition in various body tissues. In the human body, it has been proved to be a toxicant, giving rise to both cytological and physiological effects such as inhibiting many important enzymes, producing ROS and inducing oxidative stress, DNA damage and cell apoptosis. At levels of 10 mg m^{-3}, Ag is immediately dangerous to life and health.

Li and Dai *et al.* reported a robust PEC aptasensor for Ag^+ detection using an enhanced ZnO nanorod-based photoelectrochemistry by *in situ* generated AgBr *via* layer-by-layer assembly. As shown in Fig. 11, poly(C) was self-assembled onto the PDDA film *via* electrostatic interactions on a ZnO nanorod-array electrode, and the presence of Ag^+ would induce the formation of Ag^+-mediated poly(C) due to the high specificity of C–Ag^+–C. Then, the addition of Br^- would result in the *in situ* generation of AgBr, which is a visible-light responsive semiconductor. The coupling of AgBr and ZnO nanorod arrays resulted in enhanced photoelectric conversion efficiency by means of an extended visible light response, fast separation of charge carriers and light scattering in the nanorod arrays. And the detection range is 0.4–12.8 nmol L^{-1} with a detection limit of 150 pmol L^{-1}. This strategy of employing *in situ* generated narrow-bandgap semiconductors paves a new way for PEC sensing.[82]

2.7 Detection of calcium (Ca) ions

The Ca element is highly abundant both in the environment and in organisms. Compared with other metals, the Ca ion and most Ca compounds have low toxicity. The Ca element is essential for living organisms, particularly in cell physiology where its movement serves as a signal for many cellular processes including muscle contraction, motility, fertilization, fluid secretion, sensory transduction, exocytosis, and cell death. Ca concentration is associated intimately with many biological processes including excitability, neurotransmitter release, gene transcription, cell proliferation, synaptic plasticity and hormone secretion.

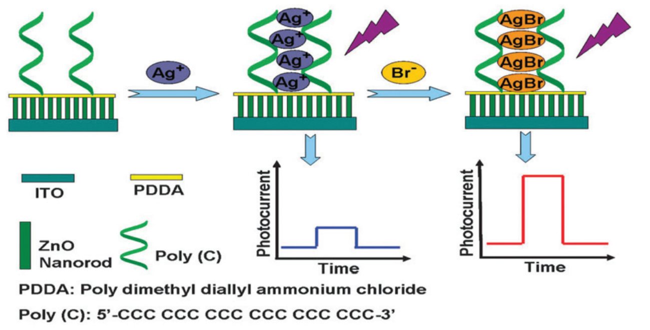

Fig. 11 The aptasensing of Ag^+ based on the *in situ* generated AgBr enhanced ZnO nanorod-based photocurrent *via* layer-by-layer assembly. (Reprinted with permission from ref. 82. Copyright 2014, Royal Society of Chemistry.)

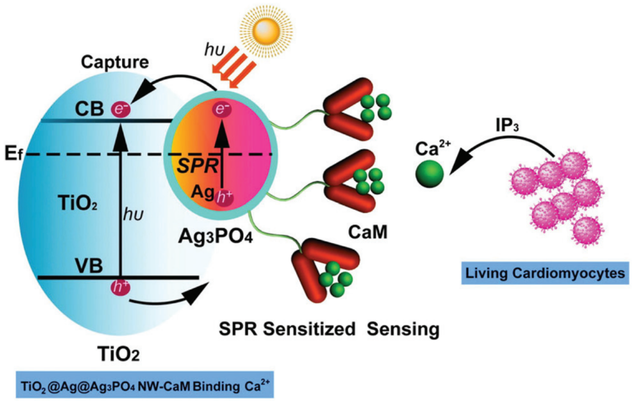

Fig. 12 Illustration of the SPR-enhanced PEC sensing mechanism for measuring Ca^{2+} by the TiO_2@Ag@Ag_3PO_4–CaM NW PEC sensors. (Reproduced with permission from ref. 83. Copyright 2015, Elsevier Publishing.)

Zheng *et al.* recently reported an innovative plasmon-enhanced PEC monitoring of Ca^{2+} from living cardiomyocytes. As shown in Fig. 12, TiO_2@Ag@Ag_3PO_4 was developed as a plasmon-based PEC sensing electrode, which exploited the benefits of TiO_2 nanowires (NWs) for high stability, facile surface functionalization, fast charge transport kinetics, and environmental benignity. Besides, the coupling of a thin layer of silver@silver phosphate (Ag@Ag_3PO_4) core–shell NPs would promote the photoabsorption and charge transport of TiO_2 NWs. The resulting synergistic effects on the composite resulted in a good PEC sensing performance of Ca^{2+} ions in both buffer solutions and living cardiomyocytes. Specifically, for the electron and hole transfer, the unique structure of Ag@Ag_3PO_4–TiO_2 NWs could offer strong surface plasmon resonance for electrochemical field effect amplification. The Ag@Ag_3PO_4 NPs are photo-excited due to plasmon resonance, and charge separation is accomplished by the transfer of photo-excited electrons from the Ag@Ag_3PO_4 NPs to the conduction band of TiO_2 NWs and the simultaneous transfer of electrons from a donor in the solution. Meanwhile, Ca^{2+} binding could enhance the transfer of photo-generated holes from TiO_2 NWs to an acidic protein calmodulin (CaM), making possible selective and sensitive Ca^{2+} recognition down to the level of 2.3 μM.[83]

2.8 Detection of potassium (K) ions

Ka ions are necessary for the function of all living cells and play an important role in living organisms. K levels influence multiple physiological processes, including resting cellular-membrane potential and the propagation of action potentials

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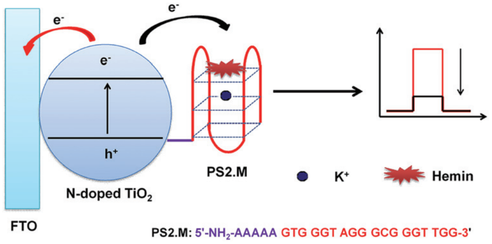

Fig. 13 The formation of the G-quadruplex/hemin complex with the promotion from K^+ decreased the photocurrent generated by the excitation of N-doped TiO_2. (Reprinted with permission from ref. 84. Copyright 2015, Royal Society of Chemistry.)

in neuronal, muscular, and cardiac tissues, hormone secretion and action, systemic blood pressure control, glucose and insulin metabolism, acid–base homeostasis, *etc.* K depletion or excess can cause numerous abnormalities, including an abnormal heart rhythm, various electrocardiographic abnormalities, *etc.*

Pei *et al.* reported a PEC detection of K^+ through quenching of photoinduced electrons based on a G-quadruplex/hemin complex. As shown in Fig. 13, the decreasing photocurrent from photoinduced electron transfer by the formation of a G-quadruplex/hemin complex in the presence of K^+ was utilized as a sensing signal for label-free PEC detection of K^+, and a linear relationship of photocurrent intensity *versus* K^+ concentration from 0.5 to 10 mM was obtained.[84]

3. Summary and outlook

Metal ions are of interest due to their serious harmfulness or unique biological importance to humans and the environment. The PEC technique offers a sensitive platform for the detection of metal ions and various signaling mechanisms have been proposed. Recent years have particularly witnessed rapid advances in the PEC detection of metal ions. This review has introduced the fundamentals and recent progress in this field, and the analytical applications are summarized on the basis of different ion species. As demonstrated, PEC detection of metal ions enables the analysis of a wealth of ion targets, and most of the reported studies fulfill the requirement of WHO's detection limits of heavy metal ions and some studies were successfully applied to track the changes within living systems. Now, as indicated by the increasing number of scientific papers, more efforts have been devoted to the development of advanced PEC detection of metal ions and its elegant analytical and bioanalytical application toward specific metal ions. With the rapid progress of PEC detection, we believe that this research area will become more dynamic and important results will be achieved continually.

Indeed, since the PEC detection of metal ions is still in its inception phase, there are a lot of opportunities to exploit and challenges to overcome, such as: (a) tailoring the nanomaterials/biomolecules/ions hybrid systems for innovative detection strategies with higher sensitivity and selectivity, *e.g.*, the ingenious use of various functional ion-dependent DNAzymes and related DNA molecules; (b) developing new protocols for the detection of many other metal ions including arsenic, zinc, iron, manganese, tin, *etc.*, and for the multiplexed detection of different metal ions;[85] (c) each physicochemical form of an element exhibits different bioavailability and toxicity properties, and therefore selective differentiation among various metal species is needed for some ion species, *e.g.* Cr(III)–Cr(VI) and Ti(I)–Ti(III);[86] (d) applying the PEC detection of metal ions to biological samples like urine, saliva, blood, *etc.* and to living systems; (e) the reported methods aim only at the detection of metal ions, while the design of novel dual-function PEC detection of metal ions capable of simultaneous removal of these targeted toxic metal ions seems to be of great significance; (f) real application of this technique for practical purposes, *e.g.*, in continuous monitoring of water bodies for toxic metal ions; (g) development of robust detection systems capable of high reusability and mass production for commercialization.

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