Electrochemistry Communications 57 (2015) 18–21

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

A study of the photodeposition over Ti/TiO_2 electrode for electrochemical detection of heavy metal ions

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ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 17 April 2015
Accepted 27 April 2015
Available online 6 May 2015

Keywords:
Photodeposition
Ti/TiO_2 electrode
Electrochemical detection
Heavy metal ions

ABSTRACT

Here we reported that UV light irradiation can significantly enhance sensitivity of Ti/TiO_2 electrode for determination of trace heavy metal ions (such as Cu^{2+}, Pb^{2+} and Cd^{2+}) owing to the photodeposition of metal ions on the surface of electrodes. The sensitivity of heavy metal ions can be selectively enhanced over the Ti/TiO_2 electrode, which is attributed to matching between potential of heavy metal ions and the position of the conduction band of TiO_2.

1. Introduction

With the development of industry and agriculture, heavy metal pollution of the natural environment has attracted the public's attention due to its toxicity for living organisms, accumulation, and low rate of clearance [1,2]. Thus, the precise identification and detection of trace heavy metal ions in environmental samples are increasingly important. In the past few years, a large amount of methods, such as atomic absorption spectroscopy (AAS) [3], atomic fluorescence spectrometry (AFS) [4], hyper-Rayleigh scattering [5], and inductively coupled plasma mass spectrometry (ICP-MS) [6], electrochemical methods [7,8], and so on, have been utilized to detect heavy metal ions. Among these techniques and methods, anodic stripping voltammetry (ASV) is especially adopted because of its low cost, easy operation, high sensitivity and the ability of quick measurement [9–11]. The sensitivity of ASV comes from the pre-concentration of the analyte (metal ions) on the working electrode by an electrochemically and adsorptive way [12]. The pre-concentration allows an increase of sensitivity of other 2 or 3 orders of magnitude, making it feasible to operate with lower analyte concentrations [12].

However, it is still a challenging work to further improve the selectivity and sensitivity of ASV approach to fulfill determination need for trace levels of many metals. To achieve the above objective, the chemical modification of electrode surface by various materials as general approach is widely used, such as the use of carbon nanostructured materials [13,14], mesoporous silica [15], high adsorptive γ-AlOOH@SiO_2/Fe_3O_4 [16], polypyrrole/RGO nanocomposite [17], silver [18], Sb nanoparticles [19], and gold nanoparticles [20,21]. Progress in electrochemical determination of trace heavy metal ions requires new approaches to achieve enhanced control over the selectivity and sensitivity of electrode. However, so far, previous researches mostly regarded on onefold chemical modification of electrode, few studies have been done to enhance selectivity and sensitivity of electrode materials utilizing photoelectric effect [22]. Here, we found that the sensitivity of Ti/TiO_2 electrode for some metal ions was selectively enhanced by light irradiation owing to matching between potential of metal ions and conduction band levels of semiconductor.

2. Experimental section

2.1. Preparation of electrodes

Titanium flake (99.7% pure, Yunjiemetal Co., China), 10 mm × 10 mm × 1 mm in size as the titanium electrode, was polished with abrasive SiC paper (#800–#2000), degreased by sonicating in acetone and ethanol, followed by rinsing with ultrapure deionized water. To obtain Ti/TiO_2 electrode, the Ti flake was heat-treated in a muffle furnace s at 400 °C for 4 h.

2.2. Apparatus

Electrochemical experiments were recorded using a CHI 660E potentiostat/galvanostat (ChenHua Instruments Co., Shanghai, China) with a standard three-electrode system. A platinum plate

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http://dx.doi.org/10.1016/j.elecom.2015.04.015
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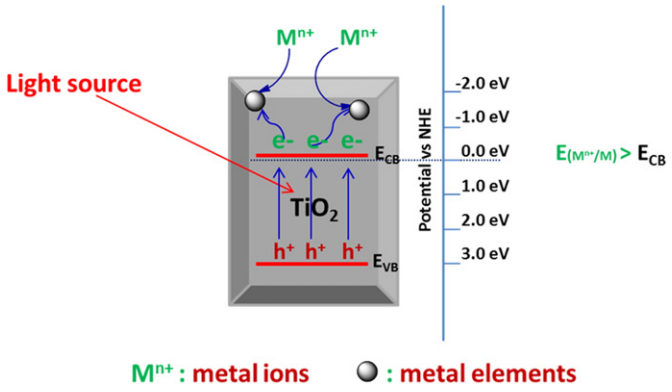

Scheme 1. Mechanism of photodeposition of metal ions on the surface of Ti/TiO2 electrodes.

and a Ag/AgCl (KCl satd) reference electrode were used as counter electrode and reference electrode.

3. Test methods

Anodic stripping voltammetry was used for the detection of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}. (1) Photo-deposited pre-concentration step: first, heavy metal ions were deposited into electrodes by light irradiation using mercury lamp as light source (effective wavelength of is 254 nm) for certain times in 0.1 M Na_2SO_4. Then, these accumulated metals were stripped to metal ions by electrochemical anodic stripping under the following experimental conditions: potential range of −1.2 to 0.3 V; increment potential = 4 mV; amplitude = 50 mV; pulse width = 0.2 s; sample width (s) = 0.0167; pulse period(s) = 0.5; quiet time = 2 s; sensitivity (A/V) = 0.001. (2) For the purpose of comparison, the reference experiment has been performed at the same experimental condition, only photo-deposited pre-concentration step is absent in this process.

4. Results and discussion

In a typical preconcentration step, the modes of metal preconcentration on the working electrode can be summarized by an electrochemically and adsorptive way. In our preconcentration step, the photoelectric effect was used to realize enrichment of metal ions on the surface of electrode. Thanks to this photoelectric effect the metal ion concentration is achieved in volume very much smaller as compared to the volume of the solution. The working principle of the photoelectric effect is based on in situ photodeposition of metal ions on the surface of Ti/TiO_2 electrode in preconcentration step, as illustrated in Scheme 1. It is well known that the internal photoelectric effect can occur in semiconductor when ultraviolet light falls on certain semiconductor (energy of incident radiation is higher than the band gap energy of semiconductor). In which process the semiconductor absorbed photons result in the excitation of electrons from the valence band to the conduction band. If the position of conduction band is more negative than potential of heavy metal ions ($E(^{n}_{M}{}^{+}/_{M}) > E_{CB}$), the reduction of each adsorbed metal ions occurs at the interface by acceptance of electrons from the conduction band (seeing Scheme 1). It is noteworthy that the photodeposition has been used since the decade of the 70s by the pioneer work of Bard [23] to prepare supported-metal catalysts and photocatalysts as well as to recover noble metals and to remove metal cations from aqueous effluents [24,25]. Thus, photodeposition of heavy metal ions as accumulation means can be used in preconcentration procedure of ASV [22].

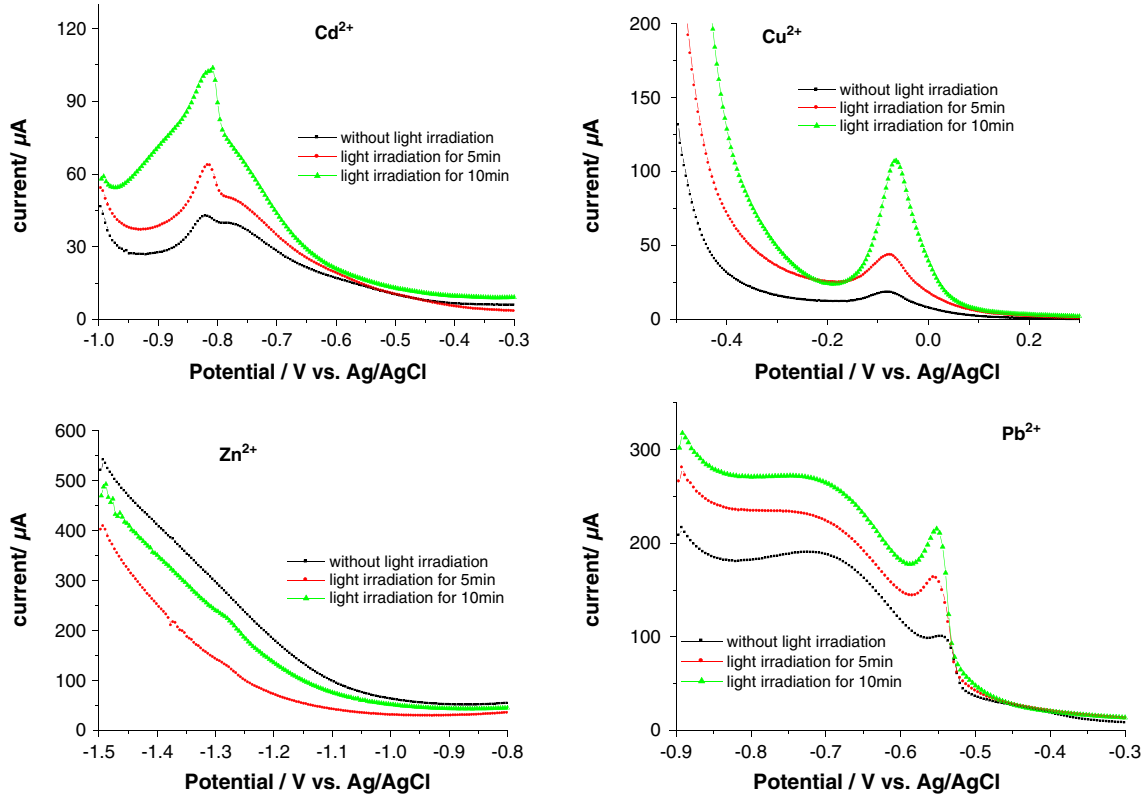

Fig. 1. Effect of light irradiation upon ASV response behavior of Ti/TiO_2 electrodes for the detection of heavy metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} with concentration of 1.0 μM, pH = 3.5).