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Photoelectrochemical cell for simultaneous electricity generation and heavy metals recovery from wastewater

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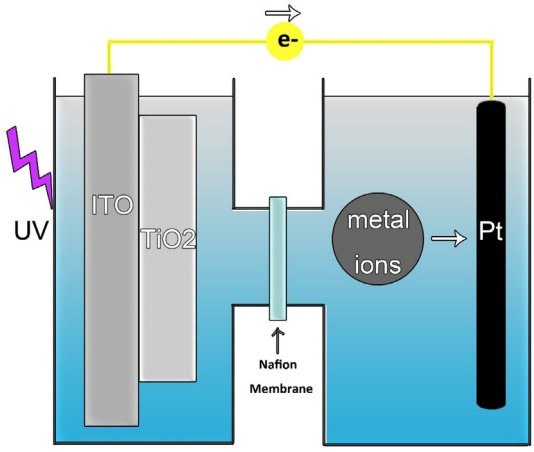
HIGHLIGHTS

- Polymer capped TiO_2 photoanode consumes photogenerated holes.
- Heavy metals reduce on the cathode according to their reduction potentials.
- Simultaneous recovery of heavy metals and production of electricity.
- Industrial wastewater treatment and production of renewable energy.

GRAPHICAL ABSTRACT



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ABSTRACT

The feasibility of simultaneous recovery of heavy metals from wastewater (e.g., acid mining and electroplating) and production of electricity is demonstrated in a novel photoelectrochemical cell (PEC). The photoanode of the cell bears a nanoparticulate titania (TiO_2) film capped with the block copolymer [poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol)] hole scavenger, which consumed photogenerated holes, while the photogenerated electrons transferred to a copper cathode reducing dissolved metal ions and produced electricity. Dissolved silver Ag^+, copper Cu^{2+}, hexavalent chromium as dichromate $Cr_2O_7^{2-}$ and lead Pb^{2+} ions in a mixture (0.2 mM each) were removed at different rates, according to their reduction potentials. Reduced Ag^+, Cu^{2+} and Pb^{2+} ions produced metal deposits on the cathode electrode which were mechanically recovered, while $Cr_2O_7^{2-}$ reduced to the less toxic Cr^{3+} in solution. The cell produced a current density J_{sc} of 0.23 mA/cm^2, an open circuit

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voltage V_{oc} of 0.63 V and a maximum power density of 0.084 mW/cm^2. A satisfactory performance of this PEC for the treatment of lead-acid battery wastewater was observed. The cathodic reduction of heavy metals was limited by the rate of electron-hole generation at the photoanode. The PEC performance decreased by 30% after 9 consecutive runs, caused by the photoanode progressive degradation.

1. Introduction

Uncontrolled release of heavy metals into water as a result of industrialization is an environmental problem of global concern, which poses significant risk to humans, plants and animals [1,2]. For example, the uncontrolled release of toxic mercury in 1950s and 1960s in Japan from the production of acetaldehyde caused adverse effects to the inhabitants of Minamata, a small fishing and farming village in Japan [3]. Other heavy metals such as cadmium, copper, lead *etc.* from industrial processes (for instance, lead can easily escape into environment by improper handling of lead-acid batteries) are also frequently, threatening the ecosystem [4]. Since most conventional wastewater treatment processes, especially those based on conventional biological methods, are ineffective in removing heavy metals [5], new approaches are necessary in order to develop sustainable solutions.

The rapid industrial development and its long-term sustainability calls for most of heavy metals to be recovered as highly desirable recyclable resources. For this purpose, advanced oxidation processes including photocatalysis have been investigated for the effective removal of metal ions [6–8]. In photocatalysis the absorption of photons by a semiconductor photocatalyst generates electron-hole pairs [9] and in turn highly reactive radical species, which lead to the oxidation of organic wastes [10]. A typical photocatalyst is nanostructured titanium dioxide (TiO_2). Photocatalysis is also a potentially efficient method to recover metals from wastewater, which occurs through the reduction of the dissolved metal ions to their metallic state by interaction with photogenerated electrons, in the presence of a hole scavenger [11]. However, current laboratory studies have not been translated to real applications in wastewater treatment, since the hole scavengers are often relatively costly reagents such as methanol and $NaHCO_3$ [12] which makes their use unrealistic in industry. Early studies performed with suspensions of nanoparticle photocatalysts [13–16] were not practical, since the separation of the suspended catalyst from the aqueous suspension, and of the metals from the solid, are highly challenging [17]. Clearly, the development of a robust technology to recover metals by photocatalysis requires the immobilization of the photocatalyst on a support to favour the recovery of the deposited metals. The metal reduction process involves the migration of electrons, therefore, it may also be possible to generate electricity during the recovery of metals from the wastewater [18,19]. Within this contest, the recovery of heavy metals from wastewater by *photoelectrocatalysis* has the potential to simultaneously address three issues, including (1) pollution prevention of heavy metals, (2) metal resources conservation and (3) renewable energy generation.

To address this challenge, in this study we developed a novel photoelectrochemical cell (PEC) carrying a nanoparticulate polymer capped titania photoanode and a Pt cathode (Fig. 1) which were connected by an external circuit. Simultaneous electricity generation and metal recovery was observed when the photoanode was exposed to UV irradiation. The performance and underlying mechanism of this innovating cell for environmental remediation with simultaneous generation of renewable energy are presented in this study. Previous studies in literature utilizing PEC have focused primarily on the removal or organic contaminants [18] and this is one of the few focusing on the removal and recovery of heavy metals from wastewater with simultaneous production of electricity.

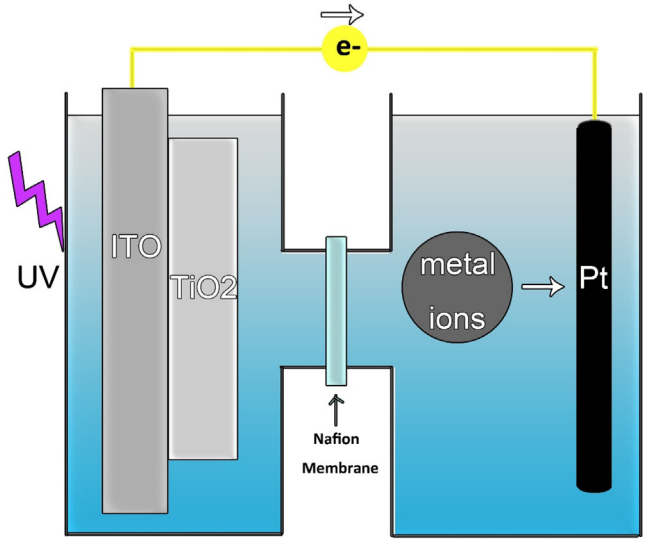

Fig. 1. Schematic illustration of the PEC for the purpose of simultaneous metal recovery and energy production.

2. Experimental

2.1. Chemicals

Titanium chloride ($TiCl_4$), poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) (P123), polyvinyl alcohol (PVA, Mw ≈ 22,000) and diethylene glycol (DEG) were obtained from Sigma-Aldrich. Copper sulfate ($CuSO_4$), copper nitrate ($Cu(NO_3)_2$), silver nitrate ($AgNO_3$), silver sulfate (Ag_2SO_4), nickel nitrate ($Ni(NO_3)_2$), nickel sulfate (Ni_2SO_4), lead nitrate ($Pb(NO_3)_2$) and $K_2Cr_2O_7$ were purchased from Fisher and used as received. ITO glass (2.3 mm of thickness, 2.25 cm^2 of area, 8 Ω/sq) from Dyesol Glass was cleaned with 2-propanol and distilled water several times before use. Ultrapure water (18 MΩ cm) was used throughout all the experiments.

2.2. Synthesis of nanoparticulate TiO_2 photoanode

The TiO_2 nanocrystals were synthesized according to a recent study [20]. In brief, a mixture of $TiCl_4$ (1 mL), NH_4OH (1 mL), P123 (0.6 g) and DEG (20 mL) was heated at 220 °C in air with vigorous stirring (600 rpm) for 3 h. After cooling down to room temperature, a light-brown mud-like precipitate was obtained upon addition of acetone and centrifugation. Finally, the sample was washed with acetone and ethanol to remove any residual organic species and re-dispersed in 2 mL H_2O. This procedure was repeated multiple times to produce a 18 mL stock solution. The presence of P123 in this synthesis plays a multiple role: it limits the growth of TiO_2 nanocrystals, it caps them and, most importantly, it acts as sacrificial electron donor to scavenge the photogenerated holes [20,21].

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