Applied Catalysis B: Environmental 207 (2017) 35–41

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Homogeneous photoconversion of seawater uranium using copper and iron mixed-oxide semiconductor electrodes

Seunghoon Lee[a,b], Unseock Kang[a,b], Guangxia Piao[a,b], Soonhyun Kim[c], Dong Suk Han[d], Hyunwoong Park[a,b,e,*]

[a] School of Energy Engineering, Kyungpook National University, Daegu 41566, Republic of Korea
[b] School of Architectural, Civil, Environmental, Energy Engineering, Kyungpook National University, Daegu 41566, Republic of Korea
[c] Division of Nano and Energy Convergence Research, Daegu Gyeongbuk Institute of Science and Technology, Daegu 42988, Republic of Korea
[d] Chemical Engineering Program, Texas A&M University at Qatar, Education City, Doha, P.O. Box 23874, Qatar
[e] Advanced Institute of Water Industry, Kyungpook National University, Daegu 41566, Republic of Korea

ARTICLE INFO

Article history:
Received 9 September 2016
Received in revised form 9 January 2017
Accepted 2 February 2017
Available online 3 February 2017

Keywords:
Photoelectrochemical
Resource recovery
Electron shuttle
p-type
Nuclear waste

ABSTRACT

Sunlight-driven conversion of hexavalent uranium (U(VI)) in seawater is achieved with mixed p-type CuO and $CuFeO_2$ ($CuO/CuFeO_2$) photocatalyst film electrodes synthesized *via* electrodeposition (ED) of Cu(II) and Fe(III), followed by annealing in air. The mixed photocatalysts exhibit a double-layer configuration with crystalline structures of CuO and $CuFeO_2$. On irradiation of the $CuO/CuFeO_2$ electrodes (held at −0.5 V vs. SCE) with solar simulated light (air mass 1.5; 100 mW cm^{-2}), the U(VI) concentration decreases with time, while the total amount of uranium in solution does not change. This indicates that virtually all conversion reactions of U(VI) occur in the bulk solution, while surface reactions are limited due to insignificant adsorption of U(VI). U(VI) conversion leads to the mixed production of lower oxidation states U^{4+}, $U^{14/3+}$, and $U^{16/3+}$ at a ratio of 42:28:30, with an overall Faradaic efficiency of ∼98%. The kinetics and induction time for U(VI) conversion are significantly influenced by the conditions of photocatalyst synthesis ($CuO/CuFeO_2$, CuO, and $CuFeO_2$; ED times of 2–4 h), the applied potential value (−0.4, −0.5, and −0.6 V vs. SCE), and the seawater condition (air-equilibrated vs. N_2-purged; pH 3–10.4). Based on the obtained results, O_2 is proposed to play a key role in shuttling photogenerated electrons between the electrodes and U(VI). In addition, the existence of an induction time is discussed in terms of material and reaction pathway.

1. Introduction

As carbon-neutral energy has emerged as the key to the sustainable growth of global communities, nuclear power has received growing attention worldwide [1–3]. Despite the long debate on safety and impact on the natural environment and human societies, nuclear power is still considered an alternative to fossil-fuel-based power because of its immediate CO_2 mitigation, both nationally and internationally. Uranium, a primary nuclear fuel, is a relatively common element in the Earth's crust and is traded securely under scrutiny [3–5]. Nevertheless, increases in the demand for energy security and political conflicts revisit the sustainability of the traditional supply chain.

In this regard, seawater uranium has received renewed attention in terms of securing the uranium supply because of its vast amount in oceans (45×10^8 ton, ∼1000 times the territorial reservoir). Although the natural uranium concentration in seawater is as low as ∼3 ppb [3], its uniform distribution in oceans encourages the development of recovery technology. The most common recovery process is the traditional sorption of U(VI), which exists as hydroxyl-carbonated uranyl anions (*e.g.*, $(UO_2)_2(OH)_3CO_3{}^{-}$ and $UO_2(CO_3)_3{}^{4-}$), in air-equilibrated seawater at pH ∼8.2, using various sorbents, including amidoxime [6], oxides [7,8], polymers [6,9], and sediments [10]. Sorption recovery is practical and promising; however, it does not change the oxidation states of U(VI). Considering that UO_2 is the favored chemical form for nuclear power operations, the recovered U(VI) requires post-chemical conversion for further utilization as a fuel. To address this challenge, photocatalytic recovery and simultaneous conversion of U(VI) using TiO_2 have often been studied [11–14]. However, most studies were performed in deionized water or well-controlled aqueous media,

---

[*] Corresponding author at: School of Energy Engineering, Kyungpook National University, Daegu 41566, Republic of Korea.
E-mail address: hwp@knu.ac.kr (H. Park).

http://dx.doi.org/10.1016/j.apcatb.2017.02.004
0926-3373/

which limits insight into the photoconversion mechanism in real seawater.

Recently, we reported the photoelectrochemical recovery and simultaneous conversion of U(VI) in seawater using porous TiO_2 film electrodes [15]. Under simulated sunlight irradiation, U^{6+} underwent stepwise reduction to $U^{14/3+}$ and U^{4+} (coordinated to oxygen) in an 8:2 ratio on the TiO_2 electrode surface; seawater has a similar uranium composition. The Faradaic efficiency of the uranium reduction was estimated at nearly 100%, with most reactions occurring on the TiO_2 surface (~95% of total uranium). However, the use of TiO_2 raises some technical issues. Firstly, TiO_2 is an n-type semiconductor with the valence and conduction bands bent downwards. Therefore, TiO_2 is not appropriate for direct injection of the majority carriers (*i.e.*, electrons) to the interfacial solution. An application of negative bias can induce upward bending of the bands, leading to an overlap between the Fermi level and the conduction band edge. Secondly, the distribution of uranium on the surface and in solution, requires additional post-separation and collection steps. It would be more practical if reduced uranium accumulated in one phase (surface vs. solution).

With this in mind, we attempted to convert seawater uranium using mixed p-type CuO and p-type $CuFeO_2$ ($CuO/CuFeO_2$; CFO) film electrodes. CFO is composed of earth-abundant elements and possesses a suitable energy level configuration capable of efficiently transferring photogenerated electrons to interfacial acceptors. Both the semiconductors have often been used for reduction reactions in non-saline aqueous media [16,17]. In this study, we have explored the applicability of mixed p-type electrodes to seawater uranium photoconversion.

2. Experimental section

2.1. Fabrication of photoelectrodes

Mixed CuO and $CuFeO_2$ electrodes ($CuO/CuFeO_2$; CFO) were fabricated on fluorine-doped SnO_2 ($F:SnO_2$, FTO) soda lime glass (Pilkington, ~50-nm-thick FTO layer) *via* electrodeposition, as reported elsewhere [16]. In brief, FTO substrates (1.5 cm × 3 cm; active area exposed to solution ~0.78 cm^2) were placed in aqueous perchlorate solution ($KClO_4$, 50 mM, Aldrich) containing $Cu(NO_3)_2{\cdot}3H_2O$ (4 mM, Aldrich) and $Fe(ClO_4)_3{\cdot}H_2O$ (12 mM, Aldrich). They were then held at −0.36 V vs. SCE (saturated calomel electrode) for 2 h by a potentiostat/galvanostat (CompactStat, Ivium). A platinum gauze was used as the counter electrode. After drying in air, the as-deposited samples were annealed at 650 °C for 3 h in air. For comparison, $CuFeO_2$ electrodes were also fabricated by annealing the as-deposited samples at 650 °C for 2 h under an Ar atmosphere. For the fabrication of CuO electrodes, electrodeposition was performed in aqueous perchlorate solution with $Cu(NO_3)_2{\cdot}3H_2O$ (4 mM, Aldrich), followed by annealing at 650 °C for 2 h under an air atmosphere.

2.2. Photoelectrochemical seawater uranium conversion

Hexavalent uranium (U(VI)) stock solutions (30 or 100 ppm) were prepared weekly by dissolving uranyl nitrate ($UO_2(NO_3)_2{\cdot}6H_2O$, purity >98.0%, Sigma Aldrich) in natural seawater derived from the East Sea, Korea (latitude: 36.13°, longitude: 129.40°). Before using, the sampled seawater was filtered through 0.45-μm PTFE membranes (Millipore) to remove particulate matter. Detailed information on the ionic composition of seawater is available elsewhere [15]. CFO, SCE, and Pt foil were placed in a customized Teflon reactor with air-equilibrated seawater (50 mL) in the absence or presence of U(VI) at varying pH values (3, 6, 8.2, and 10.4; unless otherwise specified, ~8.2). Potentials swept at a scan rate of 50 mV s^{-1} or constant potentials were applied to the CFO electrode using an electrochemical workstation (CompactStat, Ivium) in the dark or under simulated light of air mass 1.5 light (AM 1.5). A 150-W Xenon arc lamp (ABET Tech.) equipped with an AM 1.5 filter was used as the light source with a light intensity of 100 mW cm^{-2} (1 sun), unless otherwise specified. Light was irradiated on the backside of the CFO electrodes (FTO side). If necessary, N_2 (>99.9%) was purged through the solution during experiments.

During the photoelectrochemical (PEC) experiments at constant potentials (−0.4, −0.5, and −0.6 V vs. SCE; hereafter SCE is omitted for simplicity, unless otherwise specified), aliquots (0.5 mL) were intermittently sampled for uranium analysis while recording currents. Quantification of U(VI) was completed using a spectrophotometric method with Arsenazo III ($(HO)_2C_{10}H_2(SO_3H)_2(N{=}NC_6H_4AsO_3H_2)_2$) as a chelating indicator of U(VI) [15]. This method has been shown to be accurate, reliable, and selective for hexavalent uranium [18,19], with no interference from seawater ions [20–22]. Details of the analytical method are described in the *Supplementary Information*. In addition, the total uranium remaining in seawater was quantified using inductively coupled plasma (ICP) spectrometry (Perkin Elmer, Optima 7300DV). The ICP standard solution of uranium (100 ± 10 ppm, GFS Chemicals) in 5% nitric acid was used for the measurements. To examine the oxidation states of uranium in solution, hydrous titania adsorbents with a high surface area (>300 $m^2\,g^{-1}$) were prepared following a literature procedure [15]. The Faradaic efficiency of U(VI) conversion was estimated using the following equation:

$$\text{Faradaic efficiency } (\%) = \frac{\left[U^{(6-n)+}\right](\text{mol}) \times n}{\text{total current (A)} \times \text{time (s)}} \times F \times 100$$

where, $U^{(6-n)+}$ refers to uranium species with an oxidation state of $(6-n)+$, n is the number of electrons, and F is the Faraday constant (96,485 C mol^{-1}).

2.3. Surface characterization

The surface morphology and composition of CFO were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) equipped with energy-dispersive X-ray spectroscopy (EDS). The crystalline patterns of CFO were examined by X-ray diffraction (XRD, Rigaku D/Max-2500). The electrophoretic mobilities of CFO particles collected from the as-synthesized electrodes were measured to estimate their zeta potentials as a function of pH using an electrophoretic light scattering spectrometer (Zetasizer, Malvern) equipped with a He–Ne laser and thermostated flat board cell [23].

3. Results and discussion

3.1. Photocatalyst characterization

As-fabricated CFO films possessed a porous, double-layer structure with a ~0.5 μm thick underlayer and a ~3 μm thick porous overlayer (Fig. 1a). A uniformly formed underlayer acted as a seed layer, on which particles grew and interconnected, creating a blossom-like porous morphology (Fig. 1b). This double-layer configuration is unique, particularly in aqueous electrodeposition processes [16]. EDS analysis indicates that Cu and Fe were deposited simultaneously (Fig. 1c) and that their composition was uniform over the entire surface (Fig. 1d–f). However, the atomic ratio of Cu and Fe was not stoichiometric (Cu/Fe = ~1.55; see Fig. S1), suggesting that the synthesized sample was not a pure spinel (*e.g.*, $CuFe_2O_4$) or delafossite (*e.g.*, $CuFeO_2$). XRD characterization of the as-fabricated CFO films was performed to examine their crystalline structure (Fig. 2). Most of the XRD peaks were assigned