Synergistic Bilayer-modified Electrode and Pulse Electrochemistry for Efficient Uranium Extraction from Seawater

Authors: Peng, Jian-Yi, Chen, Ms. Qin, Chen, Xiaomei, Ms. Zi-Yue Zhu, He, Ms. Jing, Ms. Qin-Qin Fan, Zhen-Ju Jiang, Wang, Dr. Yu, Dr. Jing Feng, Feng, Dr. Jing

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Abstract

The extraction of uranium from seawater is crucial for sustainable nuclear energy but remains challenging due to low concentration, carbonate competition, and energy-intensive processes. Herein, this study developed and systematically evaluated a novel electrode material, CF@MTPN, coupled with the energy-efficient double potential step technique (DPST) for the highly efficient extraction of uranium from seawater. CF@MTPN was fabricated through sequential self-assembly of iron-tannic acid (Fe-TA) network and an iron-phytic acid (Fe-PA) complex on carbon felt. In simulated seawater (5 mg L -1 uranyl, 2 mM Na 2 CO 3 , pH 8.1), CF@MTPN achieved rapid uranium removal efficiencies of 90.3% (potentiostatic technique, PST) and 93.3% (DPST) within 15 min, with corresponding extraction capacities of 96.12 and 99.31 mg g -1 d -1 , respectively. Notably, during the DPST process (0 V/-1.3 V), current oscillations led to the detachment of the Fe-PA layer from the control electrode CF@MPN, alongside progressive oxidation of the bare CF surface. In contrast, the introduction of an inner Fe-TA layer in CF@MTPN effectively resolved these stability issues, allowing CF@MPN to maintain its structural integrity throughout an extended DPST operation. Moreover, DPST dramatically enhanced the Faradaic efficiency by 430% over PST by effectively suppressing the competing hydrogen evolution reaction. Practical viability was confirmed through a continuous-flow experiment with 20 L of natural seawater, achieving a uranium recovery of 60.0 g and a high extraction capacity of 3.62 mg g -1 d -1 over 5 h. This work presents a synergistic material and process solution for efficient, stable, and energy-conscious uranium extraction from seawater.

Full Text

Preamble

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Jian-Yi Peng[1], Qin Chen[1], Xiao-Mei Chen[1], Zi-Yue Zhu[1], Jing He[1], Qin-Qin Fan[1], Zhen-Ju Jiang[1],[2], Yu Wang[3], Jing Feng[1],[2]

Abstract

The extraction of uranium from seawater is crucial for sustainable nuclear energy but remains challenging due to low concentration, carbonate competition, and energy-intensive processes. Herein, this study developed and systematically evaluated a novel electrode material, CF@MTPN, coupled with the energy-efficient double potential step technique (DPST) for the highly efficient extraction of uranium from seawater. CF@MTPN was fabricated through sequential self-assembly of iron-tannic acid (Fe-TA) network and an iron-phytic acid (Fe-PA) complex on carbon felt. In simulated seawater (5 mg L^{-1} uranyl, 2 mM Na_2CO_3, pH 8.1), CF@MTPN achieved rapid uranium removal efficiencies of 90.3% (potentiostatic technique, PST) and 93.3% (DPST) within 15 min, with corresponding extraction capacities of 96.12 and 99.31 mg g^{-1} d^{-1}, respectively. Notably, during the DPST process (0 V/−1.3 V), current oscillations led to the detachment of the Fe-PA layer from the control electrode CF@MPN, alongside progressive oxidation of the bare CF surface. In contrast, the introduction of an inner Fe-TA layer in CF@MTPN effectively resolved these stability issues, allowing CF@MPN to maintain its structural integrity throughout an extended DPST operation. Moreover, DPST dramatically enhanced the Faradaic efficiency by 430% over PST by effectively suppressing the competing hydrogen evolution reaction. Practical viability was confirmed through a continuous-flow experiment with 20 L of natural seawater, achieving a uranium recovery of 60.0 g and a high extraction capacity of 3.62 mg g^{-1} d^{-1} over 5 h. This work presents a synergistic material and process solution for efficient, stable, and energy-conscious uranium extraction from seawater.

Keywords: Seawater uranium extraction · electrochemical extraction · double potential step technique · phytic acid · iron-tannic acid network

Introduction

Nuclear power, characterized by its ultra-low greenhouse gas emissions, has been extensively developed over the past few decades to provide large-scale electricity [1]. Its total power generation capacity is expected to increase significantly in coming decades, and may increase by as much as 82% by 2050 to meet the demands of emerging markets and global population growth [2]. As a key nuclear fuel, uranium plays an indispensable role in the nuclear fuel cycle and is widely used in nuclear power plants worldwide [3]. However, according to the International Atomic Energy Agency (IAEA), known terrestrial uranium reserves are insufficient to meet the rising consumption demands, potentially causing supply shortages within this century [4, 5]. Given that seawater contains over one thousand times more uranium than terrestrial reserves, researchers have focused on developing efficient extraction technologies to recover uranium from seawater [6, 7]. Furthermore, uranium is a severe environmental pollutant due to its bioaccumulation, non-degradability, and persistence, posing serious ecological and human health risks even at low concentrations [8]. Consequently, the effective separation, enrichment, and reuse of uranium from contaminated sources have emerged as a crucial complementary strategy, serving the dual purposes of sustainable nuclear fuel acquisition and environmental remediation [9, 10].

Physicochemical adsorption and electrochemical methods have been utilized for uranium extraction, where capacity, kinetics, and selectivity are the general evaluation criteria [11]. Physicochemical adsorption, taking phosphate- and amidoxime-functionalized materials as the prominent reagents, immobilizes uranium onto adsorbent surfaces but is limited by slow adsorption kinetics and competitive cation adsorption (e.g., Fe^{3+}, Mg^{2+} and Ca^{2+}) [12, 13]. In contrast, electrochemical extraction has garnered significant interest due to its superior uranium enrichment capacity, fast extraction kinetics driven by the electric field, high selectivity enabled by adjusting the work voltage, and compatibility with device integration and miniaturization [14-16]. Moreover, offshore tidal and solar energy conversion technologies have reached large-scale commercial deployment (e.g., in projects like StEnSea), and this development would provide a practical power supply for electrochemical extraction processes [17-19].

The uranyl ion ($UO_2{}^{2+}$) is the dominant form of uranium in both seawater and nuclear wastewater, possessing two axial oxygen atoms and four to six coordination sites in the equatorial plane [20]. Coordination reactions are thermodynamically favorable, with common ligands including OH^-, Cl^-, H_2O, $PO_4{}^{3-}$, and $CO_3{}^{2-}$. Among these, $CO_3{}^{2-}$ exhibits the strongest binding affinity for uranyl due to combined electronic and structural effects. In seawater (pH 8.1), the $CO_3{}^{2-}$ concentration (~0.15 mM) is approximately four orders of magnitude higher than that of uranyl, leading to the preferential formation of uranyl-carbonate complexes and thereby hindering uranyl immobilization by physicochemical adsorption [21, 22]. By modulating the applied voltage, cathodes can provide tunable electron donation to uranyl and thus overcome the interference from $CO_3{}^{2-}$. However, seawater also contains abundant competing cations (e.g., Na^+, Mg^{2+}, Ca^{2+}, K^+), which inhibit uranyl electrosorption via electrostatic screening and the mass action effect. Recent studies have employed high-frequency pulsed strategy to mitigate interference from non-target species and water splitting [23-25]. However, during the pulsed electrochemical process, the interruption of the electric field can result in a reverse current, electrode passivation, and other undesirable changes in surface properties.

Enhancing electrode stability therefore requires disrupting these self-sustaining feedback loops, which can be achieved through strategic electrode material modification and precise control of the potential window. To address these stability challenges while maintaining high affinity for uranyl, we turned to a bilayer electrode design leveraging the complementary properties of phytic acid (PA) and tannic acid (TA). PA, with its six phosphate groups and flexible skeleton, can effectively form multidentate chelates with uranyl even in the presence of a high concentration of ${CO_3}^{2-}$ [26-28]. Moreover, its in situ oxidation produces ${PO_4}^{3-}$ and forms the irreversible crystalline core of $(UO_2)_3(PO_4)_2 \cdot 4.8H_2O$ and $Na_2O(UO_3 \cdot H_2O)x$ precipitate. Although it is easily soluble in water, PA has been employed as a functional layer on electrode materials (e.g., by adsorbing it onto conductive substrates like polypyrrole) for electrochemical uranium extraction [29, 30]. Unfortunately, under acidic conditions ($pH < 4$), PA is easily desorbed from these substrates. Under alkaline conditions ($pH > 9$), its phosphoester bonds (P-O-C) are susceptible to hydrolysis, resulting in structural collapse and loss of function. In the electrochemical reaction, the hydrolysis of P-O-C is accelerated by the oxidation current, leading to poor stability and phase separation of the electrode material.

Fe-TA networks have been reported as promising materials in various research fields due to their good compatibility, pH responsiveness, high adsorption capacity, ease of synthesis, and excellent stability over a wide pH range [31-34]. Fe-TA networks act as tunable buffering systems that maintain the local pH by altering their coordination states, exhibiting approximately twofold and fourfold higher buffering capacity than polyelectrolyte complexes and commercial buffer solutions, respectively [35]. Furthermore, their abundant hydroxyl groups (-O-H) can form multiple hydrogen bonds with the P=O groups of PA, leading to robust immobilization of PA even under high-voltage and low-pH conditions [36]. Physical entanglement further enhances the stability of PA immobilization. Similarly, Fe(III) ions can act as cross-linkers between PA (and/or TA) molecules, forming macromolecular networks (denoted as MPN and MTN) that significantly enhance the immobilization stability and resistance to hydrolysis of PA.

This work presents a TA- and PA-functionalized CF@MTPN electrode, which efficiently extracts uranium while exhibiting high resistance to interference from high concentrations of ${CO_3}^{2-}$. Additionally, it exhibits an intriguing electrochemical oscillatory phenomenon during the pulsed process, characterized by significantly weaker progressive oxidation and passivation compared to bare CF and CF@MPN.

Experimental Section

2.1. Chemicals

All chemicals were of at least reagent grade and were used as received without further purification. Detailed information on these chemicals is provided in the Supporting Information (Text S1).

2.2. Electrode Preparation

All electrodes were fabricated on pre-cleaned carbon felt (CF, 1.0 × 1.5 cm^2) via a sequential coordination-driven self-assembly process. The core design features a robust Fe-TA network as an inner stabilizing layer, followed by an Fe-PA complex as the outer uranium-binding layer.

A cleaned CF piece was immersed in 5 mL of aqueous TA solution (24 mM) for 10 min. Subsequently, 5 mL of $FeCl_3$ solution (24 mM) was added to form the initial Fe-TA coordination network upon gentle vortexing. The Fe-TA network on the CF substrate was stabilized by adding 10 mL of MOPS buffer (100 mM, pH 7.4). After standing for 10 min, the piece was retrieved and thoroughly rinsed with deionized water and ethanol, yielding the intermediate product CF@MTN. The as-prepared CF@MTN was further functionalized by immersing it in 2 mL of PA solution (24 mM) for 10 min. Then, 6 mL of $FeCl_3$ solution (24 mM) was added to cross-link the PA, followed by brief vortexing and a 10 min standing period. Subsequently, 10 mL of MOPS buffer was added to complete the assembly of Fe-PA. After aging for 10 min and thorough washing, the final product was obtained and denoted as CF@MTPN. For electrochemical measurements, the electrode (exposed area: 3.8 cm^2) was secured with a Pt clip. The average mass of the CF@MTPN electrode was 79.5 mg.

For comparison, a control electrode without the inner Fe-TA layer was prepared. A bare CF piece was directly subjected to the same PA/$FeCl_3$ coating procedure described above for the second step of CF@MTPN synthesis. This sample, designated as CF@MPN, was used to elucidate the critical role of the Fe-TA inner layer in enhancing electrode stability.

2.3. Characterization

Scanning electron microscopy imaging was performed on a Gemini 300 field-emission microscope (Zeiss, Germany) operating at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) was conducted on a Talos F200S microscope (FEI, USA) at 200 kV. X-ray diffraction (XRD) patterns were collected using an X'Pert PRO MPD diffractometer (Rigaku Smartlab, Japan) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were acquired on a Scientific K-Alpha spectrometer (Thermo Fisher, USA). Zeta potentials were determined with a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Austria). Water contact angles were measured at ambient temperature (~30% humidity) by the sessile drop method using a JY-PHa instrument (China). UV-Vis absorption spectra were recorded on a UV-2700 spectrophotometer (SHIMADZU, Japan). Fourier transform infrared (FTIR) spectra were obtained using a Nicolet spectrophotometer (Thermo Fisher, USA). The concentration of uranium adsorbed onto the material surfaces was quantified by inductively coupled plasma mass spectrometry (Agilent 7900, USA). The pH values of all electrolytes were measured with a PHS-2F pH meter (Leici, China). Electrochemical measurements, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS), were performed on a CHI 760E electrochemical workstation (China) employing a standard three-electrode system.

2.4. Electrochemical Measurements

All electrochemical measurements were performed using a CHI 760E electrochemical workstation under ambient conditions with a standard three-electrode configuration. The working electrodes were the as-prepared samples secured with Pt clips. A Pt wire and a saturated calomel electrode (SCE, in saturated KCl) were employed as the counter and reference electrode, respectively. CV and LSV were conducted at scan rates of 5 mV s^{-1}, respectively, unless otherwise stated. EIS measurements were carried out in a 10 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution over a frequency range from 100 kHz to 0.1 Hz. All potentials are reported versus the SCE unless specified.

2.5. Uranium Extraction Performance

The uranium concentration in solution was quantified using two complementary techniques, selected based on the solution matrix. For carbonate-free solutions, the concentration of residual ${UO_2}^{2+}$ was determined by the arsenazo III colorimetric method [37]. For solutions containing carbonate, which interferes with the colorimetric assay, inductively coupled plasma optical emission spectrometry (ICP-OES) was employed. All experiments were performed in triplicate, and the reported data are the average values. The uranium extraction efficiency (Removal, %) was calculated using Equation (1):

$$\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 (mg L^{-1}) is the initial concentration of uranium, and C_t (mg L^{-1}) is the concentration at time t.

2.6. Physicochemical Adsorption Experiment

Adsorption experiments were conducted at ambient temperature. Three pieces of the sample (1.0 × 1.0 cm^2 each) were added to 60 mL of uranyl solution (5 mg L^{-1}) under constant stirring. At predetermined time intervals, aliquots of the solution were withdrawn. The residual uranium concentration in these aliquots was analyzed by ICP-OES. The uranyl removal efficiency was calculated according to Equation (1). All experiments were performed in triplicate, and the reported data are the average values.

Results and Discussion

3.1. Material Characterization

Fig. 1 [Figure 1: see original paper]. (a) SEM and (b) High-resolution SEM of CF@MTPN. Scanning TEM and corresponding EDX elemental mapping images of (c) CF@MTN and (d) CF@MTPN. (e) XRD patterns of CF, CF@MPN, CF@MTN and CF@MTPN. XPS spectra in the (f) P 2p, (g) O 1s and (h) Fe 2p regions for CF@MTPN. FTIR spectra of (i) CF@MTN and (j) CF@MTPN. (k) Contact angles of water on the surfaces of CF, CF@MTN, CF@MPN and CF@MTPN after dripping 5 s. (l) Nyquist plots of CF, CF@MTN, CF@MPN and CF@MTPN.

The SEM images reveal that CF@MTPN exhibits a fibrous morphology with a diameter of 19.24 ± 0.53 m (Fig. 1a), and a rough surface decorated with numerous irregular nanoparticles (Fig. 1b). To study the formation process of CF@MTPN, SEM-EDS elemental mapping was used to investigate the surface element distribution of the intermediate CF@MTN and the final CF@MTPN. After the self-assembly of the Fe-TA complex on CF, the resulting CF@MTN shows uniform distributions of O and Fe elements (Fig. 1c). Subsequent self-assembly of the Fe-PA complex to form CF@MTPN resulted in a homogeneous distribution of O, P, and Fe (Fig. 1d). The EDX spectrum of CF@MTPN confirms the presence of C, O, P, and Fe on its surface, with weight percentages (wt.%) of 90.20, 8.10, 0.08, and 1.62, respectively (Fig. S1). As shown in Fig. 1e, the XRD patterns of CF, CF@MTN and CF@MTPN all exhibit two broad peaks at 24.5° and 44.3°, corresponding to the (002) and (100) crystal planes of carbon, respectively [38, 39]. The absence of new diffraction peaks after surface coating, compared to the pristine CF, suggests that the Fe-TA and Fe-PA coatings are amorphous in nature.

The XPS survey spectrum of CF@MTPN confirms the presence of C, O, P, and Fe on its surface (Fig. S2). In the P 2p spectrum (Fig. 1f), the peak at 132.8 eV corresponds to the phosphate ester group (-$OPO_3{}^{2-}$) of PA [40]. The O 1s spectrum (Fig. 1g) was deconvoluted into components corresponding to C-O/P-O-C and Fe-O bonds [41], further verifying the successful anchoring of the Fe-PA complex onto the CF@MTN surface. As shown in the Fe 2p spectrum (Fig. 1h), the multiplet splitting presents characteristic satellite features for both Fe $2p_3/_2$ and Fe $2p_1/_2$, located approximately 13.8 eV above their respective main peaks. The spectrum was fitted with peaks characteristic of Fe(II) (714.3 and 728.2 eV) and Fe(III) (710.4 and 724.4 eV) [42].

FTIR spectroscopy was employed to further confirm the successful modification. The spectrum of CF@MTN (Fig. 1i) shows two weak peaks at 1718 and 1448 cm^{-1}, ascribed to the C=O stretching vibration and the aromatic skeleton vibration of TA, respectively, indicating the formation of the Fe-TA complex on CF [43]. Similarly, the spectrum of CF@MTPN (Fig. 1j) exhibits characteristic peaks of PA at 1638 and 1092 cm^{-1}, assigned to the P=O and P-O-C vibrations [44], respectively, confirming the successful incorporation of the Fe-PA complex.

A significant drawback of carbon-based materials for electrochemical applications is their inherent hydrophobicity, as only the fraction of the surface wetted by the electrolyte contributes to the overall performance [45, 46]. To evaluate this property, the sessile drop method was conducted to compare the wettability of CF, CF@MTN, CF@MPN and CF@MTPN. As shown in Fig. 1k, pristine CF is hydrophobic, with a water contact angle of 131.6°. The Fe-TA coating rendered CF@MTN hydrophilic with the contact angle decreasing to 87.8° within 5 s of droplet deposition. CF@MPN, functionalized with Fe-PA, showed enhanced hydrophilicity with the contact angle decreasing to 44.6° within 5 s of droplet deposition. Remarkably, CF@MTPN—featuring the bilayer structure—demonstrated superhydrophilic behavior.

The interfacial wettability is intrinsically linked to electrochemical processes. Charge transfer dynamics, including specific adsorption, surface redox reactions, and complex interfacial interactions between the electrode, electrolyte ions, and solvent molecules, collectively influence surface tension and wettability [47]. EIS, often represented by Nyquist plots, is a powerful technique for characterizing these parameters and revealing the interfacial structure of the electrode/electrolyte interface [48]. Fig. 1l illustrates the EIS results for CF, CF@MTN, CF@MPN, and CF@MTPN, measured with an alternating-current amplitude of 5 mV at the open-circuit potential. The charge transfer resistance (Rct), derived from the semicircle diameter by fitting the data to an equivalent circuit model (Fig. S3) using Zview 2 software, is below 3 Ω for all electrodes, indicating highly efficient interfacial charge transfer.

3.2. Electrochemical Characterization

Fig. 2 [Figure 2: see original paper]. (a) Zeta potentials of CF, CF@MTN, CF@MPN and CF@MTPN in pure water. (b) CV curves of CF@MTPN in 0.1 M Na_2SO_4 solution at different scan rates. (c) Evaluation of the EDL capacitances for CF, CF@MTN, CF@MPN and CF@MTPN. (d) Voltammograms recorded on CF@MTN, CF@MPN and CF@MTPN at 30 mV s^{-1}, and (e) on CF@MTPN at various scan rates. The electrolytes contain 0.1 M KCl and 10 mM $[Fe(CN)_6]^{3-,4-}$. (f) Digital photos of the solutions before and after reaction. (g) FTIR spectra of $K_4[Fe(CN)_6]$ and the obtained precipitate. (h) The calibration curves of CF@MTPN between the peak current and the square root of scan rate in the $[Fe(CN)_6]^{3-,4-}$ redox reaction. (i) CV curves of CF@MTPN in 0.1 M Na_2SO_4 solution containing different concentrations of uranyl. (j) Scanning TEM and corresponding EDX elemental mapping images of the used CF@MTPN.

As shown in Fig. 2a, the Zeta potentials of CF, CF@MTN, CF@MPN and CF@MTPN in pure water were measured to be -8.44 ± 1.16, -26.18 ± 1.02, -29.92 ± 1.20, and -28.94 ± 1.18 mV, respectively. The significantly more negative Zeta potentials of the modified electrodes indicate successful coating, which introduces abundant negatively charged functional groups (e.g., phenolate and phosphate). This enhanced surface negativity is expected to favor the adsorption of cationic uranyl species.

The electrochemical properties of these electrodes were further evaluated by CV measurements in 10 mM $[Fe(CN)_6]^{3-},^{4-}$ at a scan rate of 50 mV s^{-1}. As shown in Fig. S4, the CV curve of CF@MTPN shows a prominent redox couple, with an oxidation peak at 0.66 V and a reduction peak at -0.23 V, corresponding to the $[Fe(CN)_6]^{3-},^{4-}$ redox reaction. The CV shapes suggest that CF@MPN and CF@MTPN might have lower electroactive surface areas but potentially faster electron transfer kinetics than CF@MTN. The EDL capacitances of the electrodes were evaluated using CV in 0.1 M Na_2SO_4 at various scan rates (CF: Fig. S5; CF@MTN: Fig. S6; CF@MPN: Fig. S7; CF@MTPN: Fig. 2b). The hydrophobic CF exhibited a very low EDL capacitance of only 0.25 mF cm^{-2} [49]. CF@MTN, coated with Fe-TA networks, showed the highest capacitance of 15.7 mF cm^{-2}. CF@MPN, coated with Fe-PA complex, had a lower capacitance of 7.9 mF cm^{-2}. Notably, CF@MTPN, featuring both Fe-TA and Fe-PA layers, displayed an intermediate capacitance of 13.0 mF cm^{-2}. This intermediate value suggests that the outer Fe-PA layer in CF@MTPN may partially limit ion access to the underlying Fe-TA layer compared to CF@MTN.

When the voltage window was expanded to -2 to 2 V, the CV profiles of CF@MTN, CF@MPN, and CF@MTPN in 10 mM $[Fe(CN)_6]^{3-},^{4-}$ revealed a significant change: a new reduction peak emerged at approximately 0.26 V (Fig. 2d), which is attributed to the reduction of Fe(III) species. Fig. 2e shows the CV curve of CF@MTPN alongside photographs of the solution before and after the reaction. A yellow precipitate formed continuously during the scan (Fig. S8). FTIR analysis of this precipitate (Fig. 2f) showed characteristic peaks assignable to $Fe(OH)_3$ and $K_4[Fe(CN)_6]$ [50].

To investigate the reaction kinetics, the peak currents were plotted against the square root of the scan rate ($^1/^2$). The oxidation peak current (I) of $[Fe(CN)_6]^{4-}$ exhibited a linear relationship with $^1/^2$ (I = 5.21 $^1/^2$ -3.63, R^2 = 0.998), as did the reduction peak current (I) of $[Fe(CN)_6]^{3-}$ (I = -5.58 $^1/^2$ + 3.65, R^2 = 0.999) (Fig. 2g). These linear dependencies confirm that both the oxidation and reduction processes are diffusion-controlled [51]. A similar phenomenon was observed for CF@MTPN in uranyl nitrate solution. As shown in Fig. 2h, the peak currents at approximately -0.5 and -1.2 V increase gradually with increasing uranyl concentration. SEM-EDS mapping of the electrode after use (Fig. 2i) revealed a uniform distribution of P, Fe, and U elements, confirming the effective co-deposition and enrichment of uranium.

3.3. Electrochemical Uranium Extraction

Fig. 3 [Figure 3: see original paper]. (a) CV curves of CF@MTN, CF@MPN and CF@MTPN electrodes in 0.1 M Na_2SO_4 solution containing 5 mg L^{-1} uranyl. (b) XPS U 4f spectrum of CF@MTPN after use. CV curves of CF@MTPN, (c) in which PA chelates with different metal ions and (d) in which PA chelates with different quantities of Fe(III). CV curves of CF@MTPN,

(e) in which TA chelates with different metal ions and (f) in which TA chelates with different quantities of Fe(III). (g) Schematic illustration of the preparation process of CF@MTN, CF@MPN and CF@MTPN.

Fig. 4 [Figure 4: see original paper]. (a) LSV curves of CF@MTPN in 0.1 M Na_2SO_4 with and without 5 mg L^{-1} uranyl. (b) Chronoamperometric curves and (c) the corresponding uranyl removal efficiency and charge consumption for 35 min potentiostatic adsorption process using CF@MTPN. (d) The influence of Na_2CO_3 in the physicochemical adsorption. (e) Uranium extraction performance by the electrochemical (-0.5 V) adsorption of CF@MTN, CF@MPN and CF@MTPN. LSV curves of (f) CF, (g) CF@MTN, (h) CF@MPN, and (i) CF@MTPN in 0.1 M Na_2SO_4 for consecutive rounds. Inset shows the electrochemical oxidation and initiative reduction mechanism for these electrodes.

The electrochemical behavior of uranyl ions was evaluated on CF@MTN, CF@MPN, and CF@MTPN electrodes in 0.1 M Na_2SO_4 containing 5 mg L^{-1} uranyl. While no distinct redox peaks were observed in the CV curves of CF@MTN and CF@MPN, CF@MTPN exhibited well-defined redox peaks (Fig. 3a), highlighting its superior activity for uranium electrodeposition. XPS analysis was employed to investigate the chemical states of elements on the CF@MTPN electrode surface before and after uranium electrodeposition (Fig. S9). The survey spectra revealed the emergence of two new peaks at 392.9 eV and 382.2 eV after electrodeposition, corresponding to U $4f_5/_2$ and U $4f_7/_2$ [52, 53], respectively, confirming the successful uptake of uranium. High-resolution scanning of the U 4f region (Fig. 3b) indicated the presence of mixed valence states, including U(IV), U(V), and U(VI). Based on the combined CV and XPS results, the cathodic peak at approximately -1.2 V can be attributed to the reduction of U(VI) to lower valence states, while the peak at -0.5 V is likely associated with the electrochemical adsorption of uranyl species onto the electrode surface.

To quantitatively evaluate the uranium extraction performance of the electrodes, the concentration of uranyl in the electrolyte was monitored using the arsenazo III colorimetric method. A calibration curve for the arsenazo III method was established using standard uranyl solutions prepared in the absence of carbonate (Fig. S10a), which exhibited an excellent linear relationship ($y = 0.07509x - 0.01323$, $R^2 = 0.999$) (Fig. S10b).

To further investigate the uranium electrodeposition behavior, CV was performed on different electrodes using the setup shown in Fig. S11 [54]. The optimization began with the outer Fe-PA layer (with the resulting electrodes denoted as CF@MTP' N). The choice of metal center significantly influenced the electrochemical response, with Cu(II) and Fe(III) yielding the highest reduction current associated with uranyl adsorption (Fig. 3c). Furthermore, optimization of the molar ratio of PA to Fe(III) revealed that a 1:3 ratio generated the maximum current response (Fig. 3d). Subsequently, the inner Fe-TA layer was optimized separately (with the resulting electrodes denoted as CF@MT' PN). Similarly, the choice of metal center was critical, again showing Cu(II) and Fe(III) to be the most effective (Fig. 3e). The molar ratio of TA to Fe(III) was also found to be optimal at 1:1, yielding the strongest CV signal for uranyl adsorption (Fig. 3f). Based on the practical advantage of easier separation, iron was ultimately selected over copper as the metal center for both coordination layers. A control experiment with CF@MPN (which contains only a Fe-PA layer and lacks the Fe-TA inner layer) confirmed the vital role of the bilayer structure, as it showed a significantly weaker response (Fig. S12). A schematic of the overall preparation process for CF@MTN, CF@MPN and CF@MTPN is provided in Fig. 3g.

The LSV curves of CF@MTPN (Fig. 4a) revealed a significantly higher current density in the presence of 5 mg L^{-1} uranyl at potentials more negative than -0.35 V, indicating additional electron consumption for uranyl reduction/adsorption. Chronoamperometric tests were conducted at controlled potentials from -0.1 to -0.6 V (Fig. 4b). The corresponding uranium removal rates and charge consumed (Q) are displayed in Fig. 4c, identifying -0.5 V as the optimal potential. At this optimal potential, CF@MTPN exhibited rapid kinetics, removing 96.6 ± 2.3% of uranyl within 35 min (Fig. S13). In the absence of carbonate, this electrochemical process achieved a high extraction capacity of 44.07 mg g^{-1} d^{-1} (1.05 mg cm^{-2} d^{-1}), which was significantly superior to physicochemical adsorption alone, which achieved only 14.2 ± 2.8% removal and a capacity of 6.48 mg g^{-1} d^{-1} (0.15 mg cm^{-2} d^{-1}). The presence of 2 mM Na_2CO_3 had a minor inhibitory effect on the electrochemical adsorption at -0.5 V but a greater impact on the physicochemical process (Fig. 4d). Quantitatively, the electrochemical extraction capacity in the presence of carbonate remained high at 42.61 mg g^{-1} d^{-1} (1.01 mg cm^{-2} d^{-1}), whereas the physicochemical adsorption capacity was only 2.55 mg g^{-1} d^{-1} (0.06 mg cm^{-2} d^{-1}).

Furthermore, the LSV responses of CF@MTN, CF@MPN, and CF@MTPN differed significantly (Fig. S14), which translated to marked differences in adsorption performance. At -0.5 V, the uranyl removal efficiencies after 35 min were 32.3%, 29.2%, and 96.3% for CF@MTN, CF@MPN, and CF@MTPN, respectively, unequivocally demonstrating the superior performance of the bilayer CF@MTPN electrode (Fig. 4e).

To elucidate the differences in adsorption performance, the surface properties of CF, CF@MTN, CF@MPN, and CF@MTPN were investigated using consecutive LSV. The first LSV cycles (Fig. S15) revealed distinct behaviors: CF exhibited a weak current; CF@MTN and CF@MTPN showed strong oxidation peaks at 0.42 and 0.62 V, respectively; and CF@MPN displayed only a weak peak at 1.1 V. Analysis over multiple cycles provided insights into the redox processes. CF exhibited a weak current and stepwise oxidation above 1.0 V (Fig. 4f). For CF@MTN, ten consecutive cycles (Fig. 4g) revealed a reversible oxidation peak at 0.40 V, attributable to hydroxyl group oxidation. The spontaneous reduction current upon interrupting the electric field indicates excellent surface antioxidant capacity and a reversible electron/proton transfer process. Moreover, the progressive increase in both oxidation and reduction current over cycles suggests an activation process, likely due to enhanced ion accessibility rather than mere electrolyte migration.

The behavior of CF@MPN differed significantly (Fig. 4h). The initial anodic peak at 1.1 V is assigned to electric-field-promoted hydrolysis of PA, even at neutral pH. This hydrolysis generates hydroxyl groups, which are then oxidized in the subsequent cycle at 0.40 V, accompanied by spontaneous reduction. Notably, CF@MTPN exhibited a strong initial oxidation peak at 0.62 V (Fig. 4i), which would be attributed to hydroxyl group oxidation, with the positive shift compared to subsequent cycles (0.40 V) being due to mass transport effects. The consistent observation of spontaneous reduction confirms the regeneration of hydroxyl groups and underscores superior antioxidant capacity compared to CF@MPN, as well as better reversibility than CF and CF@MTN. This conclusion is further supported by the tenth LSV cycles (Fig. S16), which show that CF@MTPN maintains the highest concentration of electroactive hydroxyl groups.

3.4. Double Potential Step Technique for Enhanced Extraction

Fig. 5 [Figure 5: see original paper]. (a) LSV curves of CF@MTPN in 0.1 M Na_2SO_4 and 2 mM Na_2CO_3 electrolyte: effect of 5 mg L^{-1} uranyl addition. (b) Chronoamperometric curves of CF@MTPN during PST processes at controlled potentials ranging from -0.5 to -1.5 V. Performance of CF@MTPN in the PST and DPST processes: (c) Q and (d) uranium extraction efficiency. Inset shows the operating procedure of DPST. (e) LSV analysis of electrolytes from the DPST processes using a fresh CF@MTPN electrode. Pulsed current profiles of CF@MTPN over the first minute for steps from 0 V to (f) −0.5 V and to (g) −1.3 V, respectively. (h) Chronoamperometric curves for bare CF and (i) CF@MPN during DPST from 0 V to −1.3 V.

As shown in Fig. 5a, the addition of 2 mM Na_2CO_3 did not obscure the clear differences in the LSV curves of CF@MTPN with and without uranyl, sustained indicating electron consumption attributable to uranium extraction. Subsequently, potentiostatic (PST) and double potential step (DPST) techniques were employed to extract uranium from simulated seawater (0.1 M Na_2SO_4, 5 mg L^{-1} uranyl, and 2 mM Na_2CO_3, pH 8.1). Fig. 5b presents the chronoamperometric curves of PST processes for CF@MTPN at potentials from −0.5 to −1.5 V. At -1.5 V, the electrode current increased significantly over time, which is attributed to a sharp drop in solution pH that promotes the hydrogen evolution reaction (HER). This pH drop likely results from vigorous oxygen evolution at the counter electrode (Fig. S17). Visible hydrogen bubbles on the CF@MTPN electrode at -1.5 V (Fig. S18) further confirm significant HER activity. From an energy efficiency standpoint, HER is an undesirable competing reaction that should be minimized. Pulse voltammetry has been widely employed in numerous studies to mitigate this issue [55, 56].

Figs. S19–S24 show the chronoamperometric curves of the DPST processes

(-0.5 to -1.5 V) for CF@MTPN at a frequency of 400 Hz, with a power-on to power-off time ratio of 3:2. Fig. 5c compares Q during the PST and DPST processes, with the inset illustrating the operating procedure of DPST. The DPST processes exhibit more stable currents and significantly lower Q compared to PST, along with highly efficient uranium extraction (Fig. 5d). In 15 min, CF@MTPN achieved uranium removal efficiencies of 90.3% and 93.3% using the PST and DPST methods (-1.3 V), respectively. The corresponding extraction capacities were 96.12 mg g^{-1} d^{-1} (2.28 mg cm^{-2} d^{-1}) for PST and 99.31 mg g^{-1} d^{-1} (2.36 mg cm^{-2} d^{-1}) for DPST. Most importantly, at the optimal potential of -1.3 V, DPST enhanced the Faradaic efficiency by 430% compared to the PST, as calculated from the Q values. This dramatic enhancement underscores the superior energy efficiency of the pulsed electrochemical approach.

To further assess the solution after electrochemical extraction, the electrolyte obtained from each DPST process was analyzed by LSV using a fresh CF@MTPN electrode (Fig. 5e). The reduction current intensity at -1.0 V decreased in the following order based on the potential applied during electrolyte generation: -0.5 V > -0.7 V > -0.9 V > -1.2 V -1.5 V > -1.3 V. This trend demonstrates that the spent electrolyte from processes at more negative potentials contains less residual uranyl, confirming the extraction efficiency. Moreover, the sensitive response of the electrode to varying uranyl concentrations highlights its potential for detecting uranyl in carbonate-containing aqueous solutions.

Fig. 5f displays the pulsed current profile of CF@MTPN during the initial minute of the DPST process (periodically switching between 0 V and -0.5 V). The current oscillates periodically, with its amplitude stabilizing after approximately 0.2 s. Notably, a reverse current is observed immediately upon switching off the applied voltage. This is attributed to the discharge of the electrical double layer (EDL), as cations (e.g., Na^{+}) that had migrated to the cathode under the electric field diffuse back into the bulk solution. A similar current behavior was observed for CF@MTN and CF@MPN (Figs. S25 and S26), consistent with a universal EDL formation and relaxation mechanism.

When the cathodic potential was increased to -1.3 V, the current amplitude of CF@MTPN also stabilized rapidly (Fig. 5g). In this case, the reduction current amplitude significantly exceeded the oxidation current, indicating Faradaic reduction processes—such as uranyl reduction and HER—contribute alongside EDL charging. Crucially, digital photos of the electrode during the DPST process at both -0.5 V and -1.3 V show no visible gas bubbles (Fig. S27). In direct comparison to the PST process (Fig. 5c and Fig. S18), where vigorous HER was evident, the DPST process effectively suppresses this undesirable side reaction.

In a separate experiment, the DPST process (periodically switching between 0 V and -1.3 V) applied to bare CF resulted in a gradual increase in the pulsed current amplitude (Fig. S28). This suggests the progressive transformation of the originally hydrophobic CF surface via electrochemical oxidation, rendering it more hydrophilic. Contact angle measurements confirmed this, showing a decrease from 131.6° to 64.0° after use (Fig. S29). As shown in Fig. 5h, the pulsed current on CF under the same DPST conditions was much lower than that on CF@MTPN (Fig. 5g) and CF@MTN (Fig. S30), consistent with its inferior wettability and lower capacitance. CF@MTN (Fig. S30) exhibited a higher pulsed current than CF@MTPN (Fig. 5g), which correlates with its higher EDL capacitance. For both CF@MTN and CF@MTPN, the reduction current amplitude exceeded the oxidation current, indicating concurrent Faradaic reduction reactions alongside capacitive charging.

Fig. 5i shows the chronoamperometric curve of CF@MPN during the DPST process. The current amplitude remained stable for the first 210 s. Around this point, a sharp decrease occurred, accompanied by the visible detachment of the modification layer from the electrode. Subsequently, the current behavior resembled that of bare CF, gradually increasing as the exposed carbon fiber surface was oxidized.

The superior performance of CF@MTPN for uranium extraction can be attributed to the synergistic effect of the Fe-TA layer and the DPST technique. The Fe-TA layer not only enhances the uranium extraction efficiency but also significantly improves the electrode stability, as evidenced by its intact structure after testing compared to the severe detachment observed for the CF@MPN electrode. Moreover, the DPST process itself is a key factor in enhancing the energy efficiency. The Q for CF@MTPN during DPST was significantly lower than during PST, while still achieving high extraction efficiency. This combination of low energy input and high output, coupled with the observed absence of bubbles on the electrode surface, confirms that the DPST process effectively mitigates HER compared to the conventional PST method.

3.5. Performance Evaluation in Natural Seawater

Fig. 6 [Figure 6: see original paper]. (a) Reaction device for the continuous uranium extraction from natural seawater. (b) XPS U 4f spectrum, and (c) Scanning TEM and corresponding EDX elemental mapping images of the used CF@MTPN. DPST is periodically switched between 0 V and -1.3 V at a frequency of 400 Hz with the power-on to power-off time ratio of 3:2.

To validate the practical applicability of the DPST extraction method based on the CF@MTPN electrode, a continuous-flow reaction system (Fig. 6a) was employed to extract uranium from 20 L of natural seawater. In this setup, a circulation pump transported seawater from a reservoir to the electrochemical reaction cell and back, maintaining a dynamic flow at a constant rate (5 mL min^{-1}). After 5 h of continuous operation, the chemical state of the extracted uranium on the CF@MTPN electrode was investigated by XPS. As shown in Fig. 6b, the recovered uranium was predominantly in the U(V) state. STEM and corresponding EDX elemental mapping (Fig. 6c) confirmed a homogeneous distribution of P, Fe, O, Na, and U on the electrode surface. The EDX spectrum (Fig. S32) showed that the wt.% of C, N, O, P, Fe, Na, and U were 49.10, 11.30, 28.20, 1.90, 7.60, 1.00, and 0.90, respectively.

The electrode was subsequently regenerated by immersion in 1.0 M Na_2CO_3 solution for 12 h. ICP-OES analysis of the eluent determined the total amount of recovered uranium to be 60.0 g, corresponding to an extraction efficiency of 90.88%. The calculated extraction capacity was 3.62 mg g^{-1} d^{-1} (0.086 mg cm^{-2} d^{-1}), which compares favorably with most reported adsorbents and electrocatalytic materials for seawater uranium extraction (Table S1). Regeneration by Na_2CO_3 solution effectively restored the composition of CF@MTPN, as shown by EDX spectroscopy (Fig. S33), which indicated wt.% of 88.32% (C), 9.75% (O), 0.09% (P), and 1.84% (Fe). SEM imaging (Fig. S34) confirmed that the morphology of the regenerated CF@MTPN remained similar to that of the pristine electrode. The excellent regenerability was further corroborated by FTIR (Fig. S35), XRD (Fig. S36) and XPS (Fig. S37) analyses, which showed nearly identical spectra before and after use. Finally, the LSV curve of the regenerated electrode in simulated seawater (Fig. S38) exhibited a clear enhancement in current density in the presence of uranyl, confirming the full retention of its electrochemical activity for uranium extraction.

Conclusion

This study successfully developed and systematically evaluated a novel electrode material, CF@MTPN, coupled with the electrochemical DPST for the highly efficient extraction of uranium from seawater. The bilayer modification structure of CF@MTPN, fabricated through sequential self-assembly of Fe-TA and Fe-PA complexes on CF, demonstrated superior performance. In simulated seawater (5 mg L^{-1} uranyl, 2 mM Na_2CO_3, pH 8.1), CF@MTPN achieved optimal efficiencies of 90.3% and 93.3% for uranium removal within 15 min using the PST and DPST methods, respectively. The corresponding extraction capacities were 96.12 mg g^{-1} d^{-1} (2.28 mg cm^{-2} d^{-1}) for PST and 99.31 mg g^{-1} d^{-1} (2.36 mg cm^{-2} d^{-1}) for DPST. Notably, the DPST enhanced the Faradaic efficiency for uranium extraction by 430% compared to PST. This improvement successfully addresses the low energy efficiency issue inherent in PST caused by the competing HER. The stable current and absence of gas bubble formation on the electrode surface during DPST collectively confirm that energy is more effectively directed toward the target uranium extraction reaction rather than side reactions.

The practical viability of this system was demonstrated in a continuous-flow experiment using 20 L of natural seawater. Over 5 h, a high uranium extraction efficiency of 90.88% was achieved, corresponding to an extraction capacity of 3.62 mg g^{-1} d^{-1}, which compares favorably with most reported adsorbents and electrocatalytic materials. Moreover, the electrode could be efficiently regenerated with Na_2CO_3 solution, with the regenerated electrode largely retaining its original compositional, morphological, and electrochemical properties.

In summary, this work, through innovative electrode design and advanced electrochemical process, provides an effective and promising solution to key challenges in seawater uranium extraction—namely, carbonate inhibition, stability, and energy consumption. It establishes a solid theoretical and technical foundation for the sustainable recovery of valuable yet potentially hazardous metals.

Declarations

Conflict of interest: The authors declare that they have no competing interests.

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