Supporting Information

Enhanced degradation of arsanilic acid and *in situ* recovery of inorganic arsenic in a two-stage bioelectrochemical process

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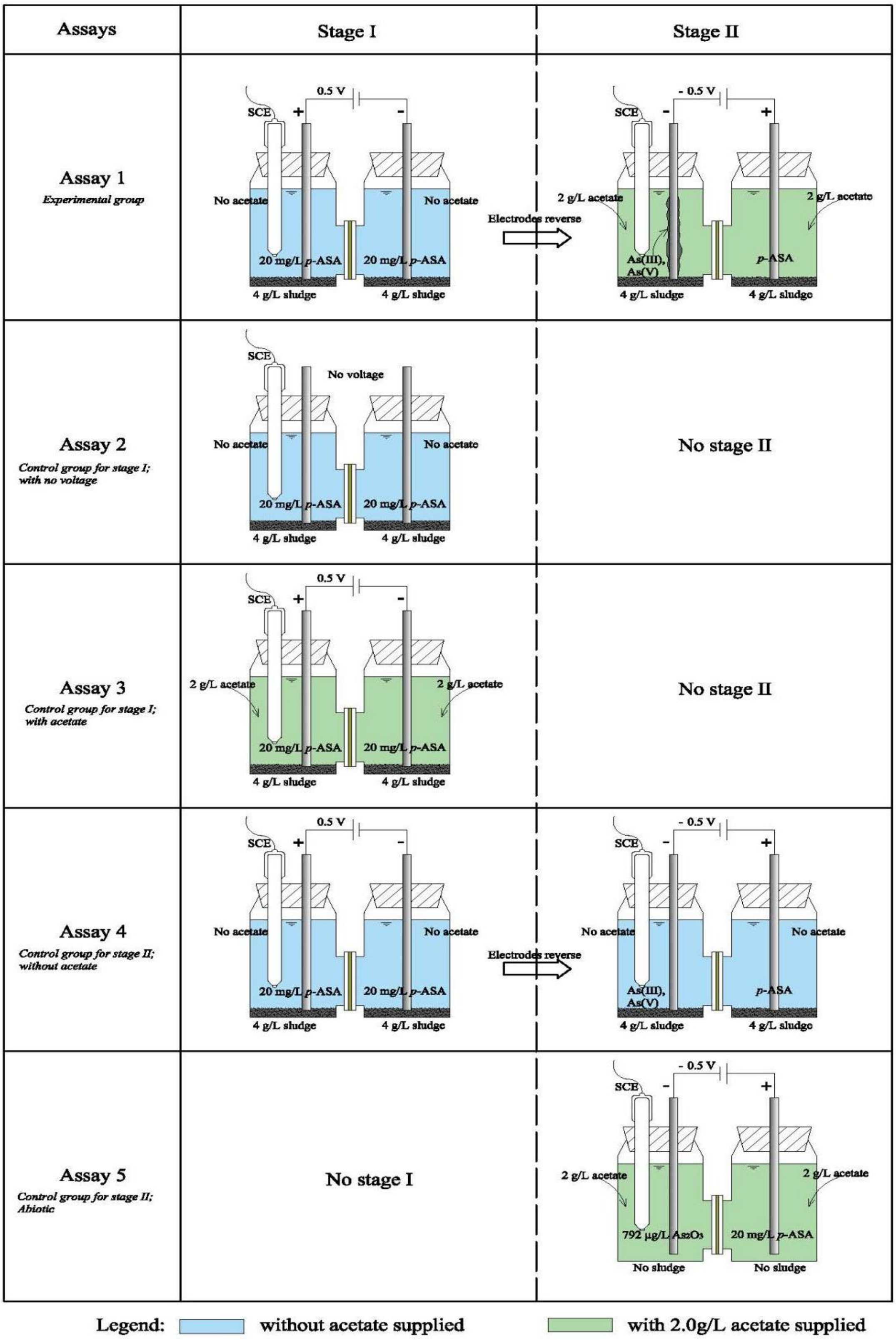

Fig. S1 Schematics of the BES reactor and the two-stage operation.

Solid-phase extraction procedure and GC-MS operational conditions

Solid-phase extraction was performed using C18 cartridges (Cleanert^{TM} S C18, Agela Technologies, China), with 100 mL of liquid samples slowly passed through the cartridges. After extraction, the cartridges were air-dried and then eluted using 10 mL of dichloromethane. The eluted solution was concentrated to 1.0 mL by N_2 flushing, followed by derivatization with 50 μL of bis(trimethylsilyl)-trifluoroacetamide (BSTFA, purity >90%, Sigma-Aldrich, the USA) for 12 h at room temperature. The temperature-program for the GC column was as follows: held at 40℃ for 3 min, then increased by 10℃/min to 280℃, where it was held for 5 min. The mass spectrometer was set to analyze within the m/z range of 20 − 500.

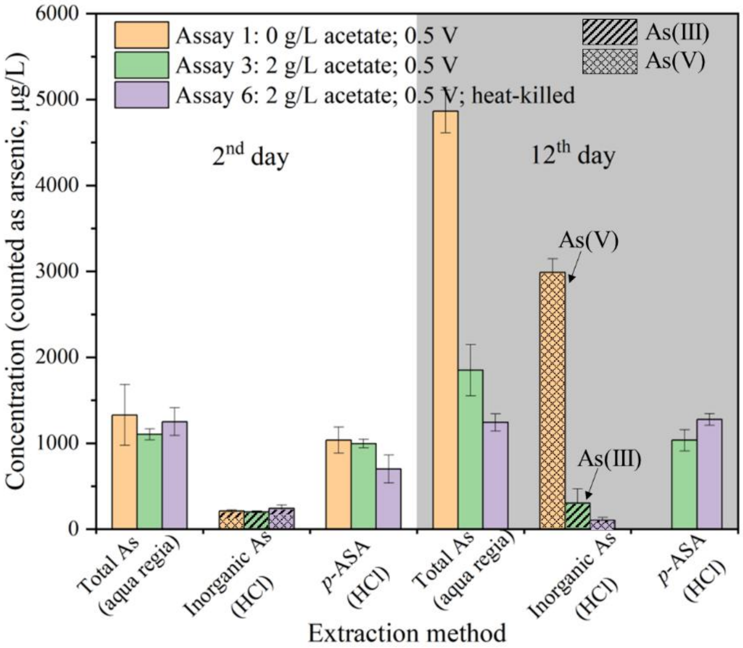

Fig. S2 Inorganic arsenic and *p*-ASA extracted from the sludge on the 2nd and 12th day. Note: Assay 6 was a new adsorption control using heat-killed sludge.

Extraction method for Fig. S2

The reactors were gently shaken to obtain a uniform mixture of sludge and liquor. Subsequently, 10 mL samples were collected from the chamber. After centrifugation at 3000 r/min for 5 min at 4℃, the supernatant was decanted, and the *p*-ASA concentration was determined using HPLC. The sludge at the bottom was then remixed with 20 mL of deionized water and subjected to ultrasonic treatment in a bio-mixer to break up the microbial cells. Aqua regia or HCl was then added to the tubes for extraction, which is shown as follows:

1) Aqua regia: 2.5 mL of suspension liquor was collected from the tube, mixed with 5 mL of aqua regia (50%), and digested under 100℃ of water bath for 2 h.

2) HCl: 2.5 mL of suspension liquor was collected from the tube, mixed with 5 mL of HCl (5%), and placed in a bench shaker operating at 100 r/min for 10 h.

After extraction, AFS and HPLC were used to determine the concentrations of inorganic arsenic and *p*-ASA dissolved from the sludge, respectively.

Implication of Fig. S2

Aqua regia transformed all the organoarsenics, including *p*-ASA, into inorganic arsenic. Therefore, the concentration of arsenic after aqua regia extraction represented the total arsenic in the sludge. HCl gently dissolved the arsenic in the sludge by changing the pH conditions of the solution. From the data, it is deduced that the majority of arsenic was present in the form of *p*-ASA on the 2nd day, while only inorganic arsenic was present in the sludge on the 12th day due to complete *p*-ASA degradation.

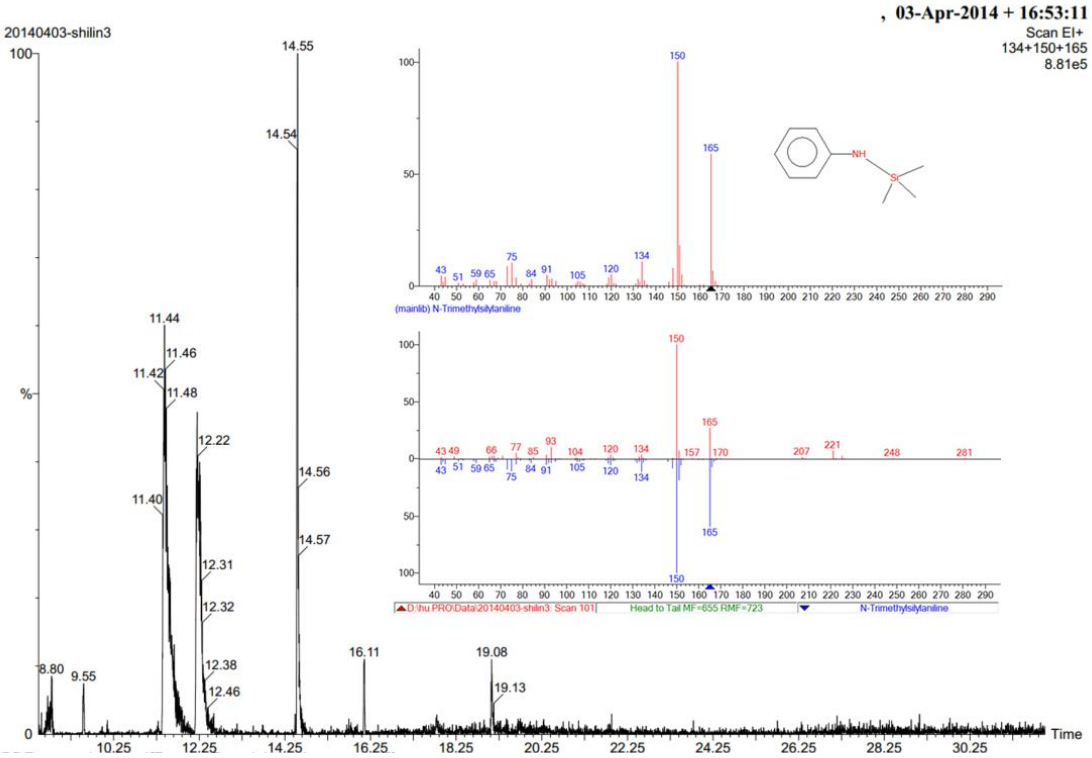

Fig. S3 GC-MS analysis of intermediates from *p*-ASA degradation in Assay 1.

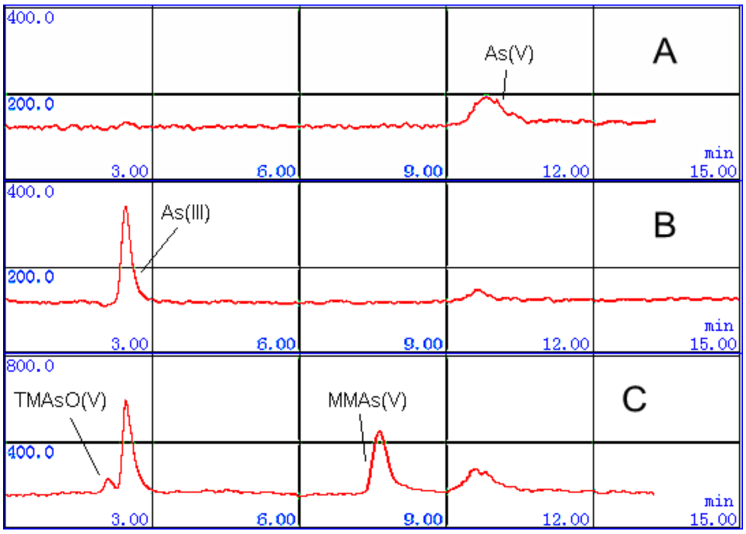

Fig. S4 Speciation of arsenic in Assay 1 on the 10th day (A), 15th day (B) and 22th day (C).

Calculation of the electrode potential in real conditions

Standard potential:

$$\mathrm{H_3AsO_4{+}2H^+{+}2e^-} \longrightarrow \mathrm{HAsO_2{+}2H_2O}\ E^0_{298}{=}0.560\mathrm{V}\ \text{(S1)}$$

$$\mathrm{HAsO_2{+}2H^+{+}3e^-} \longrightarrow \mathrm{As{+}2H_2O}\ E^0_{298}{=}0.248\mathrm{V}\ \text{(S2)}$$

$$\mathrm{As{+}3H^+{+}3e^-} \longrightarrow \mathrm{AsH_3}\ E^0_{298}{=}-0.238\mathrm{V}\ \text{(S3)}$$

Calculation:

$$\begin{aligned}
\varphi^{15d}_{As(V)/As(III)} &= \varphi^{\theta}_{308} - \frac{RT}{zF}\ln\prod a^{v} \\
&= \varphi^{\theta}_{308} - \frac{8.314J\cdot mol^{-1}\cdot K^{-1}\times 308.15K}{2\times 96485.31C\cdot mol^{-1}}\times 2.3\times \lg\frac{[\mathrm{HAs}O_2]}{[\mathrm{H_3AsO_4}][H^+]^2} \\
&= 0.56 - 0.0305\times\left\{\lg\frac{483}{131} - 2\lg 10^{-7.5}\right\} = 0.56 - 0.0305\times(0.5667+15) \\
&= 0.085V
\end{aligned}$$

$$\begin{aligned}
\varphi^{22d}_{As(V)/As(III)} &= \varphi^{\theta}_{308} - \frac{RT}{zF}\ln\prod a^{v} \\
&= \varphi^{\theta}_{308} - \frac{8.314J\cdot mol^{-1}\cdot K^{-1}\times 308.15K}{2\times 96485.31C\cdot mol^{-1}}\times 2.3\times \lg\frac{[\mathrm{HAs}O_2]}{[\mathrm{H_3AsO_4}][H^+]^2} \\
&= 0.56 - 0.0305\times\left\{\lg\frac{49.35}{470.89} - 2\lg 10^{-7.5}\right\} \\
&= 0.56 - 0.0305\times(-0.9796+15) = 0.132V
\end{aligned}$$

$$\begin{aligned}\varphi_{As(III)/As(0)}^{15d} &= \varphi_{308}^{\theta} - \frac{RT}{zF}\ln\prod a^{v} \\ &= \varphi_{308}^{\theta} - \frac{8.314J\cdot mol^{-1}\cdot K^{-1}\times 308.15K}{3\times 96485.31C\cdot mol^{-1}}\times 2.3\times \lg\frac{1}{[\mathrm{HAs}O_2][H^+]^3} \\ &= 0.248 - 0.0204\times\left\{\lg\frac{1}{0.000483/75} - 3\lg 10^{-7.5}\right\} \\ &= 0.248 - 0.0204\times(5.1911+22.5) = -0.317V\end{aligned}$$

$$\begin{aligned}\varphi_{As(III)/As(0)}^{22d} &= \varphi_{308}^{\theta} - \frac{RT}{zF}\ln\prod a^{v} \\ &= \varphi_{308}^{\theta} - \frac{8.314J\cdot mol^{-1}\cdot K^{-1}\times 308.15K}{3\times 96485.31C\cdot mol^{-1}}\times 2.3\times \lg\frac{1}{[\mathrm{HAs}O_2][H^+]^3} \\ &= 0.248 - 0.0204\times\left\{\lg\frac{1}{0.00004935/75} - 3\lg 10^{-7.5}\right\} \\ &= 0.248 - 0.0204\times(6.1818+22.5) = -0.344V\end{aligned}$$

$$\begin{aligned}\varphi_{As(0)/AsH_3}^{22d} &= \varphi_{308}^{\theta} - \frac{RT}{zF}\ln\prod a^{v} \\ &= \varphi_{308}^{\theta} - \frac{8.314J\cdot mol^{-1}\cdot K^{-1}\times 308.15K}{3\times 96485.31C\cdot mol^{-1}}\times 2.3\times \lg\frac{a(AsH_3)}{[H^+]^3} \\ &= -0.608 - 0.0204\times\left\{\lg\frac{p(AsH_3)}{p^{\theta}} - 3\lg 10^{-7.5}\right\} \\ &= -0.608 - 0.0204\times(-2+22.5) = -1.026V\end{aligned}$$

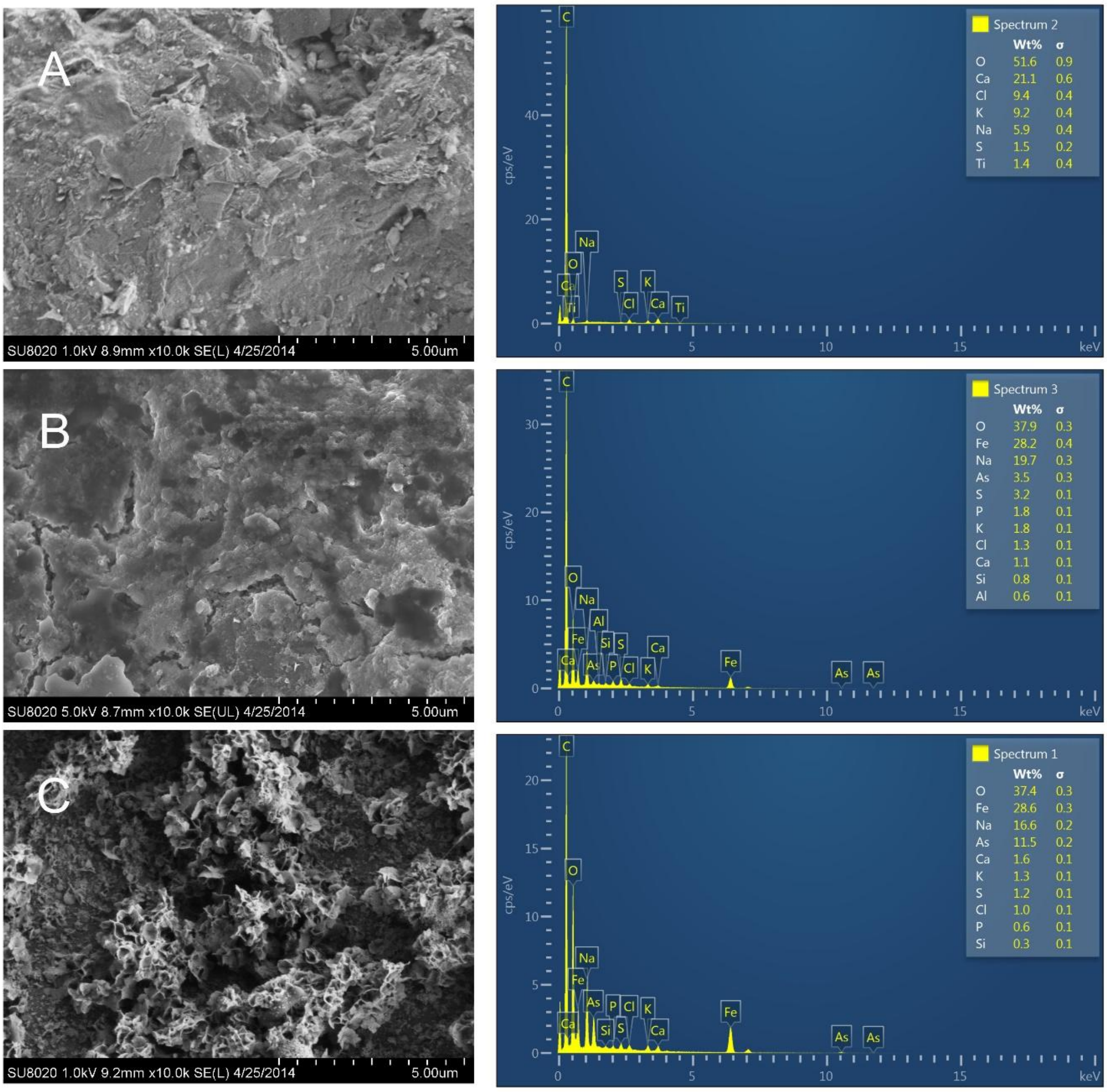

Fig. S5 Corresponding EDS scan of the electrodes described in the article. (A) is the anode before Stage I, (B) is the anode after Stage I, while (C) is the cathode after Stage II.

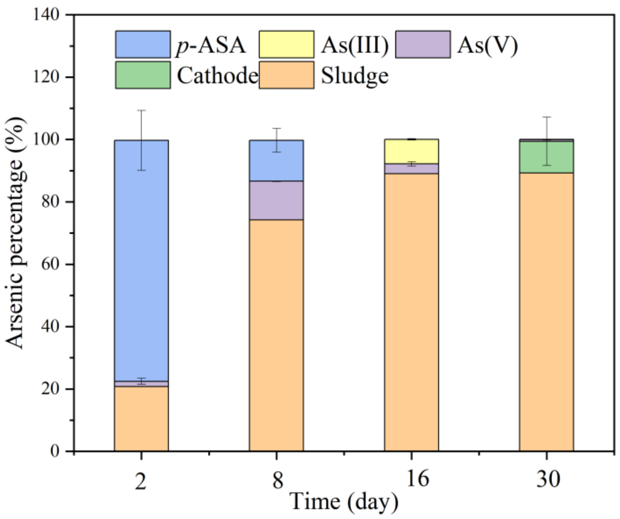

Fig. S6 Distribution of arsenic in the working chamber of Assay 1 on the 2nd, 8th,16th and 30th day (calculated based on the arsenic concentration in Assay 1).

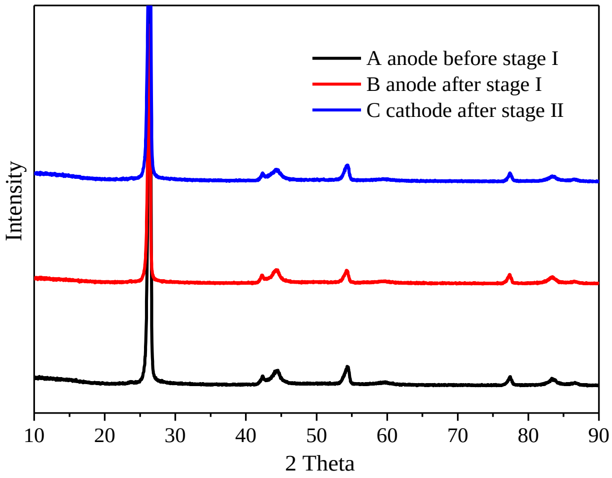

Fig. S7 The XRD spectra of different electrodes that are described in the article. A is the anode before Stage I, B is the anode after Stage I, while C is the cathode after Stage II.

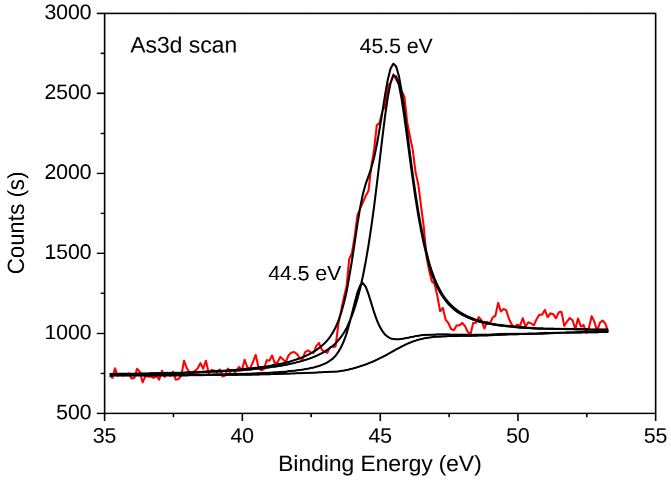

Fig. S8 XPS spectra of the cathode after Stage II.

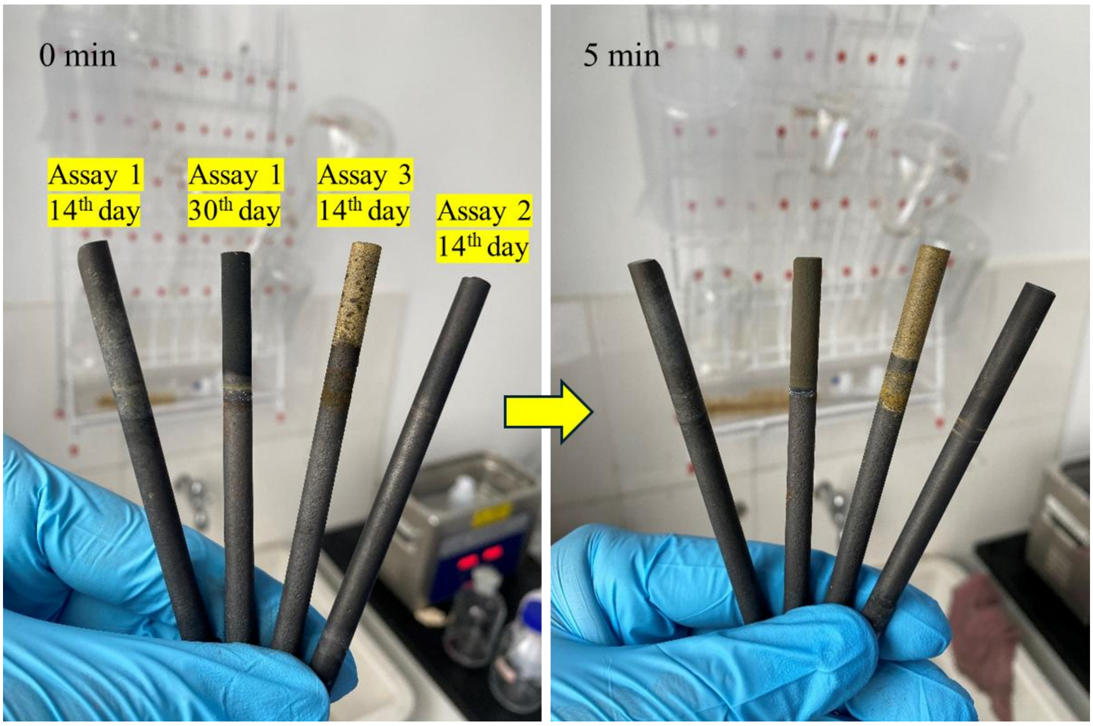

Fig. S9 Photographs of the fresh working electrodes collected from the reactor and naturally dried after 5 min.