

A sunlight assisted dual purpose photoelectrochemical cell for low voltage removal of heavy metals and organic pollutants in wastewater

Gwangjun Kim, Ebenezer T. Igunnu and George Z. Chen*

Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

* Email: george.chen@nottingham.ac.uk

Supporting information

S1. XRD pattern of WO₃

The WO₃ powder used in this work was purchased from Aldrich-Sigma. In addition to SEM inspection (Fig. 4), the powder was analysed by XRD before and after heating at 200 °C in air for 30 min. Almost identical XRD patterns were obtained, and the pattern of the heat treated powder is shown in Fig. S1.

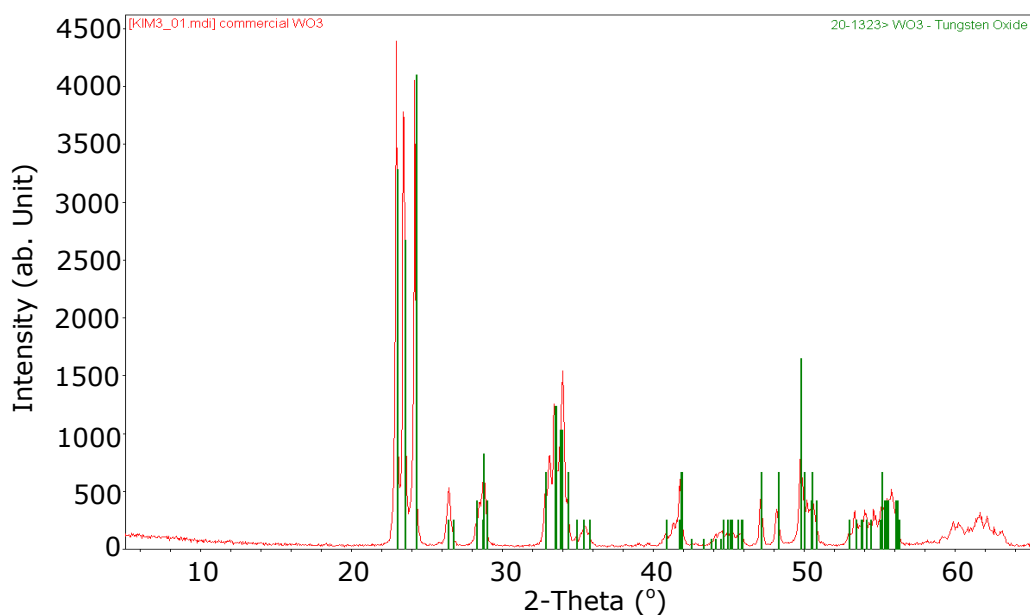


Fig. S1. XRD pattern (red line) of the WO₃ powder after heating in air for 30 min. The green vertical lines are the standard pattern of WO₃.

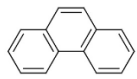
S2. Processing synthetic oil field produced wastewater in the dual purpose PEC

Wastewater is widely produced from oil and gas fields and contains typically brine, heavy metals and various organic species, particularly polyaromatic compounds [45,46]. To test the dual purpose PEC for processing the oil field produced wastewater, a synthetic wastewater sample was prepared, consisting of brine, multiple heavy metal ions, and a typical polyaromatic compound, phenanthrene. Table S1 gives the composition of this synthetic wastewater. Because of the greater chemical stability of phenanthrene compared to MB, the

dual purpose PEC was assembled using the previously reported TiO₂/CNT composite [11,12,14] as the photoanode catalyst, and the same Pt disc electrode as the cathode.

The test was carried out at 1.0 V cell voltage under dark and irradiation of the simulated sunlight. The results are presented in Fig. S2, confirming in general the technical feasibility of simultaneous deposition of the heavy metals and degradation of phenanthrene. It is noticed that the conversion was fairly fast [e.g. ca. 15 % in 10 min, see Fig. S2 (b)]. This can be at least partly attributed to the much higher ionic strength in this simulated wastewater sample as shown in Table S1, which helped reduce resistance and speed up electrolysis.

Table S1. Composition of synthetic wastewater in simulation of that produced from oil field.

Compound	NaCl	MgCl ₂	CaCl ₂	CuCl ₂	PbCl ₂	NiCl ₂	FeCl ₂	Phenanthrene 
Content	1.0 M	1.0 M	1.0 M	1000 ppm	1000 ppm	1000 ppm	1000 ppm	1.6 mg/L \approx 1.6 ppm (close to saturation)

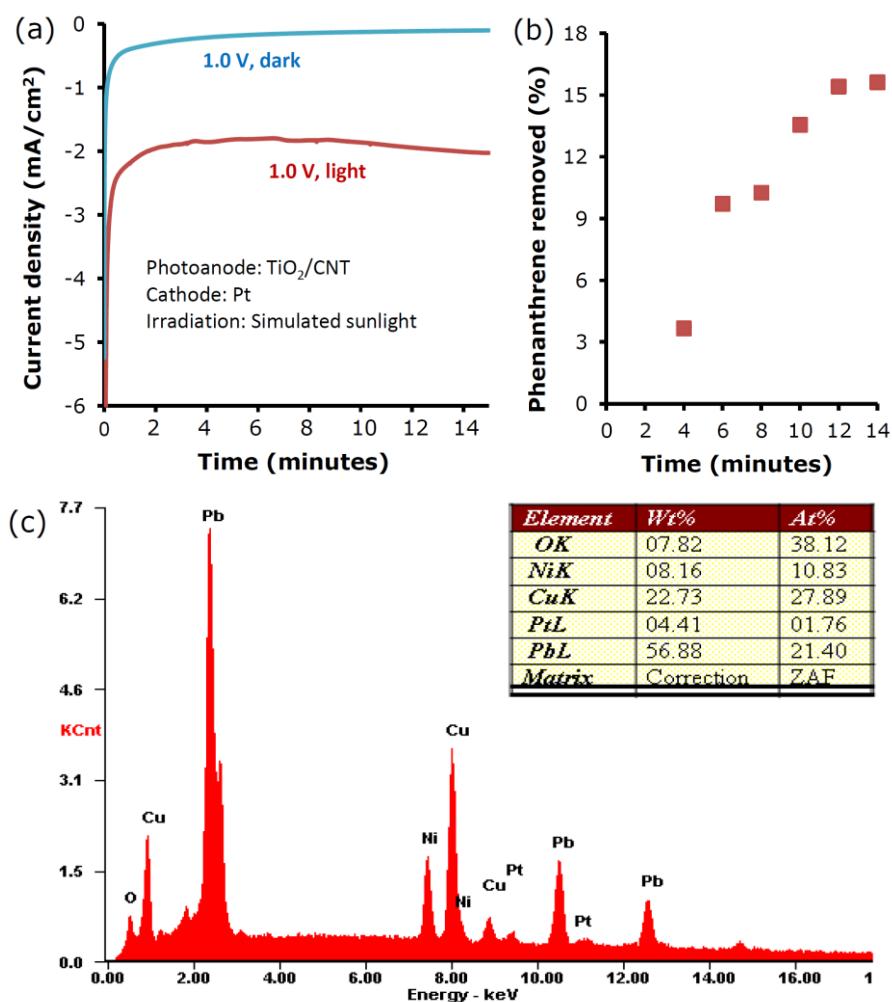


Fig. S2. Application of a dual purpose PEC with a Pt cathode and a TiO₂/CNT photoanode for processing simulated oil field produced wastewater containing phenanthrene, Pb²⁺, Cu²⁺, Ni²⁺ and Fe²⁺ ions and brine (see Table S1). (a) Current – time plots recorded at a cell voltage of 1.0 V under dark and light conditions. (b) UV spectroscopy determined variation of the phenanthrene content with electrolysis time. (c) EDX spectrum recorded on the Pt cathode after 15 min electrolysis.

It is worth noting that the EDX spectrum and the analysis data (At.%) in Fig. S2 (c) indicate that Cu was the most deposited metal, followed by Pb and Ni. The absence of Fe on the EDX spectrum is not surprising because the Fe^{2+}/Fe couple has the most negative standard potential (-0.44 V vs. SHE) in comparison with Cu^{2+}/Cu (0.34 V), Pb^{2+}/Pb (-0.13 V), and Ni^{2+}/Ni (-0.25 V). This finding also confirms that the PEC is capable of selectively removing heavy metals from the wastewater via the application of different cell voltages.

S3. UV spectra of simulated wastewater before and after treatment in the PEC

The absorbance decrease in the visible range of the UV-Vis spectra in Fig. 15 (b) indicates decolouration which may result from either or both of partial oxidation and complete mineralisation, or even reductive conversion of MB to LMB. According to the literature, partial oxidation is commonly featured by formation of smaller aromatic molecules (cf. Fig. 16) which are colourless but generally expected to absorb UV light [44]. LMB is also colourless but absorbs UV at 256 nm [47]. Thus, if partial oxidation and/or LMB formation were the only or dominant processes for the observed decolouration, the UV range of the UV-Vis spectra should have indicated approximately constant or even increased absorbance. As shown in Fig. S3, both the MB [Fig. 3S (a)] and phenanthrene [Fig. 3S (b)] containing water samples (i.e. simulated Wastewater A as described in Table 1 and that in Table S1, respectively) exhibited significant absorbance decrease with the electrolysis time in the respective PECs. Unfortunately, some chloro-complexes of transition metal ions, such as CuCl_3^- , can interfere UV measurements [M. A. Khan, M. J. Schwing-Weill, Stability and electronic spectra of the copper(II) chloro complexes in aqueous solutions, *Inorg. Chem.* 15 (1976) 2201-2205.]. This is exemplified in Fig. S3 (a) by the UV spectra of different water samples containing either or both CuCl_2 and NaCl , but no MB. Such interferences from chloro-metal complex ions compromise the quantitative significance of the UV spectra in Fig. 3S. However, the consistent absorbance decreases on these UV spectra with electrolysis time are still valid qualitative evidence supporting the conclusion that the degradation of MB or phenanthrene in the PECs went through both partial oxidation and complete mineralisation.

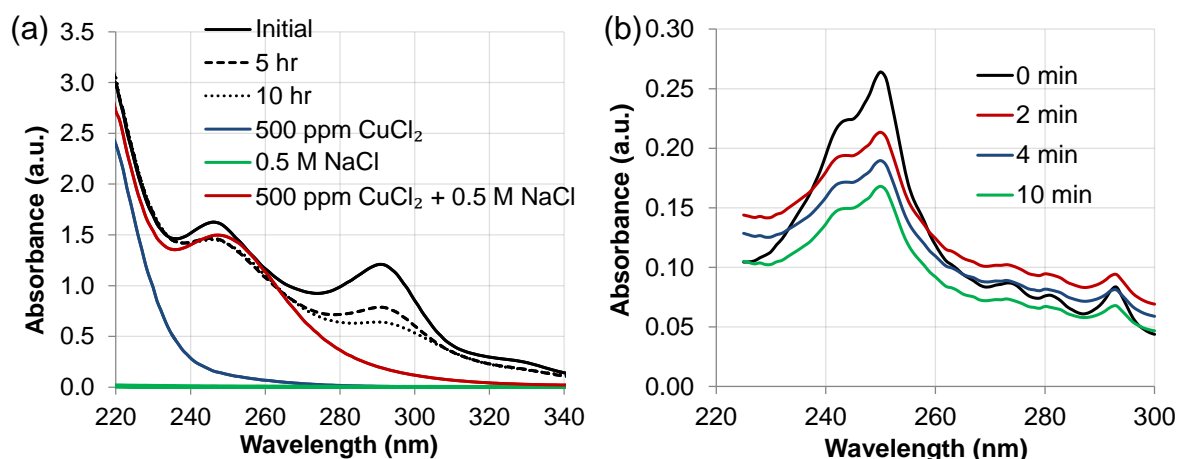


Fig. S3. UV spectra of (a) MB containing water samples (cf. Table 1 and Fig. 15), and (b) phenanthrene containing water samples [cf. Table S1 and Fig. S2 (b)] obtained before and after electrolysis under irradiation in the respective PECs. The UV spectra of three water samples without MB are superimposed in (a) for comparison.

S4. Further discussion

Scale up consideration. It is worth mentioning that the cathodic current should be balanced with the current of the photoanode to maximise the utilisation of photocatalysis. The cathodic current is a function of the concentration of reducible species in an electrolyte (e.g. Cu^{2+}), and the size of the cathode while the anodic current is a function of several factors, including the amount of photocatalysts and their performance, and also the intensity and wavelength of the light. In addition, an overall cell current is dependent on the cell voltage. Thus, optimisation of these parameters is required for a specific application of the dual purpose PEC.

Use of supporting electrolyte. The use of a supporting electrolyte (0.5 M NaCl) in this work was to enhance the ionic conductivity of the simulated wastewater. This component is itself relevant to, for example, the brine containing wastewaters from oil and gas fields as mentioned above [46]. However, the supporting electrolyte is not a necessity because the dual purpose PEC can be driven by a relatively small voltage and low current density (e.g. 0.4 V and 2 mA/cm^2). Further, the PEC can be designed and engineered into a thin layer structure with relatively short distance between the photoanode and the cathode to minimise the solution resistance.

Future research. The research reported in this paper is at its very infancy stage, and many efforts are required to improve both the fundamental understanding and technological practicality. One of the fundamental needs is the qualitative and quantitative analyses of the anodic process and product(s) that can help identify the reaction pathways. UV-Vis spectroscopy is a powerful tool for this purpose because many organic compounds are UV-Vis responsive. It is also very suitable for uses in laboratory where the total amount of samples is often very small. The challenge is that not all organic compounds (pollutants or decomposition products) are UV-Vis responsive, and interferences are also expected from transition metal ions via complex formation. Thus, a more comprehensive analysis should obviously include other techniques such as total carbon (TC) and total organic carbon (TOC) and GC-MS.

On the practical aspect, the engineering match between the wastewater composition and the photoanode catalyst will be crucial. It is well known that many organic compounds are excellent ligands to form complexes with heavy metal ions. Although no sign of complex formation was observed in this work, it is technically important because complex formation will likely make it more difficult to deposit the metal and also decompose the organic pollutant, and increase the energy input to drive the process.

Last, but not the least, results from this study showed very high charge efficiency for metal deposition at the cathode, whilst the anodic charge efficiency was not a simple electrochemical issue. Therefore, it remains a challenge to determine what process variables are relevant to the improvement of the process efficiency, which should consider at least both the removal efficiency (C/C^0) and charge (or energy) efficiency that requires identification of the degradation products.