



A simple and effective strategy to fast remove chromium (VI) and organic pollutant in photoelectrocatalytic process at low voltage



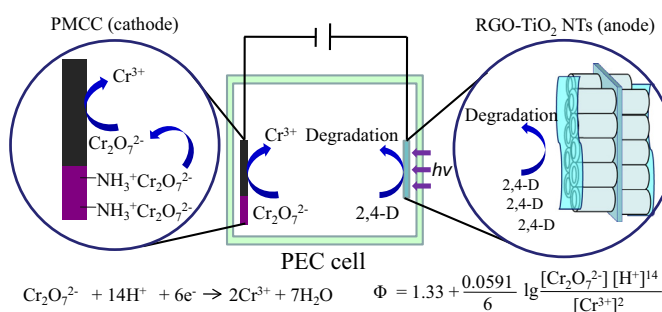
Chengbin Liu*, Yangbin Ding, Wenqun Wu, Yarong Teng

State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China

HIGHLIGHTS

- High enrichment of negatively charged metal species onto cathode.
- Fast removal of Cr(VI) in PEC process at low voltage.
- The synergistic effect on simultaneous removal of heavy metals and organic pollutants.
- Good longevity of electrodes with stable working performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 22 June 2016

Accepted 11 July 2016

Available online 12 July 2016

Keywords:

Simultaneous removal
Heavy metals
Organic pollutants
Low voltage
Fast removal

ABSTRACT

Photoelectrocatalytic (PEC) process is a rising approach to simultaneous removal of heavy metals and organic pollutants. However, electric field plays a dual role in the reduction of negatively charged metal species (e.g., $\text{Cr}_2\text{O}_7^{2-}$): Reduction driving force makes metal species move to cathode; electric field force pulls negatively charged species to anode. The reduction reaction of Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$) strongly depends on the concentration of both $\text{Cr}_2\text{O}_7^{2-}$ and H^+ on the surface of cathodes. The reduction of Cr(VI) in conventional PEC process must enhance proton concentration with a mass of strong acid or prolong reaction time. A highly effective PEC system was constructed with amino-modified carbon cloth as cathode and reduced graphene oxide functionalized TiO_2 nanotube arrays as photo-anode. The amino groups could concentrate protons to form quaternary ammonium cations which could adsorb $\text{Cr}_2\text{O}_7^{2-}$ ions through electrostatic interaction. The graphene functionalized anode greatly accelerated the mass transfer of organic pollutants onto photo-anode. Resultantly, Cr(VI) and 2,4-dichlorophenoxyacetic acid (2,4-D) could be removed faster at lower cell voltage compared with conventional PEC process and the electric energy consumption decreased by at least 50%. Furthermore, the proposed PEC process could be repeatedly utilized with highly stable working performance. This work would give a new insight into the development of cost-effective PEC process for treatment of Cr(VI)-containing wastewater.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Wastewaters are often highly complex in composition with various pollutants such as heavy metals and organic species. The

* Corresponding author.

E-mail address: chem_cbliu@hnu.edu.cn (C. Liu).

treatment of wastewater contaminated with both heavy metals and organic pollutants is a challenge. In recent years, photoelectrocatalytic (PEC) process combining electrochemical (EC) and photocatalytic (PC) processes for simultaneous removal of heavy metals and organic pollutants has undergone rapid development [1–5]. For positively charged metal ions (such as Cd^{2+} , Cu^{2+} and Ni^{2+}) [2,3,5,6], the metal ions can forwardly move to cathode under electric field, which is favorable for the reduction at cathode. However,

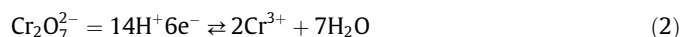
for negatively charged metal species (e.g. toxic $\text{Cr}_2\text{O}_7^{2-}$), they tend to move to anode under electric field, which goes against the reduction at cathode. Furthermore, according to Nernst equation (Eq. (1)), the reduction of negatively charged metal ions would be increasingly difficult due to more negative redox potentials as the concentrations of metal ions become lower and lower. The reduction reaction of Cr(VI) strongly depends on the concentration of both $\text{Cr}_2\text{O}_7^{2-}$ and H^+ (Eqs. (2) and (3)). Although the reduction of Cr(VI) can be enhanced by adjusting the pH value to be lower with a mass of strong acid or prolonging reaction time [7,8], it is unpractical and not cost-effective in the treatment of practical wastewater. Therefore, enhancing the adsorptive ability of both $\text{Cr}_2\text{O}_7^{2-}$ and H^+ onto the surface of cathodes in PEC process is necessary to remove $\text{Cr}_2\text{O}_7^{2-}$ to low concentration levels. Nevertheless, there has been no effort to make.

Additionally, the reactions on anode and cathode in PEC process should complement and promote each other. The fast transfer of photogenerated electrons to conductive substrate of anode is essential. Although considerable efforts have been made in photocatalytic anodes [9–11], the immobilization of photocatalysts on electrode substrate by casting or dipping method could lead to the falling of photocatalysts from electrode substrate and also make barriers of charge transport by residual adhesive. Furthermore, the high adsorptivity of photocatalysts towards hydrophobic organic pollutants should be good for the degradation of organic pollutants [12–14]. However, hydrophilic characteristic of inorganic semiconductor materials shows poor affinity toward organic molecules [15,16]. So the design and preparation of photocatalytic anodes still merits attention.

A highly effective PEC system was here constructed with polyethylenimine-modified carbon cloth (PMCC) as cathode and reduced graphene oxide functionalized TiO_2 nanotube arrays (RGO– TiO_2 NTs) as anode (Scheme 1a and b). The amino groups of PMCC cathode could effectively adsorb protons through protonation reactions and consequently enrich $\text{Cr}_2\text{O}_7^{2-}$ ions by electrostatic interactions to promote the reduction of Cr(VI). Compared with conventional PEC process (Scheme 1c), the proposed PEC process promoted the moving of $\text{Cr}_2\text{O}_7^{2-}$ ions to cathode. The in situ

growth of TiO_2 nanotube arrays on titanium plate availed the transport of photogenerated electrons from TiO_2 to conductive titanium substrate [17]. Graphene greatly accelerated the mass transfer of organic pollutants onto photo-anode [18,19]. Compared to conventional PEC system, the proposed PEC system could faster remove Cr(VI) and 2,4-dichlorophenoxyacetic acid (2,4-D, a highly stable and toxic organic pollutant) at lower voltage.

$$\varphi = \varphi^0 + \frac{0.0591}{n} \lg \frac{[\text{O}]}{[\text{R}]} \quad (1)$$



$$\varphi = 1.33 + \frac{0.0591}{6} \lg \frac{\text{Cr}_2\text{O}_7^{2-} [\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2} \quad (3)$$

2. Materials and methods

2.1. Chemicals and materials

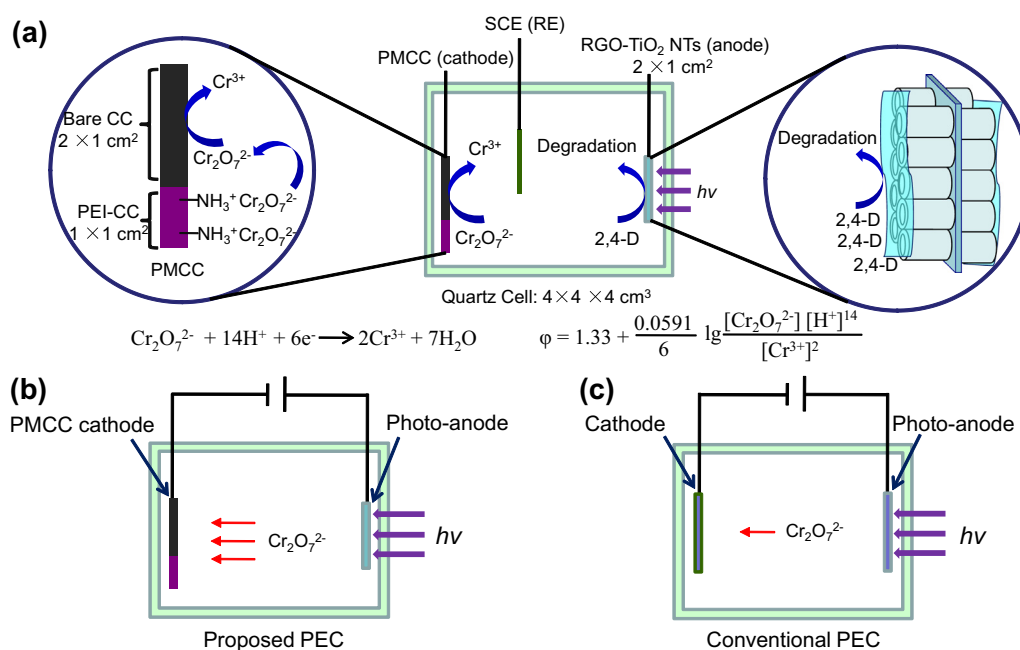
Titanium foil (99.8%, 0.25 mm thickness) and polyethylenimine (PEI) with MW of 25,000 were purchased from Sigma-Aldrich, and other reagents and materials are used as received. Deionized water was used for preparation of all aqueous solutions.

2.2. Preparation of TiO_2 NTs

TiO_2 NTs were prepared by anodization of Ti foil in an electrolyte containing 0.1 M NaF and 0.5 M NaHSO_4 at 15 V for 3 h, resulting in the TiO_2 NTs with a pore size of 90–100 nm, a length of 320 nm and an efficient electrode area of $2 \times 1 \text{ cm}^2$ on each side. The as-anodized TiO_2 NTs were sintered at 500 °C for 3 h.

2.3. Preparation of RGO– TiO_2 NTs

Graphite oxide (GO) prepared from graphite powder by modified Hummers method [20] was exfoliated in a 0.1 M, pH



Scheme 1. Illustration of the photoelectrochemical cell (PEC) used for experiments in this work (a), and schematic representation of dichromate migration in the proposed PEC (b) and conventional PEC (c).

Download English Version:

<https://daneshyari.com/en/article/145236>

Download Persian Version:

<https://daneshyari.com/article/145236>

[Daneshyari.com](https://daneshyari.com)