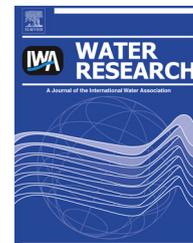




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Electrocatalytic activity of Pd-loaded Ti/TiO₂ nanotubes cathode for TCE reduction in groundwater

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ABSTRACT

A novel cathode, Pd loaded Ti/TiO₂ nanotubes (Pd–Ti/TiO₂NTs), is synthesized for the electrocatalytic reduction of trichloroethylene (TCE) in groundwater. Pd nanoparticles are successfully loaded on TiO₂ nanotubes which grow on Ti plate via anodization. Using Pd–Ti/TiO₂NTs as the cathode in an undivided electrolytic cell, TCE is efficiently and quantitatively transformed to ethane. Under conditions of 100 mA and pH 7, the removal efficiency of TCE (21 mg/L) is up to 91% within 120 min, following pseudo-first-order kinetics with the rate constant of 0.019 min⁻¹. Reduction rates increase from 0.007 to 0.019 min⁻¹ with increasing the current from 20 to 100 mA, slightly decrease in the presence of 10 mM chloride or bicarbonate, and decline with increasing the concentrations of sulfite or sulfide. O₂ generated at the anode slightly influences TCE reduction. At low currents, TCE is mainly reduced by direct electron transfer on the Pd–Ti/TiO₂NT cathode. However, the contribution of Pd-catalytic hydrodechlorination, an indirect reduction mechanism, becomes significant with increasing the current. Compared with other common cathodes, i.e., Ti-based mixed metal oxides, graphite and Pd/Ti, Pd–Ti/TiO₂NTs cathode shows superior performance for TCE reduction.

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1. Introduction

Trichloroethylene (TCE) is a widespread chlorinated solvent contaminant in the subsurface. Groundwater contaminated with TCE threatens public health because of its toxicity and carcinogenic effects (Brüning and Bolt, 2000). Removal of TCE from contaminated groundwater has been approached by

different strategies, such as air stripping (He et al., 2004), in situ chemical oxidation (Tsai et al., 2009; Waldemer et al., 2007) and reduction (Cope and Benson, 2009; Phillips et al., 2010), and biological processes (Dong et al., 2009; Goltz et al., 2005). Electrochemical transformation processes attract great interest for transformation of TCE in groundwater in recent years (Carter and Farrell, 2009; Chen et al., 2003; Lohner

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et al., 2011; Mao et al., 2011, 2012; Mishra et al., 2008; Petersen et al., 2007; Yuan et al., 2012). The anode and cathode act as a source and a sink of electrons, respectively, by donating or accepting electrons to or from dissolved contaminants or other aqueous species. As a result, an electrolytic system can induce oxidation and/or reduction of contaminants. Oxidation at the anode and reduction at the cathode have been reported for TCE transformation (Carter and Farrell, 2009; Mishra et al., 2008; Mao et al., 2011). For anodic oxidation, it is difficult to achieve complete mineralization, with degradation intermediates which are generally less toxic accumulate (Carter and Farrell, 2009). With respect to reduction at the cathode, TCE can be transformed to nontoxic ethene or even ethane (Mishra et al., 2008; Mao et al., 2011). Hence, cathodic reduction attracts more interest for TCE remediation when compared with anodic oxidation (Al-Abed and Fang, 2007; Chen et al., 2003; Mishra et al., 2008; Mao et al., 2011, 2012; Petersen et al., 2007).

TCE can be reduced at the cathode surface by electron transfer from the cathode directly or by the surface-adsorbed H formed from water electrolysis. Direct transfer of electrons from the cathode surface to TCE is typically difficult due to energy barriers. Surface-adsorbed H can be combined quickly to form H₂ when common cathode materials, i.e., carbon and Fe, are used because of their weak ability to adsorb H (Zeng and Zhang, 2010). To increase the electrocatalytic activity of a cathode towards TCE reduction, options include facilitating direct reduction on the cathode surface by increasing the overpotential of hydrogen evolution, or enhancing the catalytic hydrodechlorination process by elevating the adsorption and storage of H on the cathode. Cathode surface can be coated by noble metals to increase the electrocatalytic activity. Pd has shown superior capacity for adsorption and storage of H over other noble metals due to its relatively lower binding energy with H (Bechthold et al., 2012; Cwiertny et al., 2006; Shao, 2011). Pd coated materials are effective for the hydrodechlorination of chlorinated contaminants in aqueous solution (Cui et al., 2008; Fang and Al-Abed, 2008; Gasella and Contursi, 2007; Wang and Wang, 2009; Yang et al., 2007). Aside from the retardation of H combination, the H₂ produced from the cathode can be further adsorbed on Pd and dissociated into two atomic H (Chaplin et al., 2012), contributing to contaminant reduction (Yang et al., 2007; Zheng et al., 2012; Yuan et al., 2012).

One challenge for the application of Pd coated cathode is the binding strength of Pd particles with the base material. Porous materials, such as porous carbon (Cui et al., 2008; Fang and Al-Abed, 2008; Gasella and Contursi, 2007; Wang and Wang, 2009), nickel foam (Yang et al., 2007) and ceramic (Chen et al., 2003) have been used as bases for Pd coating, which results in a strong binding. However, using porous materials for groundwater remediation could be difficult or even impractical because of the weak dimensional stability and difficulties in large-scale fabrication. Ti plate or mesh, a very stable metallic material, has been widely used as a base material for dimensionally stable electrodes (DSE). However, the smooth surface of Ti plate or mesh is not able to hold Pd particles tightly. Recently, it is reported that ordered TiO₂ nanotubes (TiO₂NTs) arrays, with inner diameter of 20–100 nm and length of 0.5–20 μm, can grow on Ti surface by

anodization (Hou et al., 2010; Li et al., 2009; Li and Shang, 2010; Liu et al., 2008). The TiO₂NTs arrays are able to load nanoparticles tightly with high electrocatalytic activity. For example, Ti/TiO₂NTs loading PbO₂ and SnO₂ were highly efficient for the anodic oxidation of refractory pollutants (Lei et al., 2010; Zhao et al., 2009, 2010), and loading Cu₂O and ZnFe₂O₄ significantly increased the efficiency of photoelectrocatalytic degradation (Hou et al., 2009, 2010). Pd nanoparticles were also successfully loaded into the TiO₂NTs, which were prepared from TiO₂ nanoparticles by hydrothermal methods, for methanol oxidation (Dong et al., 2009; Wang et al., 2005; Xue et al., 2009). However, Ti/TiO₂NTs have never been used as the cathode or the base of a cathode for contaminant reduction.

From the analysis, it is rational to load Pd nanoparticles into TiO₂NTs grown on Ti plate, providing a Ti-based cathode with high electrocatalytic activity for contaminant reduction. By this means, Pd nanoparticles can be presumably loaded into the nanotubes, which can increase the binding tightness and mechanical stability. As Pd efficiently catalyzes the hydrodechlorination of TCE (Chaplin et al., 2012), it can be hypothesized that Pd loaded Ti/TiO₂ nanotube (Pd–Ti/TiO₂NTs) array cathode has a good electrocatalytic activity towards TCE reduction. In this study, a Pd–Ti/TiO₂NTs array cathode was prepared and characterized. The electrocatalytic activity of the Pd–Ti/TiO₂NTs cathode for TCE reduction was tested under different conditions. The mechanism of TCE reduction was elucidated. The performance of this cathode on TCE reduction was ultimately compared with other cathode materials.

2. Materials and methods

2.1. Chemicals

TCE (99.6%), trans-1,2-dichloroethylene (trans-DCE, 100 μg/mL in methanol), cis-1,2-dichloroethylene (cis-DCE, 100 μg/mL in methanol), 1,1-dichloroethene (0.2 mg/mL in methanol) and vinyl chloride (100 μg/mL in MeOH) were purchased from J&K Scientific. The gas standards including ethene and ethane (100 ppmv in nitrogen) were purchased from Chuangwei Company, China. Palladium acetate was purchased from Shanxi Kaida Chemical Reagent Co., Ltd., China. Pt plate (1 cm length, 1 cm width and 0.1 mm thickness, Wuhan Corrtest, China), Ti plate (2 cm length, 1 cm width and 0.05 mm thickness), Ti-based mixed metal oxides (Ti/MMO) of mesh type (5 cm diameter and 1.7 mm thickness, Shanxi Kaida Chemical Ltd, China), and graphite rod (1 cm diameter and 2 cm length) were used as electrodes. Excess TCE was dissolved into 18.0 mΩ•cm high-purity water to form a TCE-saturated solution (1.07 mg/mL at 20 °C) which was used as the stock solution for preparing TCE aqueous solutions. Deionized (DI) water (18.0 mΩ•cm) obtained from a Millipore Milli-Q system was used in all experiments. All the other chemicals were above analytical grade.

2.2. Synthesis of Pd–Ti/TiO₂NTs cathode

The highly ordered TiO₂NTs were synthesized by anodization of the Ti plate in an NH₄F electrolyte according to the literature

(Prakasam et al., 2007). The Ti plate was polished by sandpaper and cleaned with DI water in an ultrasonic bath (200 W, 40 KHz) for 10 min, followed by air drying. The polished plate was immersed in a mixed acid solution ($V_{\text{HF}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}} = 1:4:5$) for 30 min and cleaned sequentially in acetone and DI water for 10 min in an ultrasonic bath. The Ti plate was used as the anode, and the Pt plate was used as the cathode with 2-cm spacing. The anodization was carried out in 300 mL of glycerine solution containing 2 g of NH_4F and 10 mL of DI water. A constant voltage of 45 V was supplied by a DC power source (GPC-6030D, Taiwan Guwei Electronic Ltd., Inc., Taiwan). The anodization continued for 2 h and was repeated three times. After washing with DI water, the as-formed Ti/TiO₂NTs were calcined in a muffle burner at 500 °C for 2 h. Pd nanoparticles were then electrodeposited to the Ti/TiO₂NTs for 30 min under conditions of 3.6 mM palladium acetate solution, pH 3 and 20 mA. The as-synthesized Pd–Ti/TiO₂NTs electrode was washed and dried at 65 °C overnight. Based on Coulomb's Law, an estimate of 19.8 mg of Pd was loaded into the Ti/TiO₂NTs.

2.3. Cyclic voltammetry of Pd–Ti/TiO₂NTs cathode

The cyclic voltammetry (CV) behavior of electrodes was scanned on a CS150 electrochemical workstation (Wuhan CorrTest Instrument, China) using a Ti/MMO electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolytes used for measurement had 2.28 mM TCE (300 mg/L), pH 7 and 40 mM NaSO₄ supporting electrolyte.

2.4. Reduction of TCE at Pd–Ti/TiO₂NTs cathode

An undivided electrolytic cell (Fig. S1 in the Supplementary Materials (SM)) was used for TCE reduction in a batch mode. A piece of Pt plate was used as the anode, and the as-synthesized Pd–Ti/TiO₂NTs was used as the cathode. A 150-mL syringe was connected to the cell, allowing for gas expansion during electrolysis. For each trial, 250 mL of 10 mM Na₂SO₄ solution was transferred into the cell, leaving 75 mL headspace. 5 mL of TCE saturated water was then added to attain an initial concentration of 163 μM (21 mg/L). The reactor was sealed immediately. The solution was stirred for 15 min to reach equilibrium. Stirring at 400 rpm was maintained using a Teflon-coated magnetic stirring bar. Constant current was maintained during electrolysis. At predetermined time intervals, 2 mL of aqueous solution was sampled and filtered through a 0.22-μm micropore filter membrane (Shanghai General Reagent Factory, China), and 1 mL of headspace gas was collected using a gas-tight syringe. All the experiments were carried out in duplicate.

As O₂ was reported to suppress TCE transformation by Pd-catalytic hydrodechlorination (Lowry and Reinhard, 2001; McNab and Ruiz Jr., 1998) and cathode reduction (Mao et al., 2011), a divided electrolytic system was used to evaluate the influence of isolating O₂ produced at the anode. The anodic and cathodic compartments were separated and connected by a salt bridge, which was filled with 3% agar solution saturated with K₂SO₄. The cathodic compartment was purged by N₂ for 20 min to remove all the O₂ in solution and headspace before

electrolysis. All other conditions were identical to those used in the undivided electrolytic cell.

2.5. Analysis

TCE and DCEs in the filtrate were measured by a Shimadzu 15C HPLC equipped with an SPD-15C UV–Vis detector and an Inertsil/WondaSil C-18 reverse-phase chromatographic column (Shimadzu). The mobile phase was a mixture of acetonitrile and water (80:20, v/v) at 1 mL/min. The detection wavelength was 210 nm. Gaseous products in the headspace were detected by a Shimadzu 2014C GC with a flame ionization detector (FID) and capillary column (30 m × 0.32 mm × 0.5 μm). 1 mL of headspace gas was injected into a 0.5 mL sample loop. The program for column temperature was set as holding column temperature at 40 °C for 3 min and heating from 40 to 140 °C at a rate of 10 °C/min, and then cooling to 40 °C at a rate of 25 °C/min. Injector and detector temperatures were set at 220 and 250 °C, respectively. Chloride ions in the solution was analyzed by an ICS1500 ion chromatograph (Dionex).

The amount of Pd in Pd–Ti/TiO₂NTs before and after electrolysis was analyzed by inductively coupled plasma time of flight mass spectrometry (ICP-TOF-MS, OptiMass 9500). The Pd loaded in Pd–Ti/TiO₂NTs was dissolved by concentrated HNO₃. The complete dissolving of Pd was confirmed by the disappearance of black color on the surface. The dissolved Pd was then measured by ICP-TOF-MS after dilution. The amount of Pd loaded on Pd–Ti/TiO₂NTs was then calculated from the total Pd dissolved in solution.

The as-synthesized and used Pd–Ti/TiO₂NTs were characterized by field scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (FSEM/EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). FSEM/EDX was performed on an FEI Sirion 200 scanning electron microscope. The samples (Ti/TiO₂NTs and Pd–Ti/TiO₂NTs) were coated with Au to increase the conductivity and were placed under high vacuum conditions. An acceleration electron voltage of 20 kV was applied to obtain the SEM images. XRD patterns were obtained by a PANalytical B. V. X'Pert PRO X-ray diffractometer with CuK radiation. The analysis was carried out at 40 kV and 100 mA at the scan step size of 0.0167° and step time of 8.62 s. XPS was performed on an 800SIMS KROTOS Electron Energy Spectrometer using monochromatic Al Kα radiation (300 W PE 25 eV) and low-energy electron flooding for charge compensation.

3. Results and discussion

3.1. Characterization of electrodes

FSEM slice image shows that TiO₂NTs grew on the Ti plate with an average nanotube diameter of about 54 nm and a tube length of about 229 nm (Fig. 1a). The nanotubes and the surface were loaded by Pd nanoparticles (Fig. 1b). Aggregation of Pd nanoparticles was observed on the surface with a diameter of about 46 nm. The fraction of Pd loaded on the surface was measured to be 30.44% (w/w) by EDX (Fig. 1c). High-resolution XPS spectrum of Pd (3d_{5/2}, 3/2) gives binding energies at 335.3 and 340.6 eV (Fig. 1d), which can be assigned to Pd⁰ (Kuvarega

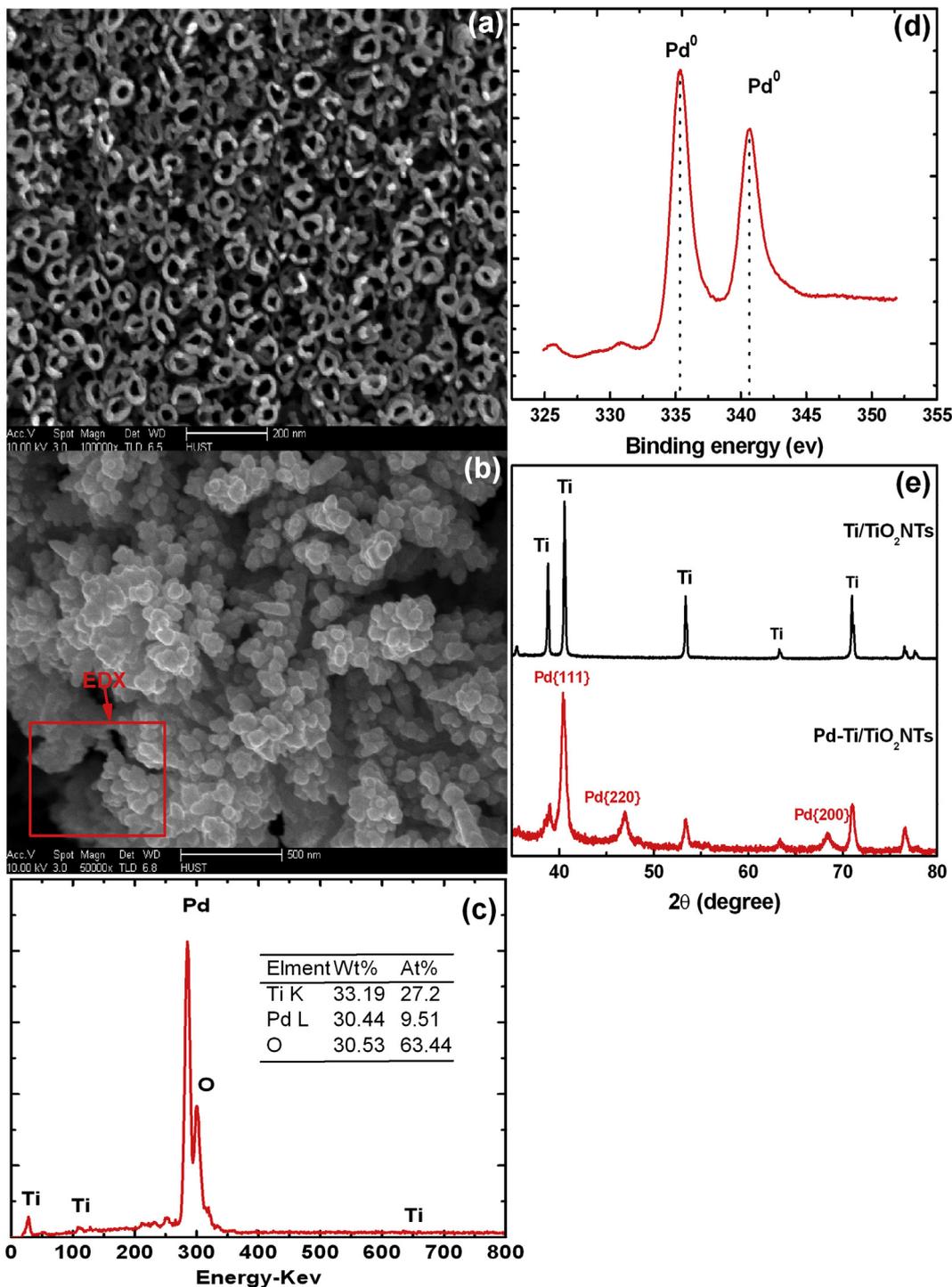


Fig. 1 – (a) FSEM for a Ti/TiO₂NTs slice, (b) FSEM of Pd–Ti/TiO₂NTs, (c) EDX of Pd–Ti/TiO₂NTs, (d) XPS spectra of Pd–Ti/TiO₂NTs, and (e) XRD patterns of Ti/TiO₂NTs and Pd–Ti/TiO₂NTs.

et al., 2011). The XPS analysis suggests an atomic content of 19.84% for Pd on the surface, which is higher than that measured by EDX (9.51%). This difference can be ascribed to the heterogeneous distribution of Pd on the surface. The total Pd loaded on the as-synthesized Pd–Ti/TiO₂NTs was dissolved by concentrated HNO₃ and measured by ICP-TOF-MS, which gives the amount of 12.8 mg Pd. This amount is less than that calculated by Coulomb's Law (19.8 mg). The XRD patterns

show five peaks at 40.4, 47.1 and 68.0° (Fig. 1e), which correspond to the {111}, {200} and {220} planes of a face-centered cubic (fcc) lattice of Pd⁰, respectively (He et al., 2009; Cui et al., 2005). The average diameter of Pd nanoparticles was calculated to be 41.5 nm by Scherrer equation, which is an approximate to that observed with FSEM. These results confirm that TiO₂ nanotubes were formed on the surface of Ti plate and Pd⁰ nanoparticles were successfully loaded.

3.2. Performance of Pd–Ti/TiO₂NTs cathode in TCE dechlorination

The electrocatalytic activity of the Pd–Ti/TiO₂NTs cathode towards TCE reduction was characterized by CV scan from 2.0 to –2.0 V (vs SCE). Without Pd loading, only the evolution of H₂ was observed for the Ti/TiO₂NTs cathode at potentials lower than –1.4 V (Fig. 2a). When Pd was loaded, the response current increased, indicating the increase in electron exchange between Pd–Ti/TiO₂NTs cathode and water. H adsorption (Eq. (1)) was often observed for a Pd cathode before H₂ evolution (Ma et al., 2009; Sun et al., 2009), but it was not observed. When

TCE was added, two irreversible reduction peaks appeared at –0.55 and –0.85 V, which can be attributed to the successive electron transfer from Pd–Ti/TiO₂NTs cathode to TCE since they did not appear in the absence of TCE. This result proves that Pd facilitated the electron transfer from the cathode surface to TCE. Oxidation peaks that occurred in the absence and presence of TCE can be assigned to the oxidation of Pd by anodization. The reduction potential of TCE under neutral conditions on the biocathode was –0.55 V (vs. SCE) (Aulenta et al., 2010), and on the carbon nanocapsules was –0.40 V (vs. SCE) (Wu et al., 2010), which are comparable to that obtained at the Pd–Ti/TiO₂NTs cathode.

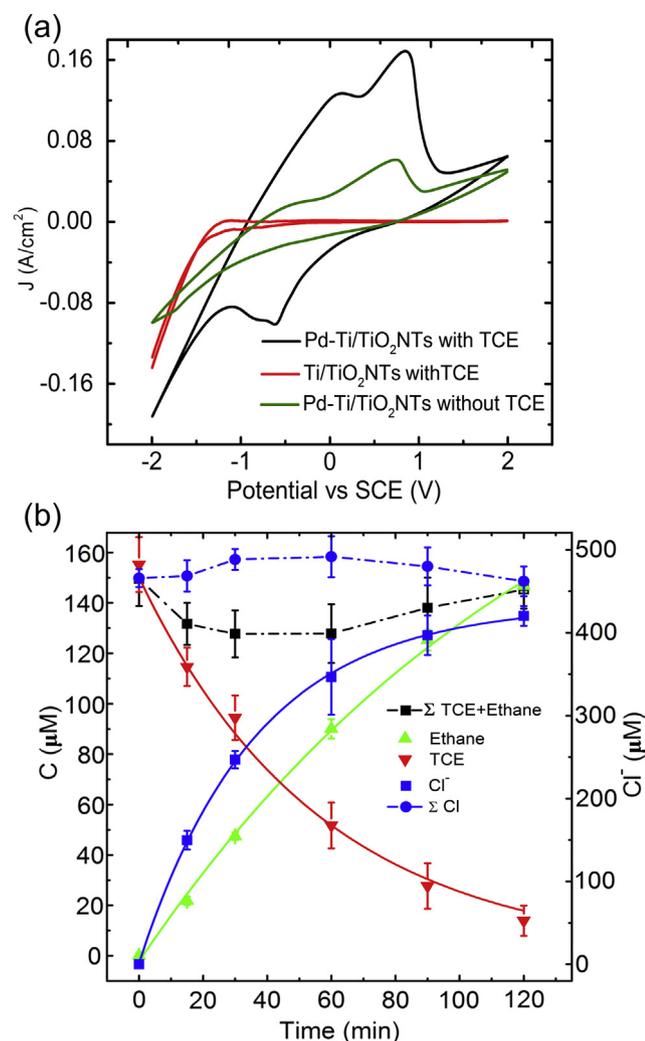
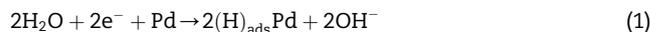


Fig. 2 – (a) CV spectrums of TCE reduction on Ti/TiO₂NTs and Pd–Ti/TiO₂NTs. The scanning conditions were based on 2.28 mM TCE, 100 mV/s scanning rate, pH 7, 500 rpm and 40 mM Na₂SO₄ as electrolyte. (b) Profiles of TCE reduction on the Pd–Ti/TiO₂NTs cathode. The reaction conditions were based on 100 mA, pH 7, 163 μM TCE and 10 mM Na₂SO₄ background electrolyte. A pseudo first-order model is used to fit the decay of TCE with time, which is expressed as $\ln(C_0/C) = kt + b$, where C_0 is the initial concentration of the reactant, C is the concentration of TCE at time t , t is the reaction time, k is the reaction rate constant (min^{-1}) and b is a constant.

TCE reduction on the Pd–Ti/TiO₂NTs cathode was further investigated in a batch mode. The aqueous concentration of TCE decreased (Fig. 2b) from 163 to 14.7 μM, with a removal efficiency of up to 91% within 120 min at 100 mA. In comparison, the removal of TCE on the Ti/TiO₂NTs cathode or without electrolysis (control) was negligible under identical conditions (Fig. S2). Ethane was measured as the sole product of TCE reduction on the Pd–Ti/TiO₂NTs cathode. During the process, the solution pH slightly declined from 7.0 to 5.5, which is consistent with the formation of HCl from TCE reduction. This variation of pH was supposed to have minimal influence on TCE reduction (Lowry and Reinhard, 2000; Munakata and Reinhard, 2007). Chlorinated intermediates such as cis-DCE, trans-DCE and VC, which are reported for TCE reduction on the cathode (Mishra et al., 2008), were not detected. The sum of TCE and ethane accounted for more than 84% of carbon balance, suggesting the quantitative transformation of TCE to ethane. Meanwhile, the cumulative concentration of Cl⁻ is equivalent to the theoretical release of 3 chlorines from TCE reduction. The decay of TCE and production of ethane and Cl⁻ followed pseudo-first-order kinetics with the rate constants of 0.0185, 0.0156 and 0.0164 min^{-1} , respectively. The similar rate constants for production of ethane and Cl⁻ are consistent with the fast transformation of TCE to ethane. As the two reduction peaks in the CV spectrum characterized a successive reduction process, it can be inferred that the intermediate was further reduced on the Pd–Ti/TiO₂NTs surface before desorption into the solution.

The rate constant of TCE transformation normalized by Pd concentration ($0.0128 \text{ g}/0.255 \text{ L} = 0.05 \text{ g/L}$) is $0.37 \text{ L gPd}^{-1} \text{ min}^{-1}$, which is in the same level as that reported by Munakata and Reinhard (2007) and one order of magnitude smaller than that reported by Lowry and Reinhard (2000) using Pd and H₂ for TCE hydrodechlorination. Water electrolysis is a conventional means of H₂ production in industry, but it is costly for large scale production. For the in situ groundwater remediation, electrolysis may provide an effective, flexible and expedient approach to supplying H₂. From this regard, electrolysis would be advantageous over external H₂ injection for Pd-catalytic reduction of TCE.

It is noted that different products were reported for TCE reduction by Pd/Fe and cathodes. TCE reduction by Pd/Fe produced 80% ethane and 20% C₃–C₆ compounds (Kim et al., 2010). Reduction by other cathodes, i.e., Ti based mixed metal oxide (Ti/MMO), iron foam and copper foam (Mao et al., 2011) and Pt or Pd-coated ceramic cathode (Li and Farrell, 2000), produced a mixture of ethane and ethene. The extent of

dechlorination is determined by the reducing ability of the system (Wu et al., 2012). More ethane can be produced under stronger reducing system. Therefore, the production of ethane indicates that the Pd–Ti/TiO₂NTs cathode has a high catalytic activity towards TCE reduction.

3.3. Effect of current on TCE reduction

TCE reduction increased significantly with increasing the electric current (Fig. 3a). The pseudo-first-order kinetic rate constants increased from 0.067 to 0.127 and 0.185 min⁻¹ when the current increased from 20 to 50 and 100 mA, respectively (Table 1). The rate constants show a linear correlation with the current within this range ($R^2 = 0.952$, Inset in Fig. 3a). There are two mechanisms for this correlation, direct and indirect reductive dechlorination. Direct reduction may occur by electron tunneling or by formation of a chemisorption complex for organic compounds with cathode materials (Li and Farrell, 2001). The possibility of direct reduction on the

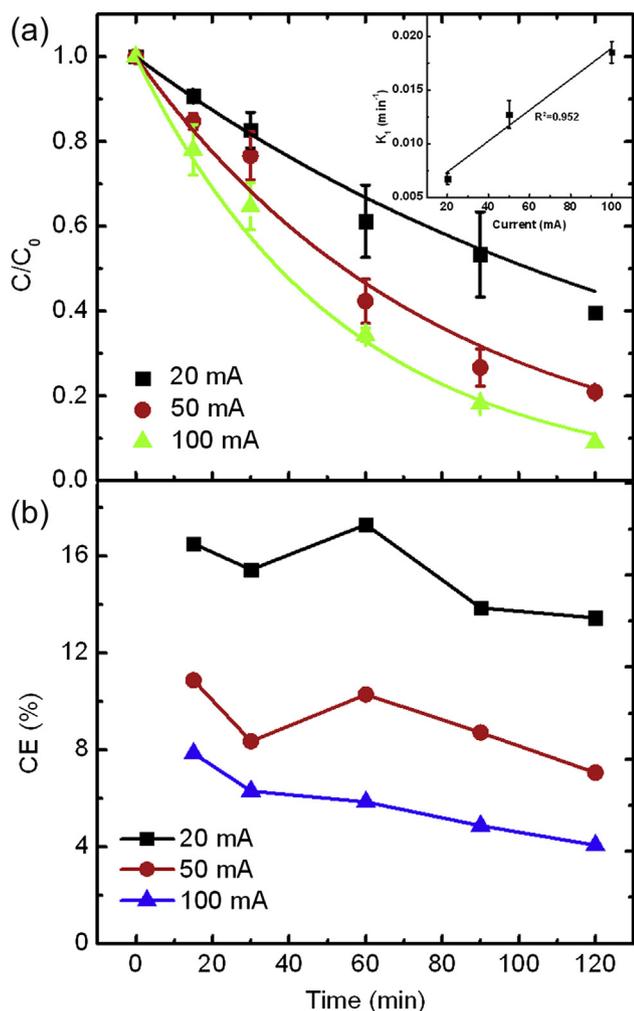


Fig. 3 – (a) TCE reduction on the Pd–Ti/TiO₂NTs cathode at different currents and (b) the corresponding transformation efficiencies. The reaction conditions were based on 163 μ M TCE, pH 7 and 10 mM Na₂SO₄ background electrolyte.

Table 1 – A summary of the results for the batch reduction experiments.

No.	Variation parameter ^a	Final pH	Residue TCE (μ M)	k_1 (min ⁻¹) ^b	R^2 for k_1
1	100 mA	5.8 \pm 0.1	14.7 \pm 2.3	0.019 \pm 0.001	0.997
2	50 mA	6.0 \pm 0.1	32.6 \pm 5.2	0.013 \pm 0.001	0.960
3	20 mA	6.1 \pm 0.1	65.2 \pm 12.7	0.007 \pm 0.001	0.973
4	10 mM NaCl	5.8 \pm 0.2	26.3 \pm 4.8	0.010 \pm 0.000	0.990
5	10 mM NaNO ₃	5.9 \pm 0.1	24.2 \pm 7.1	0.0170 \pm 0.0014	0.998
6	10 mM NaHCO ₃	5.4 \pm 0.1	44.7 \pm 9.8	0.013 \pm 0.001	0.997
7	10 mM Na ₂ SO ₃	5.2 \pm 0.1	52.9 \pm 7.2	0.010 \pm 0.002	0.993
8	10 mM Na ₂ S	5.1 \pm 0.1	94.6 \pm 4.3	0.005 \pm 0.001	0.984
9	1 mM Na ₂ SO ₃	5.4 \pm 0.1	58.4 \pm 8.8	0.090 \pm 0.001	0.797
10	1 mM Na ₂ S	5.3 \pm 0.2	65.6 \pm 7.1	0.008 \pm 0.001	0.912
11	Graphite cathode	6.2 \pm 0.1	99.0 \pm 6.4	0.005 \pm 0.001	0.698
12	MMO cathode	6.1 \pm 0.1	90.1 \pm 13.2	0.006 \pm 0.001	0.789
13	Divided system	5.5 \pm 0.1	Not detected	0.022 \pm 0.002	0.987
14	Pd/Ti cathode 1st	5.5 \pm 0.1	14.1 \pm 3.2	0.018 \pm 0.001	0.994
15	Pd/Ti cathode 2nd	6.4 \pm 0.1	128.4 \pm 6.8	0.002 \pm 0.001	0.836
16	Ti/TiO ₂ NTs cathode	6.2 \pm 0.1	132.8 \pm 4.1	0.002 \pm 0.001	0.821

a Unless otherwise stated, the reaction conditions are based on 163 μ M TCE, 100 mA current, pH 7, Pd/TiO₂NTs/Ti as cathode, 10 mM Na₂SO₄ and 120 min degradation.

b k_1 is the pseudo-first-order kinetics rate constant.

Pd–Ti/TiO₂NTs cathode is validated by the significant reduction peaks observed on the CV spectrum. Indirect reduction may occur via reaction with the atomic hydrogen adsorbed on the Pd–Ti/TiO₂NTs cathode through formation of hydride complexes (e.g., Pd–H). It is observed that the production of H₂ gas bubbles from water electrolysis increased significantly with increasing the current. The significant evolution of H₂ consumed electric charge transfer, which should have decreased the dependence of TCE reduction on the current. However, the linear dependence of TCE reduction on the current within the tested range of current suggests that production of H₂ may also contribute to TCE reduction. A comparison experiment was carried out using Ti/TiO₂NTs as the cathode, but Pd–Ti/TiO₂NTs was immersed in the solution without connection to electricity. TCE was significantly reduced (Fig. S3), but was slower than that using Pd–Ti/TiO₂NTs cathode. As Pd–Ti/TiO₂NTs was not connected to electricity, it can only catalyze the H₂ produced from the Ti/TiO₂NTs cathode for TCE hydrodechlorination. Therefore, TCE reduction can be attributed to both direct electron transfer and indirect Pd-catalytic hydrodechlorination. That is, at low current, direct electron transfer dominates the transformation as the potential for TCE reduction is less negative than that for H₂ evolution. With increasing the current, direct electron transfer reaches the maximum due to the limitation of mass transfer and the contribution of indirect Pd-catalytic hydrodechlorination becomes significant.

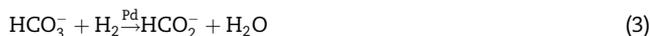
Faradic current efficiency (CE, Eq. (2)) is used to evaluate the efficiency of electric energy consumption. The current efficiency is given by

$$CE = (C_t - C_0) \times V \times zF / (I \cdot t) \quad (2)$$

Where C_t and C_0 are the concentrations of TCE at t and 0 min (mol/L), z is the number of electron transfer, F is Faradic constant (96,485 C/mol), I is current (A), t is time (s), and V is the electrolyte volume (0.255 L in this study). It is assumed that reduction of TCE to ethane requires 8 electrons (Yuan et al., 2012). Fig. 3b demonstrates that the lowest current of 20 mA always exhibits the highest current efficiency, ranging from 16.5% at 15 min to 14.5% at 120 min. In contrast, 100 mA shows 7.8% CE at 15 min and gradually decreases to 4.0% at 120 min. With increasing the current, more atomic H or gaseous H_2 are produced, which increases the reactive H but decreases the adsorption of TCE. Particularly at high current, visible H_2 evolution on the cathode surface increased the resistance of TCE adsorption, thus reducing the effective utilization of H_2 .

3.4. Effect of groundwater chemistry on TCE reduction

To further evaluate the performance of Pd–Ti/TiO₂NTs cathodes for TCE reduction in groundwater, the influence of groundwater chemistry was investigated. Compared with SO_4^{2-} , presence of Cl^- and HCO_3^- slightly inhibited TCE reduction, while the effect of NO_3^- was negligible (Fig. 4a). The negative effect of Cl^- is due to the competitive adsorption of HCl. Bicarbonate present in groundwater may compete for H_2 (Eq. (3)), resulting in a decrease in TCE reduction (Lowry and Reinhard, 2000).



Reduced sulfur compounds (RSCs) have shown a foiling effect on Pd activity (Angeles-Wedler et al., 2008; Chaplin et al., 2006; Lim and Zhu, 2008; Schuth et al., 2000). Significant foiling effect of RSCs on the Pd–Ti/TiO₂NTs cathode was also observed (Fig. 4b). With the increase in S^{2-} concentration from 0 to 1 and 10 mM, TCE decay decreased from 91 to 59 and 42%, respectively, within 120 min. Pd foiling by RSCs can be ascribed to the competitive adsorption of HS^- , modification of the electronic properties of Pd in the vicinity of sulfur atoms, and the formation of Pd–S compounds (Angeles-Wedler et al., 2008; Chaplin et al., 2006). The presence of S on the surface of Pd–Ti/TiO₂NTs cathode was proven by SEM/EDX analysis (Fig. S4). Similarly, when SO_3^{2-} concentration increased from 0 to 1 and 10 mM, TCE decay decreased from 91% to 65% and 60%, respectively, within 120 min. This foiling effect is less pronounced when compared with S^{2-} . Since the concentrations of RSCs in aquifers are generally low, i.e., <1 mM, good performance can be anticipated when using Pd–Ti/TiO₂NTs cathodes for TCE reduction. The foiling effect obtained herein is similar to those reported for Pd-catalytic hydrodechlorination (Angeles-Wedler et al., 2008; Lim and Zhu, 2008).

3.5. Effect of oxygen produced at the anode on TCE reduction

In an electrolytic system, O_2 production at the anode is inevitable when inert anodes are employed. Dissolved O_2 has

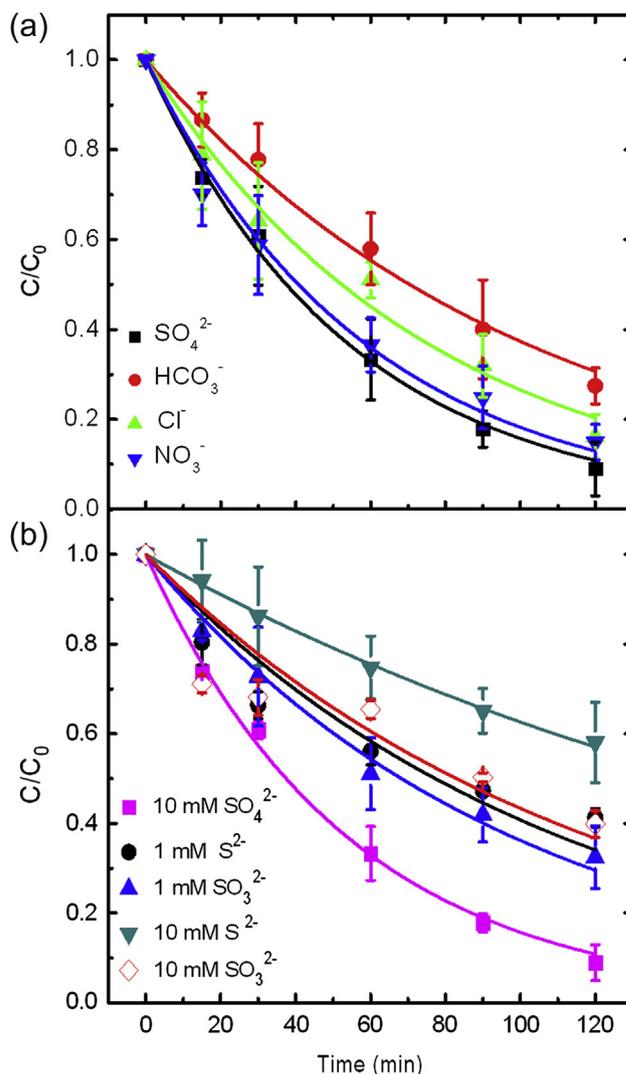


Fig. 4 – Effects of (a) anionic ions and (b) different concentrations of RSCs on TCE reduction on the Pd–Ti/TiO₂NTs cathode. Reaction conditions were based on 163 μ M TCE, 100 mA current and pH 7. Ions concentration was 10 mM unless otherwise specified.

shown great inhibition on TCE reduction by Pd and H_2 (Lowry and Reinhard, 2001; McNab and Ruiz Jr., 1998) as well as by electrocatalytic cathodes (Mao et al., 2011). Dissolved O_2 may compete with TCE for both the electrons and the atomic H on the cathode surface, thus suppressing TCE reduction. In this study, the effect of anodic O_2 was evaluated using a divided electrolytic system where the cathodic compartment was separated from the anodic compartment by a salt bridge. The O_2 in the solution and headspace was purged by N_2 prior to electrolysis. Under the same conditions, TCE reduction rate increased from 0.019 min^{-1} in the mixed system with anodic O_2 to 0.022 min^{-1} in the cathodic compartment without anodic O_2 (Fig. S5). This slight inhibition indicates that the Pd–Ti/TiO₂NTs cathode is more resistance to O_2 influence. Pd nanoparticles were loaded into the nanotubes of the cathode surface, which could decrease the accessibility of O_2 to reactive sites of Pd. In our recent study using copper foam cathode,

TCE removal decreased from >99.7% in the absence of anodic O₂ to 57.2% in the presence of anodic O₂ at the current of 90 mA (Mao et al., 2011). For TCE hydrodechlorination by Pd and H₂, it was found that TCE conversion decreased from 45.8% in the presence of 0.25 mM O₂ to 4.4% in the presence of 0.6 mM O₂ when the total concentration of H₂ and O₂ in the closed reactor was fixed at about 1 mM (Lowry and Reinhard, 2001).

3.6. Long-term performance

The long-term performance of Pd–Ti/TiO₂NTs cathodes was further evaluated by both CV scan and batch reduction experiments. For 100 successive CV scans, the peak currents of TCE reduction appeared to be constant (Fig S6), suggesting a long-lasting electrocatalytic activity of Pd–Ti/TiO₂NTs cathodes. In the batch reduction experiments, a decline in transformation efficiency with treatment durations was observed (Fig. 5). The efficiency dramatically decreased in the second application, was maintained almost constant from the second to the fifth applications, and gradually decreased afterwards.

FSEM image reveals that Pd nanoparticles aggregated after the first application (Fig. S7a). The size of Pd nanoparticles increased from about 46 nm initially to about 148 nm after usage. This change decreased the surface reactive sites on the Pd–Ti/TiO₂NTs cathode. XPS results (Fig. S7b) indicate that metallic Pd⁰ still dominated, but new peaks at 337.9 and 343.0 eV for Pd²⁺ occurred (Kuvarega et al., 2011). The oxidation of Pd⁰ to Pd²⁺, which was induced by the dissolved O₂, may decrease the catalytic activity of the Pd–Ti/TiO₂NTs cathode. The XPS peak intensities of the used Pd–Ti/TiO₂NTs were lower than the as-synthesized one, implying that some Pd nanoparticles detached from the cathode surface during treatment. The loss of Pd from Pd–Ti/TiO₂NTs cathode was validated by the decrease in the amount of Pd from 12.8 mg to 8.2 mg after first application and to 7.1 after second application (ICP-TOF-MS results). Anodic O₂ could potentially deactivate Pd–Ti/TiO₂NTs cathode. Our comparison results show that TCE reduction also decreased with treatment in the absence of anodic O₂ (Fig. S8). As a result, aggregation of Pd

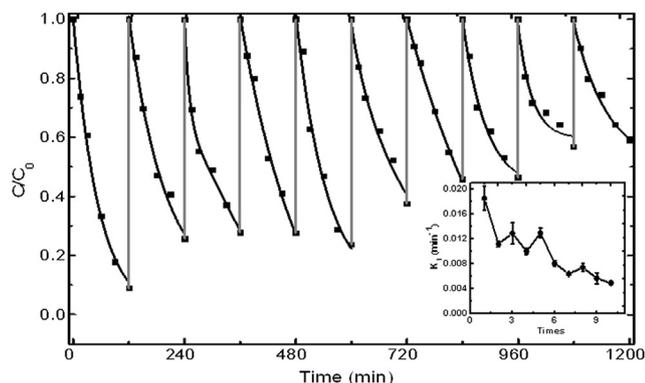


Fig. 5 – Repeated reduction of TCE on the Pd–Ti/TiO₂NTs cathode. Reaction conditions were based on 163 μM TCE, pH 7, 100 mA and 10 mM Na₂SO₄ background electrolyte. The same cathode was used for ten successively repeated applications.

nanoparticles and loss of Pd from Pd–Ti/TiO₂NTs are mainly responsible for the decrease in TCE reduction with durations. Thus, the physical structure of the Pd–Ti/TiO₂NTs cathode needs improvement so that the Pd nanoparticles can be strongly bound to the surface.

3.7. Performance comparison with conventional cathodes

The performance of Pd–Ti/TiO₂NTs cathode for TCE transformation is compared with other cathodes including Ti/MMO, graphite and Pd/Ti under identical conditions. Ti/MMO has been used for TCE reduction in groundwater (Petersen et al., 2007; Mao et al., 2011). However, in this study Ti/MMO achieved only 44.7% reduction in TCE concentration within 120 min (Fig. S9) resulting in a pseudo-first-order rate constant of 0.0056 min⁻¹. Graphite is a commonly used electrode that produced a 39.3% reduction in TCE concentration. Pd/Ti cathode shows comparable efficiency for TCE reduction in the first application, but most of the Pd particles detached from the Ti plate during treatment, leading to a very weak activity towards TCE reduction in the second application. Therefore, it can be concluded that the Pd–Ti/TiO₂NTs cathode had superior electrocatalytic activity towards TCE reduction when compared to other cathode materials such as Ti/MMO, graphite and Pd/Ti.

4. Conclusions

A novel cathode, Pd–Ti/TiO₂NTs, is synthesized and its electrocatalytic activity for TCE reduction is investigated. Pd nanoparticles can be successfully loaded onto the TiO₂ nanotubes that grow on a Ti plate. The as-synthesized Pd–Ti/TiO₂NTs cathode produces high electrocatalytic activity for TCE reduction – up to 91% removal of TCE within 120 min. Ethane is identified as the sole product of TCE transformation. At low currents, direct electron transfer is responsible for TCE reduction while the indirect mechanism of hydrodechlorination becomes significant when the current is increased. High concentrations, i.e., 10 mM, of Cl⁻ and HCO₃⁻ slightly inhibit TCE reduction. RSCs show an increasingly foiling effect on Pd activity with increasing RSCs concentration. The Pd–Ti/TiO₂NTs cathode could resist the negative influence of O₂ which is inevitably produced at the anode, and shows superior performance for TCE transformation when compared with other cathodes such as Ti/MMO, graphite or Pd/Ti. However, the electrocatalytic activity of the Pd–Ti/TiO₂NTs cathode decreases with repeated treatments, indicating that the cathode structure needs improvement.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.04.004>.

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