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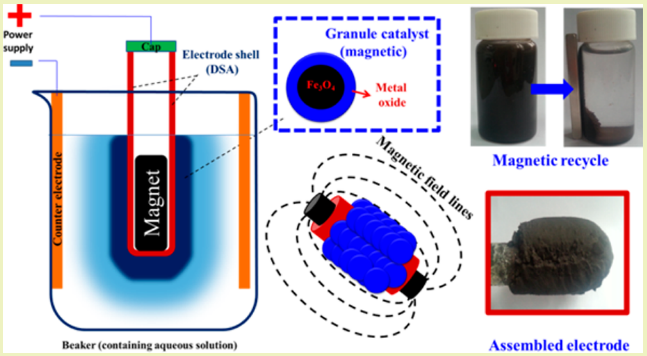
Fe_3O_4/Sb−SnO_2 Granules Loaded on Ti/Sb−SnO_2 Electrode Shell by Magnetic Force: Good Recyclability and High Electro-oxidation Performance

Dan Shao,[†,‡] Wei Yan,*[,†,‡] Xiaoliang Li,[‡] and Hao Xu*[,‡]

[†]State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[‡]Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Supporting Information



ABSTRACT: Guided by the ideas of green chemistry and green engineering, a new developed electrode with interchangeable coatings was fabricated for electrochemical oxidation (EO). This electrode consists of a permanent magnet NdFeB, a Ti/Sb−SnO_2 electrode shell and a number of magnetic Fe_3O_4/Sb−SnO_2 granules. The granules are fixed on the electrode shell by magnetic attraction force. Necessary characterizations were used to reveal the morphology, composition and magnetic property of the magnetic granules. The electrochemical properties of the new electrode were investigated by the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The performance of the new electrode and its stability in the EO process were carried out. Finally, the recyclability of the granules was also tested. Results show that the new electrode has a larger real surface area than the conventional electrode (two-dimensional electrode). The real current density on the new electrode is decreased, which results in a higher EO ability and higher electrode stability. The energy is also saved because the cell voltage is decreased. In addition, the magnetic granules could still be attracted and recycled after a long time use. This new electrode could be considered as a renewable electrode, and the lifetime of the EO system could be increased by a factor of 5 when granules are renewed timely.

KEYWORDS: *Interchangeable coating, Magnet, Tin dioxide, Green chemistry, Recycle*

INTRODUCTION

Electrochemical oxidation (EO) is a suitable wastewater treatment technology to deal with the widely distributed toxic organics or other biorefractory pollutants due to its environmental friendly feature, high efficiency, flexibility and versatility.[1−4] During the last two decades, dimensional stable anodes (DSAs) have been attributed as the most common anode materials for the EO process.[5−7] The composition of a DSA includes a metal substrate (usually titanium) and metal oxide coating material. The DSAs are widely used due to the high efficiency, mature industrial preparation technique and low economic cost.[8−11] In spite of these advantages, there are still some weaknesses in conventional EO system using DSA, such as short electrode lifetime, mass transfer limitation and low area−volume ratio.[12,13] Here, a new constructed electrode is designed that which is expected to overcome some weaknesses.

The design idea of this new electrode is originated from the consideration of anode regeneration and green chemistry. During a long time use, considerable amounts of DSA coating materials are lost through coating detachment. However, the lost but still active coating fragments could not be recycled and return to the Ti substrate. The electrode deactivation process is irreversible, and quantities of electrode materials are wasted. The scrapped anode has to be replaced by a new one to maintain the stability of the EO system, and the system operation has to be paused. If the coating material of the anode could be renewed without disturbing the system, the EO system may have a much longer service time. In addition, time and cost to fabricate another electrode are also saved.

The design of the new electrode was proposed as follows. The coating could be divided into many independent modules. Thus, the inactivation or loss of partial coating modules would not make the whole electrode collapse. As shown in Scheme 1, the new electrode consists of a strong permanent magnet core (NdFeB) as the magnetic force source, a cylinder electrode shell (a certain DSA) as the supporting material and many magnetic granules as the main catalysts. The magnetic granules (Fe_3O_4/MO_x) are expected to be fixed on the DSA by the magnetic attraction force. The underlying coating layer of the electrode shell could also be pressed on the Ti substrate firmly

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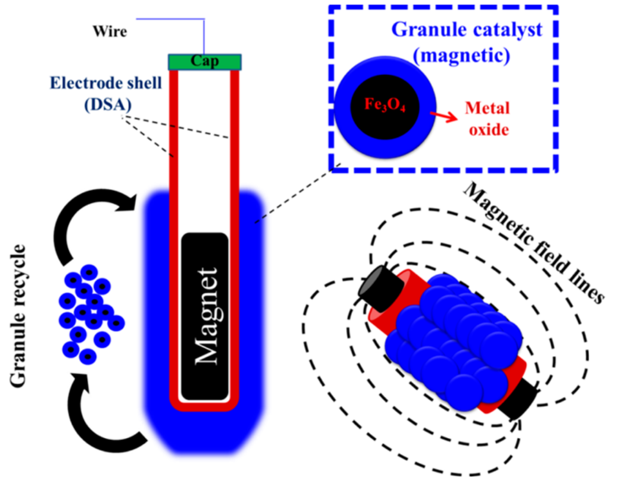
Scheme 1. Design of a New Electrode (A magnet + DSA + magnetic granules)



by the granules. We postulate the magnetic force may be the best combination force because it is easy to control this force only by controlling the magnetic field. The new electrode is expected to have two advantages. First, it is convenient to recycle and refresh the catalysts without disturbing the EO system operation. Second, compared with the conventional electrode (two-dimensional electrode, 2D electrode), the mass transfer of the new EO system may be improved and the electrode lifetime may be prolonged due to the interchangeable coating. The structure of the new electrode may be similar to the promising three-dimensional (3D) electrode because they both have granules. But unlike the 3D electrode, most granules of the new electrode are fixed on the electrode shell and they are not dispersed in the bulk solution freely. The structure of this new electrode is a transition state between that of the 2D and 3D electrodes. Therefore, the new electrode could be attributed as "2.5D electrode" (not exactly in the middle, just means a transition state), which may have characteristics of both the 2D and 3D electrodes.

To make the advantages of the new designed electrode more remarkable, we decided to use antimony doped tin dioxide ($Sb-SnO_2$) as the catalyst (MO_x) for both electrode shell coating and granule coating. This is because $Sb-SnO_2$ is a promising DSA material with high OEP (∼1.9 V vs SHE) and low cost, but the stability of this anode material is not good, which has very big improvement space.[14,15]

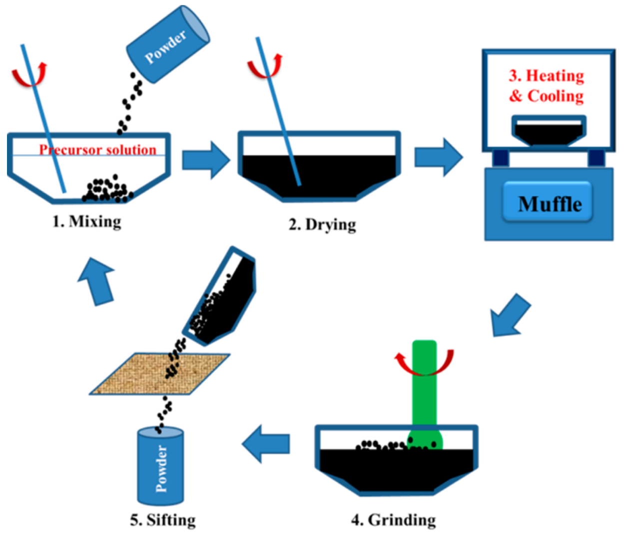
To investigate the material properties of this new 2.5D electrode, necessary characterizations of the magnetic granules were carried out. Then the electrochemical properties of this new electrode were tested. Degradation experiments of model wastewater were used to verify the performance of this novel electrode. Furthermore, the electrode stability was carefully investigated and the retrievability of the magnetic granules was investigated as well.

■ EXPERIMENTAL SECTION

Preparation of the Electrode. All reagents used are analytical pure. The conventional $Ti/Sb-SnO_2$ electrode (2D electrode) was prepared as we previously reported.[16] The Ti substrate was a cylinder shell (diameter: 1.5 cm). This procedure is easy to be reproduced because the electrodeposition and brush coating technique is easy to control. This integrative electrode was used as a control to foil the advantages of the new electrode. The loading amount of $Sb-SnO_2$ for this electrode was controlled at ∼3 mg cm^{-2}, an adequate amount. A lower version of this conventional electrode (loading amount ∼ 1.5 mg cm^{-2}) was used as the electrode shell of the new $Ti/Sb-SnO_2$ electrode

To fabricate the $Fe_3O_4/Sb-SnO_2$ magnetic granules, commercial Fe_3O_4 powder (1000 meshes, used as received) was used as the core. First, the Fe_3O_4 powder was coated by a protective layer to prevent the oxidation during the following repeated high-heat treatment. The low temperature thermal treatment of tetrabutyl orthotitanate could generate an anatase structure of TiO_2 but with very low XRD peak intensities, called TiO_x.[17] Because Ti, Sn and Sn have close atom radii,[18] during the coheated process, their oxides may combine well.[19] The coating method is carried out as follows, including five main steps illustrated in Scheme 2. First, the Fe_3O_4 powders were mixed with a solution containing 50% tetrabutyl orthotitanate (TBOT) and 50% ethanol (percent by volume) in a crucible (Step 1) and then this mixture was stirred on an electric heater (Step 2). When most of the solvent was dried, the crucible was moved into a muffle furnace and heated at 573 K for 30 min followed by a natural cooling process (Step 3). After that, the obtained bulk products were grinded to small powders again (Step 4). After that, the coated powders were sifted by a gauze screen (200 meshes) (Step 5). Then the TiO_x-coated powders were coated by $Sb-SnO_2$ with the same method. The TiO_x-coated powders were mixed with a precursor solution (1 M $SnCl_4$, 0.1 M $SbCl_3$ and 0.1 M HCl) and dried (Steps 1 and 2). Then the crucible was moved into a muffle furnace and heated at 723 K for 30 min (Step 3). Step 4 and Step 5 were the same as TiO_x coating. To obtain different loading amounts of $Sb-SnO_2$, the coating cycle could be repeated several times. Briefly, when the cycle was carried out twice, the obtained particles are called "$Sb-SnO_2(2)$" in brief. In the same manner, "$Sb-SnO_2(4)$" and "$Sb-SnO_2(6)$" represent the particles that are prepared after four and six coating cycles of $Sb-SnO_2$.

Scheme 2. Coating Cycle of Magnetic Granules (Five Steps)



When the electrode substrate shell and magnetic granules were both successfully prepared, the permanent magnet stick (NdFeB) was encapsulated into the electrode shell. Therefore, the magnetic particles would be attracted and supported by the $Ti/Sb-SnO_2$ electrode shell.

Material Characterizations. The morphology, microstructure, element content and crystalline structure of the prepared magnetic granules were analyzed by scanning electron microscopy (SEM: JSM-6390A, JEOL, Japan) equipped with an EDS (energy-dispersive X-ray spectroscopy) detector and X-ray diffraction (XRD: X'pert PRO MRD, PANalytical, Holland, Cu Kα), respectively.

Electrochemical and Magnetic Properties. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a potentiostat/galvanostat (CHI660D, Chenhua, China). The two tests were conducted in a standard three-electrode cell. The copper sheet was used as the counter electrode, and the Ag/AgCl was used as the reference electrode. The prepared electrode was installed as the working electrode. 0.5 M Na_2SO_4 aqueous solution was used as an electrolyte. In the CV test, the potential scan rate was 0.05 V s^{-1}. The determination method of electrodes' oxygen evolution potential (OEP) is illustrated in Figure S1 (Supporting Inforamtion), which is based on the CV curves of the electrodes. In the EIS test, the settings of electrodes and the system were the same as for the CV test (three-electrode system). The equilibrium potential of working electrode was set to 0 V (vs Ag/AgCl). The frequency range was 0.1 Hz to 10^5 Hz. The amplitude of the potential was 5 mV.

The magnetic property of the granules was determined by a vibrating sample magnetometer (VSM: 735 VSM Controller, Lake-Shore, USA). The powder sample was sealed in a 3 mm × 1 mm space on the vibrating stick and the mass of each sample is recorded. The range of magnet field intensity was set between −7500 and +7500 Oe.

Degradation Experiments. Analytical pure guaiacol ($C_7H_8O_2$, CAS no. 95-05-1) or Acid Red G ($C_{18}H_{13}N_3Na_2O_8S_2$, CAS no. 3734-67-6) was dissolved in pure water (18 MΩ cm) as a model wastewater sample. The pure water is fabricated in a water purification system (EPED-S2-D, EPED, China). 0.5 M Na_2SO_4 was used as the supporting electrolyte. The concentration of guaiacol or ARG was defined as 500 mg L^{-1}. The volume of each solution was 0.3 L. The adopted effective area of the anode (the exposed area of the prepared electrode substrate) was 30 cm^2. The anodic current was fixed to 0.6 A.

The current efficiency of organic degradation is used to assess the catalytic oxidizing ability of the electrode. According to Faraday's law, the current efficiency is defined as the ratio of theoretical quantity of electric charge to actual passed quantity of electric charge. Theoretical quantity of electric charge is calculated by the measured COD removal. The energy consumption (KWh per kgCOD removal) is another important index to test the electrochemical oxidation performance, which is determined by the ratio of electric consumption (KWh) and COD removal.

Accelerated Lifetime Test. The accelerated lifetime test was carried out at high current density using a potentiostat/galvanostat (LK3000A, Tianjin Lanlike, China). The fabricated electrode served as the working electrode and two copper plates were employed as both the counter electrode and reference electrode. The electrolyte was 1 M H_2SO_4 solution. The adopted effective area of the anode was defined as 2 cm^2. The constant anodic current was set at 1 A. The electrode was regarded as a deactivated electrode when the cell voltage reached to 10 V.

RESULTS AND DISCUSSION

Characterizations. Because the coating of Sb−SnO_2 cost the most time and effort, the appropriate loading amount of Sb−SnO_2 on the Fe_3O_4 core should be investigated. The Sb−SnO_2 coating is expected to cover the inner Fe_3O_4 core and the operation times should be restricted to the lowest possible number. The XRD spectra of magnetic granules with different loading amounts of Sb−SnO_2 are shown in Figure 1. The diffraction pattern varied with the coating progress. Despite of the impurity quartz (ICDD 00-001-0649), Fe_3O_4 (ICDD: 01-075-1609) is the unique composition of the initial granules. When the cycle of Sb−SnO_2 coating was carried out, Fe_2O_3 (ICDD: 01-084-0308) and Sb−SnO_2 (solid solution structure, ICDD: 01-088-2348) emerged. When the coating cycle was repeated more times, the diffraction peaks of Sb−SnO_2 increased and the peaks of Fe_3O_4 and Fe_2O_3 decreased, indicating the underlying layer was gradually covered by the new surface layer. When the coating cycle was executed six times, the XRD pattern mainly reflects Sb−SnO_2, which indicates that the magnetic core was basically covered by Sb−SnO_2 since then.

The SEM images of the prepared magnetic granules (Sb−SnO_2(6)) are shown in Figure 2a,b. The size distributions of magnetic granules are broad (approximately from 10 to 50 μm). The shape of each granule is irregular. The micromorphology of the granule surface is rough, which may benefit the catalysis. Figure 2c illustrates the EDS spectrum and element content of Sb−SnO_2(6). It is clear that the content of Sn and Sb is significant on the granule surface, which is in accordance with the XRD result. Figure 2d reflects the variation of the content of Sn, Sb, Ti and Fe along with the progress of coating process. It is clear that the content of Fe decreased when the loading amount of Sn and Sb increased and the content of the binder (Ti) first increased and then decreased. For Sb−SnO_2(6), the protection of the magnetic core Fe_3O_4 is the best. Therefore, taking both XRD and SEM results into account, the granule is qualified when the Sb−SnO_2 coating cycle was carried out at least six times. The final loading amount of Sb−SnO_2 is approximately 0.91 g g^{-1} (Fe_3O_4) for Sb−SnO_2(6).

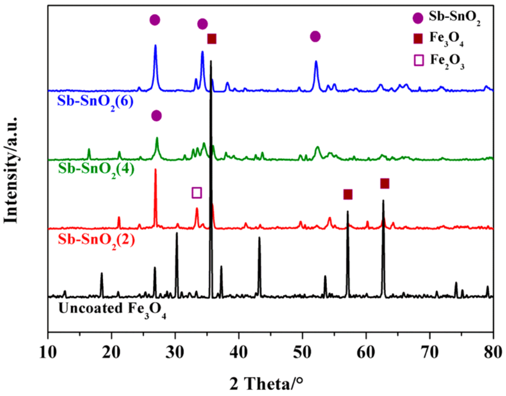
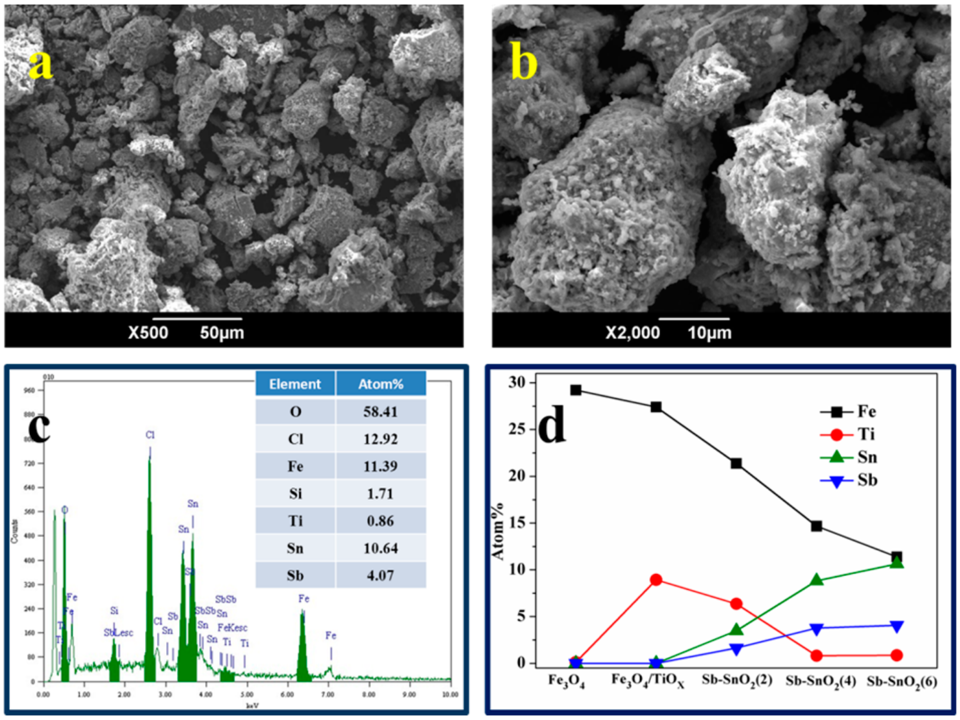


Figure 1. XRD patterns of the prepared Fe_3O_4/Sb−SnO_2 granules with different loading amount of Sb−SnO_2 (main diffraction peaks: Fe_3O_4, 18.3°, 30.1°, 35.5°, 43.1°, 57.1° and 62.6°; quartz, 20.9°, 26.6°, 50.1°, 60.0° and 67.9°; Fe_2O_3, 24.3°, 33.3°, 35.8°, 49.7°, 54.3°, 62.7° and 64.3°; Sb−SnO_2, 26.6°, 33.9°, 37.9°, 51.8°, 54.8°, 61.9°, 64.8° and 66.0°).

Magnetic Properties. It is very important to know the effect of Sb−SnO_2 loading amount on the magnetic properties of the prepared granules because these granules are expected to be attracted by the main electrode firmly. The magnetic properties of these particles were investigated with a vibrating sample magnetometer (VSM). The magnetization curves measured at 298 K are shown in Figure 3. It could be found the magnetic saturation values are 27.489 emu g^{-1} for Sb−SnO_2(2), 16.156 emu g^{-1} for Sb−SnO_2(4) and 10.558 emu g^{-1} for Sb−SnO_2(6), respectively. The decrease of magnetic value may be caused by the increased proportion of nonmagnetic component Sb−SnO_2 and repeated heating process. Nevertheless, the granules Sb−SnO_2(6) maintained sufficient magnetism so that they can still be attracted by the magnet inside the Ti/Sb−SnO_2 shell.

In consideration of the above results, the granules prepared by 6 coating cycles were used as the suitable product in further experiments because the Fe_3O_4 core is well protected by the Sb−SnO_2 coating and the magnetism of the granule is still sufficient.

Electrochemical Properties. It is also significant to examine the effect of the attracted granules on the electrochemical properties of the electrode. The oxygen evolution potential (OEP) is an important index because the oxygen evolution and electrochemical oxidation are competing



Element	Atom%
O	58.41
Cl	12.92
Fe	11.39
Si	1.71
Ti	0.86
Sn	10.64
Sb	4.07

Figure 2. SEM images of prepared granules (Sb−SnO_2(6)) and EDS result of the granules with different loading amounts of Sb−SnO_2: (a) SEM image of Sb−SnO_2(6) 500×, (b) SEM image of Sb−SnO_2(6) 2000×, (c) EDS spectra of Sb−SnO_2(6) and (d) variations of main elements content of the samples during the granule preparation process.

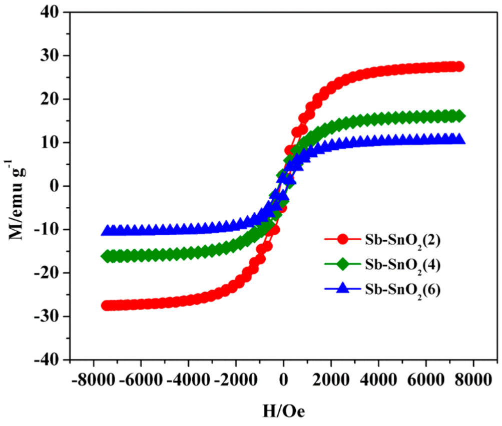


Figure 3. Magnetization curves of the prepared Fe_3O_4/Sb−SnO_2 granules with different loading amounts of Sb−SnO_2.

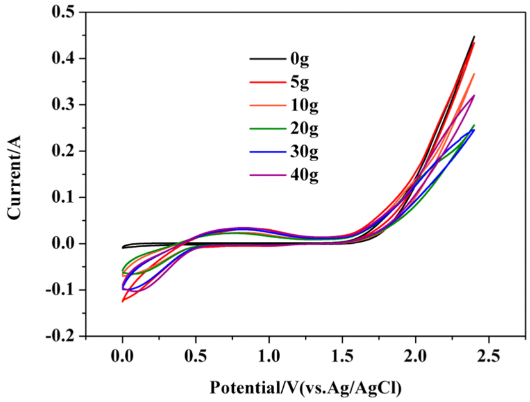


Figure 4. Cyclic voltammetry curves of the new developed Ti/Sb−SnO_2 with different loading amounts of Fe_3O_4/Sb−SnO_2 particles (0.5 M Na_2SO_4, scan rate 0.05 V s^{-1}).

reactions.[20−22] Therefore, for the electrodes, a more positive OEP means more capability of electrochemical oxidation. Figure 4 presents the cyclic voltammetry curves of new developed Ti/Sb−SnO_2 with different loading amounts of Fe_3O_4/Sb−SnO_2 particles, and the unloaded Ti/Sb−SnO_2 electrode (2D electrode) acted as the control. It could be found the OEPs of the all electrodes are similar (∼1.8 V vs Ag/AgCl). It is fortunate because the granules do not decrease the oxidation ability of the electrode. Interestingly, the enclosed area of the curve seems to be larger when more particles were loaded. The calculated mathematical areas of each CV curve are 0.0206 (0 g granule loading), 0.0598 (5 g), 0.0519 (10 g), 0.0548 (20 g), 0.0623 (30 g) and 0.0711 (40 g), respectively. The increase of CV area may indicate the increase of actual electrode surface area and active sites.[19] Especially, at the high potential range, the current response of the electrode varies when the granule loading amount increases. This variation trend of current response is related with the alteration of coating resistance and real surface area, which is discussed below.

The electrochemical impedance spectra (EIS) could reflect the function of the granules from another aspect. The attracted granules may change the condition of the electrode surface−solution interface, which could be reflected by EIS. Figure 5 illustrates the Nyquist plots of the new developed electrodes and the equivalent circuit R(RQ) for EIS data fitting. The EIS data of all tested electrodes fit the equivalent circuit R(RQ) very well. Therefore, the EIS spectra mainly represented solution resistance (R_s) connected with the parallel combination of the electrode film resistance (R_f) and the constant phase element (CPE, Q). It could be found the loading of magnetic granules changed the impedance plots. 5, 30 and 40 g of

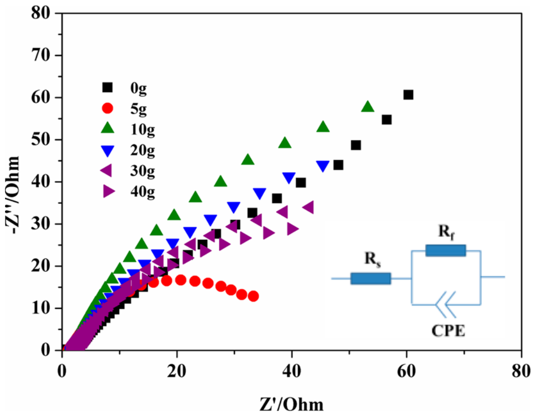


Figure 5. Nyquist plots of the new developed electrodes with different loading amount of magnetic granules and equivalent circuit R(RQ) for EIS data fitting (0.5 M Na_2SO_4, 0.01–10^5 Hz).

granules decreased the diameter of the impedance arc of the electrode. However, 10 and 20 g of granules increased the diameter of the arc. It seems that the increase of granule loading first decreases the impedance, then increases it and finally decreases the impedance. This phenomenon could be explained synthetically by two opposite factors. First, the increasing loaded 3D granules in fact could increase the surface/volume ratio of the catalyst (2D+3D) effectively compared with the conventional Ti/Sb–SnO_2 (2D electrode). The impedance is decreased by this factor. Second, there are more spaces between the increasing granules, which are filled by the electrolyte, not the solid. The impedance of the coating is then increased. The calculated values of components in equivalent circuit R(RQ) (Table 1) may prove this explanation.

Table 1. Value of Components in Equivalent Circuit R(RQ) from Impedance Data for Each Electrode with Different Loading Amount of Granules

granule loading (g)	R_s (Ω cm^2)	R_f (Ω cm^2)	Q (Ω^{-1} s^n cm^{-2})	*n*
0	1.756	474.4	0.005884	0.5771
5	1.060	50.57	0.07487	0.7351
10	1.098	263.1	0.07347	0.7372
20	1.603	209.1	0.08062	0.6934
30	2.319	138.4	0.08378	0.6965
40	1.337	96.46	0.08671	0.7031

The calculated R_f value of the 2D electrode is 474.4 Ω cm^2, which is more than that of the new developed electrode (50.57–263.1 Ω cm^2). With the increase of loading, the variations trends of R_f arc diameter are the same (474.4, 50.57, 263.1, 209.1, 138.4, 96.46; first decrease, then increase and finally decrease). Additionally, the calculated Q value mainly increased with the granule loading. The Q value of the 2D electrode is approximately 1/10 of that of the new electrode. The increase of the Q value may indicate that the new electrode has more real surface area because the capacitance shows positive relations with the size of the surface area. Interestingly, the trend of this Q value variation is in good accordance with that of the CV curve area variation. In a word, both CV and EIS results indicate that the real surface area could be well increased by the granules.

In this experiment, because the 40 g of granule loading amount exhibits the best performance (largest real surface area, relative low impedance) and has a potential positive effect on electrode stability, we selected this granule loading amount for the new electrodes adopted in the following experiments.

Degradation Experiments of Guaiacol and ARG. Because the new developed electrode has special structure and electrochemical properties, the actual effectiveness of this electrode in electrochemical oxidation may be different from the 2D electrode). Guaiacol (monomer of lignin, a relatively refractory substance,[23,24] could be used to determine which electrode has the better electro-oxidation ability. Figure 6 shows the electrochemical oxidation results of 500 ppm guaiacol (0.5 M Na_2SO_4, 0.3 L). The new developed electrode was ~20% better than the 2D electrode in COD removal. The calculated data in Table 2 also proves the superiority of the 2.5D electrode. The current efficiencies for the new developed electrode and 2D electrodes are 67.92% and 43.04% respectively, which indicates that the new electrode inhibits the side reaction better. The calculated energy consumptions

Table 2. Key Indicators of Electrochemical Oxidation Performance of Guaiacol by New Electrode and Conventional Ti/Sb–SnO_2[a]

electrode	average cell voltage (V)	average current efficiency (%)	average energy consumption (KWh kgCOD^{-1})
2.5D electrode	4.1	67.92	20.22
2D electrode	5.0	43.04	38.91

[a] Parameters: current, 0.6 A; electrode area, 30 cm^2; 500 ppm guaiacol; supporting electrolyte, 0.5 M Na_2SO_4; solution volume, 0.3 L; time period, 0–2 h.

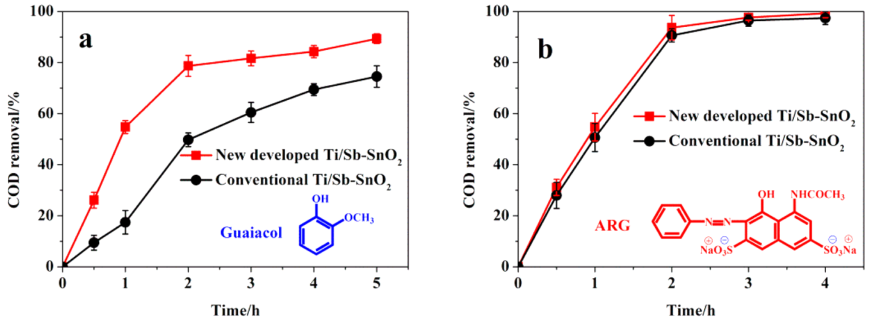


Figure 6. Electrochemical oxidation results (COD removal) of 500 ppm guaiacol and 500 ppm Acid Red G by the new electrode and conventional Ti/Sb–SnO_2 (electrode area 30 cm^2, current 0.6 A, 0.5 M Na_2SO_4, solution volume 0.3 L, room temperature).

for the new developed electrode and the 2D electrode are 20.22 KWh kgCOD^{-1} and 38.91 KWh kgCOD^{-1} respectively, which indicates that the new electrode saves more energy by providing lower cell voltage and higher efficiency.

The better performance of the new developed electrode may be attributed to the larger solid–liquid interface because the real current density on this electrode is decreased and the mass transfer condition is also improved.[25,26] Some formulas about electrochemical oxidation and oxygen evolution are good to clarify the above inferences. A certain degree of non-stoichiometry (SnO_{2-x}) is present in the Sb–SnO_2 coating.[14] When electricity is applied, the anode will generate and adsorb hydroxyl radical (·OH) through water splitting.

$$SnO_{(2-x)} + H_2O \rightarrow SnO_{(2-x)}(\cdot OH) + H^+ + e^- \qquad (1)$$

The hydroxyl radical is unstable. Then two competitive reactions happen. One is the oxygen evolution. Another is the oxidation of organic (R) where intermediate (RO) or final product CO_2 is formed.

$$2\cdot OH + \rightarrow O_2\uparrow + 2H^+ + 2e^- \qquad (2)$$

$$R + 2\cdot OH \rightarrow RO + H_2O \qquad (3)$$

It could be found that the better performance of organic oxidation (higher current efficiency) relies on the effective consumption of ·OH by organic. The rate of eq 3 is very dependent on the concentration of the organic (R) on the solid–liquid interface. Low real current density and good mass transfer condition could make the concentration of R on the solid–liquid interface of the new electrode higher than that on the 2D electrode. Because the total current is fixed, more parts of current could be utilized on the main reaction (organic oxidation) rather than the side reaction (oxygen evolution), causing the increase of current efficiency.

However, the two electrodes have similar performances in degrading Acid Red G (azo dye, easy to be electro-degraded). In Figure 6, it is found that the advantage of the new electrode is not obvious for this substance. The current efficiencies for 500 ppm ARG degradation by the two electrodes are ~65% (new electrode is ~5% higher). Above 95%, COD was removed only by 2 h of degradation. Therefore, we deduced that superiority of the 2.5D electrode may lie on the target. If the target is high concentrated and could be easily degraded, the 2.5D electrode's advantages of better mass transfer and lower real current density may be diminished. Trying to verify this, three real systems including a pulping wastewater sample (A) (COD 1500 mg L^{-1}), a textile wastewater sample (B) (COD 2000 mg L^{-1}) and a municipal sewage sample (C) (COD 300 mg L^{-1}) were adopted to test the two electrodes. Sample A mainly contained lignosulfonates and a few other salts. Sample B mainly consisted of acidic azo dyes and salts. Sample C mainly contains some oils and surfactants. The new 2.5D electrode has more obvious superiority than 2D electrode in COD removal and energy saving in treating sample A and sample C (Table S1 in the Supporting Information). The new electrode seems to be more suitable to treat more refractory substance or organic with lower concentration.

In conclusion, the magnetic granules play a key role in decreasing real current density and benefiting mass transfer. In electrochemical oxidation, the actual effectiveness of the new 2.5D electrode is better than the 2D electrode, especially for refractory substance and low COD wastewater.

Electrode Stability and Recoverability of the Granules. Electrode stability is another important index because it directly determines the application prospect of the electrode. Figure 7 illustrates the typical accelerated lifetime curves of the conventional Ti/Sb–SnO_2 and new developed electrode. The accelerated lifetime of the new developed electrode (40 g of granule loading) is approximately 24 h (additional details are also provided regarding the lifetime of other recently reported Ti/Sb–SnO_2 electrodes in the Supporting Information, Table S2), which is much higher than that of the conventional electrode (~9 h). The probable mechanism of electrode stability enhancement is illustrated in Figure S2 (Supporting Information). As discussed before, the real area of the solid–liquid interface of the new electrode is much larger than its apparent dimension. The real current density on the 2.5D electrode should be lower than that on the 2D electrode. So, the electrode stability could be enhanced because it is a common sense that the current density seriously affects the electrode stability.[27] The granules in fact share the risk of coating corrosion. Another important factor is the well coverage of the underlying Sb–SnO_2 coating by the packed granules. The granules are immobilized on the electrode firmly by a strong magnet so that the inner coating is also under pressure. Hence the combination of the Ti substrate and coating is reinforced.

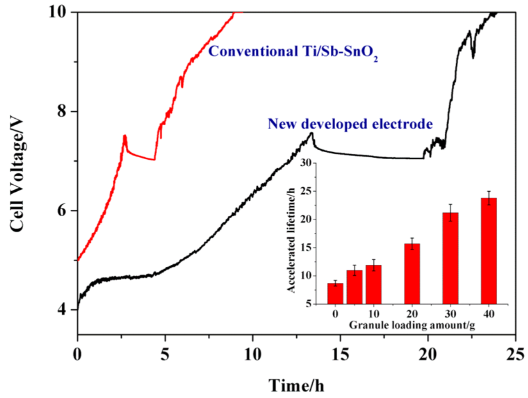


Figure 7. Typical accelerated lifetime curves of conventional Ti/Sb–SnO_2 and new electrode (1 M H_2SO_4, current density 500 mA cm^{-2}, room temperature).

When this new electrode was deactivated, it was found that almost all the coating of the underlying Ti/Sb–SnO_2 electrode shell was lost. So, under the harsh condition of the accelerated lifetime test, the electrode stability is mainly determined by the coating loss rate of the electrode shell. In addition, the color of some granules became reddish-brown, which could be attributed as the emerging Fe_2O_3 (also confirmed by XRD, Supporting Information, Figure S3). Even so, most of the granules were still attracted on the electrode by the magnet and they were still active.

In fact, it is unnecessary to let the new electrode serve as long as possible until it is deactivated. Because the new electrode has interchangeable granules, we can renew all the granules timely when the time exceeds a defined value. In an experiment, we attempted to remediate the conventional Ti/Sb–SnO_2 through a heating treatment (be calcinated at 774 K, 30 min) followed by a recoating process (additional 0.5 mg cm^{-2} loading amount of Sb–SnO_2 by electrodeposition) every 2 h and renew all the granules of the new electrode every 10 h in the accelerated lifetime test. Figure 8 illustrates cell voltage variations before and after renewal processes in the accelerated lifetime test for the two electrodes. It is obvious that the new electrode served as a fresh one even after four coating renew processes. Its total accelerated lifetime could exceed 50 h successfully. But remediation of the conventional electrode seems to fail. Its total real accelerated lifetime after five cycles was only ~6.5 h, an even lower value than that for ~9 h previously. Hence, it could be concluded that the conventional Ti/Sb−SnO_2 electrode could not be recovered, while the granule recycled for the new electrode could successfully extend the lifetime of the EO system.

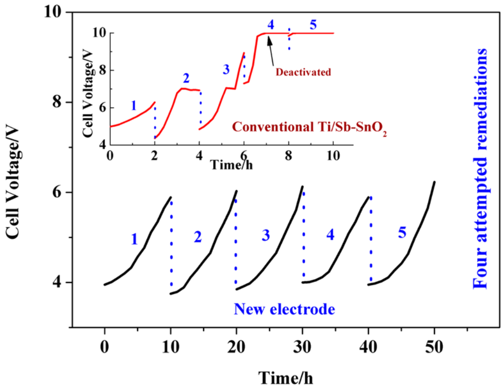


Figure 8. Cell voltage variation in five service cycles of conventional Ti/Sb−SnO_2 electrode and new electrode in the accelerated lifetime test (1 M H_2SO_4, 500 mA cm^{-2}).

The performance of the new electrode is also investigated under the practical milder condition (neutral media, relative low current density 20 mA cm^{-2}). The first batch of the new fabricated electrodes has been working for 4 months. Despite the color change of the granules, the structure and conductivity of the electrodes are still maintained. Especially, the magnetism of the granules is still fine (confirmed by magnetization curves in the Supporting Information, Figure S4). Therefore, it is convenient to recycle these granules by the magnet even when some granules are dispersed in the solution or deposited on the bottom of the reactor. Then the recycled granules could be recoated by Sb−SnO_2 and be used as new ones again. Figure 9 shows the recoverability of the fresh prepared granules and used granules (after 4 months use). All dispersed granules in the solution were attracted on the side of the bottle by the magnet or deposited on the bottom, and the initial turbid solution became clear and transparent after magnetic separation process. This phenomenon indicates that the catalytic granules are easy to be separated from the solution no matter be used or not. To determine the recovery rate of the granules, 40 g of granules was released in the solution first and then a magnet was dipped into the solution to attract these granules. After the drying and weighing of the magnet, it could be calculated that the recovery rate of the unused and used granules by (after 4 months use) could achieve 99.99% (40.00 g/40.01 g) and 96.08% (38.44 g/40.01 g) respectively, indicating the theoretical recovery rate of the magnetic granules may basically reach ~100%. Therefore, the 2.5D electrochemical oxidation system may be environmental friendly (no secondary pollution) and economic in its further practical application. Interestingly, if the permanent magnet in the electrode shell is replaced by an electromagnet, it is more flexible to modify the magnetic field strength. Therefore, the adsorption or desorption of the granules on the anode could be adjusted with more flexibility by altering the current in the electromagnet coil.

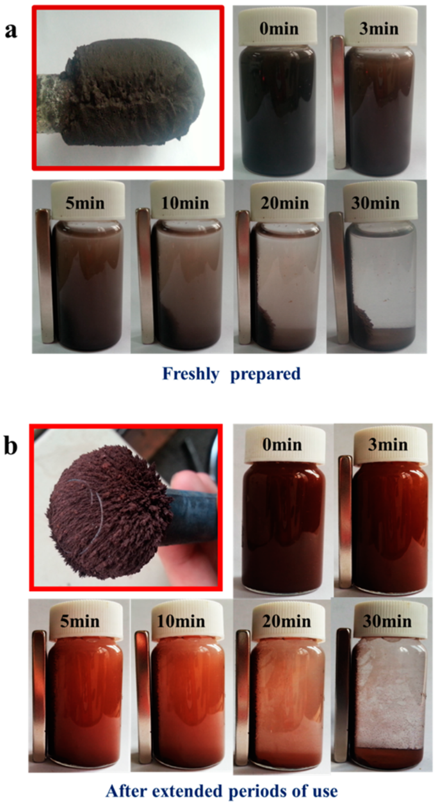


Figure 9. Photos of electrode macroscopic appearance and granule recyclability tested by a magnet: (a) freshly prepared electrode and granules and (b) used electrode and granules.

The tracking of the new electrode service is still in progress. Because the new electrode may have a long first lifetime (which is estimated to be more than 1 year, during which granules are not refreshed) under practical mild conditions, further experiments such as the coating recycle of have to be delayed. We postulate that the total lifetime of the electrode may be extended significantly after several coating recycles.

Comparisons of New 2.5D Electrode/System and Three-Dimensional (3D) Electrode/System. Because the new 2.5D electrode is superior to the 2D electrode, it is interesting to compare this 2.5D electrode with the three-dimensional (3D) electrode. The 3D electrochemical oxidation has been recognized as an effective process for wastewater treatment.[28] The 3D system is established based on the 2D system with the similar electrode materials. But it has additional granular electrodes or bed electrodes, which are filled between the anode and cathode. These granules could be polarized by the electric field and form several positive−negative charges. The 3D system has higher surface area and shorter distance of mass transfer than the 2D system, resulting in higher COD removal efficiency than that in the 2D system. Therefore, the advantages of the 2.5D system here and those of the 3D system are similar compared with those of the 2D system. Therefore, it is worth it to compare the 2.5D system with the 3D system. Some main aspects are listed below:

Polarization of Granular Catalysts. In most 3D systems, the third electrodes (granular catalysts) are separated from the main electrode.[29] Therefore, each granule has two poles (anode and cathode). Although the granules on the electrode of the 2.5D system have only one attribution (anodic in this paper) due to the direct contact with the electrode shell.

The polarization degrees of the granules in the two systems are not similar as well. In the 3D system, granules polarization degrees vary with the distance between the granules and main electrode. This heterogeneity results in the different EO abilities and different lifetimes of the granules. In the 2.5D system, all granules are polarized strongly because they are attracted on the electrode shell. All granules have similar EO ability and lifetime, which are convenient to be recycled at the same time.

Loading Style of the Granular Catalysts. The granules used in the 2.5D system are attracted on the anode surface by magnetic attraction force. Except for the recycle process, the granules are fixed tightly and could barely disperse into the bulk solution. However, most granules used in the 3D system are suspended in the bulk solution, and others are supported by the bottom or a board in the reactor.

EO Ability of the System. As reported, the COD removal efficiency in the 3D system is 10−50% higher than that in the 2D system.[26,30,31] In this study, the COD removal efficiency in the 2.5D system is 5%−55% higher than that in the 2D system.

System Regeneration. The 2.5D system is easier to regenerate than the 3D system. In the 2.5D system, granules on an anode are taken out together with the electrode shell first. And when the magnetic field is removed, the granules were separated from the electrode shell. Using this method, nearly 100% granules could be recycled and there is no need to stop the whole system. The regeneration of 3D system is relatively inconvenient. The operation of the 3D system must be stopped and the granules are taken out using other more complicated methods. The 2.5D system may be more suitable for consideration of green chemistry.

■ CONCLUSIONS

From the above investigations, we can see that the combination of DSA (Ti/Sb−SnO_2) and magnetic catalytic granules (Fe_3O_4/Sb−SnO_2) could be assembled as a new electrode (2.5D electrode). The granules have adequate magnetism to be attracted on the electrode shell. Because of the improvement in mass transfer, the 2.5D system has higher organic removal efficiency and lower energy consumption than the 2D system. Because of the flexibility of magnetic force, the recycle of magnetic granules on the new electrode could be carried out in situ and no secondary waste is produced. When the coating is renewed in time, the lifetime of the new electrode could be increased by a factor of 5. The use of this new electrode is environmentally friendly, which may give it a bright future in the green chemistry industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1 illustrates the tangent method to determine oxygen evolution potential (OEP) of the electrode. Figure S2 shows the proposed mechanism of electrode stability enhancement on new 2.5D electrode. Figure S3 shows the XRD pattern of the used magnetic granules after the accelerated lifetime test. Figure S4 shows the magnetization curve of the magnetic granules after long time use under practical condition. Table S1 shows additional information on electrochemical oxidation performance of real wastewater A, B and C by new electrode and conventional Ti/Sb−SnO_2. Table S2 lists the accelerated lifetime data for Ti based Sb−SnO_2 electrode in some recent literature. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00321.

■ AUTHOR INFORMATION

Corresponding Authors

*Wei Yan. E-mail: yanwei@mail.xjtu.edu.cn.
*Hao Xu. E-mail: xuhao@mail.xjtu.edu.cn.

Notes

The authors declare no competing financial interest.

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