A modular functionalized anode for efficient electrochemical oxidation of wastewater: Inseparable synergy between OER anode and its magnetic auxiliary electrodes

Dan Shaoa,∗, Yuanyuan Zhanga, Wei Lyub, Xinlei Zhanga, Guoqiang Tanb, Hao Xud, Wei Yand

a School of Materials Science and Engineering, Shaanxi Key Laboratory of Green Preparation and Functionalisation for Inorganic Materials, Shaanxi University of Science & Technology, Xi’an, 710021, China
b State Key Laboratory for Modification of Chemical Fibers and Polymer Materials & College of Materials Science and Engineering, Donghua University, Shanghai, 201620, China
c Department of Chemistry, University of York, York, YO10 5DD, UK
d Department of Environmental Engineering, Xidian Jiaotong University, Xi’an, 710049, China

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ABSTRACT

Oxygen evolution reaction (OER) anodes, (e.g., IrO2) are well-known inefficient catalysts for electrochemical oxidation (EO) of refractory organics in wastewater due to the high energy consumption via OER. However, in this study this kind of anode participated in a very effective EO process via a specific modular anode architecture. Traces of magnetic Fe3O4/Sb-SnO2 particles as auxiliary electrodes (AEs) were attracted on the surface of the two-dimensional (2D) Ti/IrO2-Ta2O5 by a NdFeB magnet, and thereby constituted a new magnetically assembled electrode (MAE). MAE could be renewed by recycling its AEs. The electrochemical properties as well as the EO performances of the MAE could be regulated by adjusting the loading amount of AEs. Results showed that even a small amount of AEs could increase surface roughness and offer massive effective active sites. When removing color of azo dye Acid Red G, the optimal MAE exhibited ∼1100 % and ∼500 % higher efficiencies than 2D Ti/IrO2-Ta2O5 and 2D Ti/Sb-SnO2, respectively. The superiority of the MAE was also applicable in degrading phenol. The synergy between Ti/IrO2-Ta2O5 and magnetic Sb-SnO2 particles was therefore discussed.

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1. Introduction

Electrochemical oxidation (EO) wastewater treatment technique is a clean and effective approach to realize the elimination or conversion of the hazardous and biorefractory organic pollutants in wastewater, which could either function as an independent technique or act as an appropriate supplement of biotreatment technique (Möhle et al., 2018; Martínez-Huitle and Panizza, 2018; Karlsson and Cornell, 2016; Martínez-Huitle et al., 2015; Xu et al., 2017). The economic efficiency of EO wastewater treatment technique is mainly depended on the inhibition of side reaction, i.e., oxygen evolution, which is determined by the nature of anode. Therefore, anode material with high EO selectivity towards organic pollutants (i.e., high EO ability/capability) and sustainability is desirable (Shao et al., 2020). Enhancing the intrinsic EO capability of the existing active sites and increasing the amount of effective active sites are the two main design rules for developing high-performance anodes in the recent studies, such as the modification of anode surface’s chemical composition (Fu et al., 2017; Wang et al., 2017; Adams et al., 2009; Zhang et al., 2018; Shao et al., 2014a), the construction of the porous surface structure (Fan et al., 2016; Farinos and Ruotolo, 2017; Chai et al., 2014; Zhang et al., 2019, 2017), and the directly utilization of three dimensional (3D) electrodes (Zhan et al., 2019; Zhang et al., 2013; Li et al., 2016) and so on.

For several years, we have committed to focus on Sb-SnO$_2$ coated Ti anode (Ti/Sb-SnO$_2$) since it is a promising anode with low-cost and high EO capability (Yang et al., 2017; Li et al., 2017; Sirés et al., 2014). The only drawback is the short lifetime. Many approaches had been tried to address this issue, such as inserting TiH$_x$ interlayers (Shao et al., 2014b), introducing gradient distribution of Sb and Sn elements (Shao et al., 2014c) or even change the Ti substrate to SiC (Zhang et al., 2019). However, the best lifetime performance of this kind of anode was still no more than 72 h (current density of 200 mA cm$^{-2}$, in 0.5 M H$_2$SO$_4$) during the long-term research. The obtained unacceptable performance was far below the level of mainstream anode materials’ performance.

Fortunately, we finally found a facile approach to develop a high-performance anode with additional heterogeneous active sites (Fig. 1), where a small amount of magnetic particles (auxiliary electrodes, AEs) were attracted and fixed on a 2D metal oxide coated anode (main electrode, ME) by a strong magnetic field. This new anode architecture was named as magnetically assembled electrode (MAE). The MAE EO system presents a transition state between the conventional 2D EO system and the three-dimensional (3D) EO system, so MAE has another name “2.5D electrode”. The massive additional active sites (or area) introduced from AEs could decrease the real current density, improve the mass transfer and endow the MAE with higher stability, higher EO efficiency and higher waste disposal capacity (Shao et al., 2018, 2015). As the AEs are fixed on the 2D ME by a flexible combination force, the MAE has some unique characteristics:

(i) Variability

The surface structure and composition could be varied if necessary.

(i) Adjustability

AEs loading amount could be automatically adjusted by change the magnetic field.

(i) Versatility

Combinations of different ME and AEs, as well as different AEs loading amount, could endow the MAE with versatility to handle complex and variable wastewaters.

(i) Recyclability

The EO system can be purged by cutting off the magnetic field, where the released AEs could be recycled by another magnet and new fresh AEs would be loaded on the ME again. The power source does not need to be cut off during this unique recycle process.

(i) Dispersion

Because of magnetic polar repulsion, the attracted magnetic AEs particles are highly dispersive.

(i) Modularity

Furthermore, most importantly, the modular assembly of surface catalysts and underlying bulk anode could combine the advantage and minimize the weakness of each component. For example, in our earlier

![Fig. 1. Illustrations of the magnetically assembled electrode (MAE) and its EO system.](image-url)
attempts we used Ti/PbO2 as ME and Sn-SnO2 as coating material of AEs. Thanks to the underlying Ti/PbO2, the surface Sn–SnO2 catalyst’s high EO performance was more durable. The preliminary operating mechanism of MAE was therefore proposed. The functionality of ME and AEs was regarded as the guarantee of electrode stability and the catalytic activity, respectively.

To inhibit oxygen evolution reaction (OER) and obtain sufficient energy efficiency, researchers and engineers usually use anodes with higher oxygen evolution potential (OEP), such as boron doped diamond (BDD), TiO2, Sn-SnO2 and PbO2. Therefore, in our earlier efforts to assemble MAE, only materials with high oxygen evolution potential (OEP) were chosen, i.e., Sn–SnO2 and PbO2. However, the similar EO behaviors of these higher OEP coating materials on ME and AEs brought a difficulty in distinguishing the contribution of either ME or AEs, and further digging out the real operating mechanism of the MAE will be out of the question. Therefore, we decided to use a blank background as ME to distinguish the functionality and contribution of AEs first.

It is well known that Ti/IrO2-Ta2O5 has excellent anode stability compared with other metal oxide anodes (Scialdone et al., 2009; Comminellis and Chen, 2010; Bagastyo et al., 2011; Aminu et al., 2018; Duan et al., 2016). However, this typical OER electrode with lower OEP value (compared with BDD, Sn–SnO2, etc.) inevitably shows a poor EO performance in treating refractory organic wastewater, demonstrating this active anode material is not suitable to be used for EO wastewater treatment (Scialdone et al., 2009; Bagastyo et al., 2011; Shestakova and Sillanpaa, 2017). So, in our opinion, this unserviceable Ti/IrO2-Ta2O5 was an ideal blank background to reflect the contribution of other components in MAE. However, interestingly, in the preliminary experiments this anode was found to be a qualified ME and its high OER activity (low OEP) did not bring down the EO capability of the whole MAE. In addition, ME with IrO2-Ta2O5 ME even performed better than other MAEs with Sn–SnO2 or PbO2 ME. Therefore, the inherent mechanism needs to be explored.

Herein, Fe3O4/Sb-SnO2 particles (AEs) were loaded on 2D Ti/IrO2-Ta2O5 electrode (ME). Various electrochemical properties of the new electrode with different AEs loading amount were studied. Moreover, the MAE’s EO performances towards two different types of organic pollutants were investigated and compared with those of the 2D Ti/IrO2-Ta2O5 and 2D Ti/Sn–SnO2 under different conditions. The relationships among surface composition/structure, electrochemical properties and EO degradation performance towards different hazardous pollutants were revealed. The synergy mechanism of the low OEP ME and high OEP AEs was further proposed. This new MAE was expected to combine the advantages of IrO2-Ta2O5 (relatively excellent electrochemical activity and stability) and Sn–SnO2 (high EO efficiency) and enhance the reputation of OER anode material in the energy-efficient EO treatment of refractory organic wastewater.

2. Material and methods

2.1. The assembly of the MAE

Dip coating-pyrolysis method was used to fabricate Fe3O4/Sb–SnO2 AEs as reported (Shao et al., 2018). The received commercial 2D Ti/IrO2-Ta2O5 was used as the ME. As shown in Fig. 2, a permanent magnet (NdFeB) was fixed on the back of Ti/IrO2-Ta2O5 ME and followed by loading an appropriate amount of AEs on the ME’s surface. The MAEs with different loading amount of AEs (0.05 g cm−2, 0.10 g cm−2, 0.20 g cm−2, and 0.30 g cm−2) were named as IrO2/Sn–SnO2(0.05 g), IrO2/Sn–SnO2(0.1 g), IrO2/Sn–SnO2(0.2 g) and IrO2/Sn–SnO2(0.3 g), respectively. For comparison, 2D Ti/Sn–SnO2 was prepared as reported (Shao et al., 2014b). In addition, a received commercial graphite anode with moderate OEP value was used as another comparison to investigate the synergy between IrO2-Ta2O5 and AEs. The MAE with different loading amount of AEs on graphite was also named as Gr/Sn–SnO2(xg).

2.2. Electrode characterizations

For the material characterizations, the AEs were characterized by SEM (JSM-6390A, JEOL), EDS and XRD (Cu Kα, D/max-2200PC, Rigaku), respectively. The MEs were also characterized as above. The electrochemical characterizations were carried out in a standard three-electrode cell. The working electrode (effective area 1 cm2) was the assembled MAE or the control electrode. The counter electrode was a copper plate. The reference electrode was a saturated calomel electrode (SCE). A galvanostat/potentiostat (CS-310H, CorrTest) was used to perform different electrochemical characterization experiments such as CV tests (cyclic voltammetry) and EIS tests (electrochemical impedance spectroscopy). The electrolyte was 0.5 M Na2SO4 aqueous solution. In the EIS test, the frequency was set from 103 to 0.1 Hz, 0 V (vs. SCE) was the equilibrium potential, and the amplitude of the potential was 5 mV.

2.3. Degradation of acid red G and phenol

Two different wastewater samples with 100 mg L−1 pollutant concentration and 0.25 L volume were prepared by dissolving chemical pure Acid Red G (ARG) and phenol in pure water (18 MΩ cm), respectively. The adopted effective area of the anode in this experiment section was 9 cm2. The variation of organic concentration in samples was measured directly for ARG detection or indirectly via the method of 4-amino antipyrine (National standards for environmental protection HJ503-2009, China) for phenol detection by a UV–vis spectrometer (Agilent 8453).

2.4. Sustainability of the assembled MAE

One representative MAE in this study (IrO2/Sn–SnO2(0.2 g)) was chosen in the accelerated lifetime test to examine the electrode stability of the assembled MAE. The effective anode area was 9 cm2, and the anodic current was set to 1.8 A (current density of 200 mA·cm−2), and the media was 0.5 M Na2SO4 solution. The accelerated lifetime of the electrode was regarded as the duration from the initial time to the time when the cell voltage reached to 10 V. During the accelerated lifetime test, the electrochemical characterizations (e.g., voltammetric charge) as well as the EO performance of the electrode were examined every 24 h, and the condition was as same as that in section 2.2 and section 2.3.

3. Results and discussion

3.1. Material characterizations

The SEM images of Sn–SnO2 coated AEs, 2D Ti/IrO2-Ta2O5 ME and 2D Ti/Sn–SnO2 control electrode are shown in Fig. 3a–c, respectively. The AEs was μm grade (10–20 μm), and the compact coatings of all 2D electrodes presented typical crack-mud structure. The EDS mapping images of the two 2D electrodes shown in Figure S1 and S2 clearly confirmed the composition of IrO2-Ta2O5 and Sn–SnO2. The XRD spectra are shown in Fig. 3d. For the 2D Ti/IrO2-Ta2O5 ME, it can be found that the intensity of IrO2 characteristic peaks was much higher than the one of Ti substrate, indicating the fine coverage of IrO2 coating on Ti substrate. While for Fe3O4/Sb–SnO2 AEs, only slight weak intensity of Fe3O4 characteristic peaks can be observed. It suggested the successful encapsulation of Fe3O4 core by Sn–SnO2 coating, which offered sustainable magnetism of the AEs and ensured the durability of the MAE.

3.2. Electrochemical oxidation of ARG and phenol

Two typical organic pollutants, i.e., anionicazo dye Acid Red G and phenol, were selected to study the EO performance of the assembled electrodes. It is well known that azo linkage and benzene ring of
organic pollutants can be broken by the EO treatment, in which the breakage of benzene ring is more difficult (Wang et al., 2017; Brillas and Martinez-Huitle, 2015).

Fig. 4 shows the EO performance of different electrodes on ARG removal. In Fig. 4a, we can see the different decolorization results of these electrodes as a function of time. No obvious color change could be observed for 2D Ti/IrO$_2$-Ta$_2$O$_5$ electrode during 3 h treatment, indicating 2D Ti/IrO$_2$-Ta$_2$O$_5$ was unable to break the azo linkage efficiently. Pale red solution can be found for 2D Ti/Sb-SnO$_2$ after 3 h treatment, suggesting it was much better in decolorization. Inspiringly, striking decolorization phenomenon was observed for all MAEs, with the best EO performance achieved by IrO$_2$/SnO$_2$(0.2 g) within only 30 min, i.e., 97 % of ARG removal. Under the same short treating time, only ~8 % and ~16 % ARG removals were available on the above two 2D electrodes, respectively. The obtained contrasting results revealed that loading tiny Fe$_3$O$_4$/Sb-SnO$_2$ AEs on the inferior IrO$_2$/SnO$_2$ anode could significantly enhance the ARG removal efficiency (~1100 % higher than 2D Ti/IrO$_2$-Ta$_2$O$_5$) and even made the whole electrode much better than the 2D Ti/Sb-SnO$_2$ (~500 % higher). As shown in the UV-vis spectra (Fig. 4b–d), it could also be found that the adsorption peaks of benzene ring and naphthalene ring of ARG decreased obviously on IrO$_2$/SnO$_2$(0.2 g) electrode, revealing that the MAE could break benzene ring and naphthalene ring of ARG more efficiently than the two 2D electrodes. The loading amount of AEs was found to be crucial in exerting the maximal EO power of the MAE, and 0.2 g·cm$^{-2}$ was found to be the optimal loading amount for ARG degradation (Fig. 4e). In addition, TOC decay during this treatment was also measured (Figure S3), where after 3 h treatment ~33 % TOC decay was available on IrO$_2$/SnO$_2$(0.2 g) while the value was only ~18 % on 2D Ti/Sb-SnO$_2$, further demonstrate the superiority of IrO$_2$/SnO$_2$(0.2 g) also existed in organic mineralization. Another electrode, the IrO$_2$/SnO$_2$(0.3 g), also showed competitive EO efficiency.

Different current densities, i.e., 10 mA·cm$^{-2}$ and 20 mA·cm$^{-2}$, were applied in EO treatment of ARG (Fig. 4e and f). The EO efficiency of 2D electrodes was affected by the applied current density, while the EO performance of MAE was independent. Especially, it can be found that for 2D Ti/IrO$_2$-Ta$_2$O$_5$, an anode that are more inclined to OER, higher current density would not increase the EO efficiency but benefit to OER.

Fig. 2. The assembly of the MAE in this study.

Fig. 3. SEM images and XRD patterns. (a) SEM image of the AEs (inset: accumulated AEs). (b) SEM image of the ME (2D Ti/IrO$_2$-Ta$_2$O$_5$). (c) SEM image of the control electrode 2D Ti/Sb-SnO$_2$. (d) XRD patterns of ME and AEs.
Therefore, for MAEs based on this ME, the current density of 10 mA cm\(^{-2}\) was selected and more appropriate due to its energy-saving and its equivalent or better efficiency compared with that of 20 mA cm\(^{-2}\).

Since phenol is more refractory than ARG, the superiority of the highly loaded MAEs may be more obvious in destroying phenol (Fig. 5). It is worth to mention that 2D Ti/IrO\(_2\) almost had negligible power to degrade phenol, but an appropriate small amount of AEs could improve the situation, e.g., IrO\(_2\)/SnO\(_2\)(0.3 g) and IrO\(_2\)/SnO\(_2\)(0.2 g), whose performances were even much better than 2D Ti/Sb-SnO\(_2\) (∼70 % and ∼26 % better). TOC decay (Figure S4) also demonstrated that the superiority of the above two MAEs in mineralization, where the values were ∼12 %, ∼32 %, ∼41 % and ∼27 % on 2D Ti/IRo\(_2\)Ta\(_2\)O\(_5\), IrO\(_2\)/SnO\(_2\)(0.2 g), IrO\(_2\)/SnO\(_2\)(0.3 g) and 2D Ti/Sb-SnO\(_2\), respectively, after 3 h treatment. Another phenomenon was that higher current density was unbene\(\text{fi}\)cial for 2D Ti/IrO\(_2\)Ta\(_2\)O\(_5\) because of the boosted OER side reaction. Similarly, the EO efficiency of MAE could not be increased proportionally due to the magnified OER on the ME. Therefore, in practical operation, the current density should be controlled below a critical level to gain the balance of efficiency and energy-saving.

Fig. 4. ARG removal results (100 mg L\(^{-1}\), 0.25 L, 9 cm\(^2\) electrode area). (a) UV spectra of the solution samples versus time treated by 2D Ti/IrO\(_2\)Ta\(_2\)O\(_5\) (current density 20 mA cm\(^{-2}\)). (b) UV spectra of the solution samples versus time treated by 2D Ti/Sb-SnO\(_2\) (current density 20 mA cm\(^{-2}\)). (c) Photos of the solution samples versus time. (d) UV spectra of the solution samples versus time treated by IrO\(_2\)/SnO\(_2\)(0.2 g) (current density 20 mA cm\(^{-2}\)). (e) ARG removal rate on different anode under current density of 20 mA cm\(^{-2}\). (f) ARG removal rate on different anode under current density of 10 mA cm\(^{-2}\).

Fig. 5. Phenol removal rate versus time under current density of 20 mA cm\(^{-2}\) (left) and 10 mA cm\(^{-2}\) (right) (100 mg L\(^{-1}\), 0.25 L, 9 cm\(^2\) electrode area).
3.3. Electrochemical characterizations

3.3.1. Electrochemical roughness factor (Rf)

The AEs particles not only introduce macroscopic rough surface but also bring additional microscopic roughness along the interface between ME and AEs, or between AEs themselves (interior defects). The Rf value could reflect the impact of AEs on the real roughness of the whole electrode and is an indication of the real surface area of the electrode (Duan et al., 2015; Montilla et al., 2004; Chen et al., 2017). The data of Rf value was calculated from the narrow range CV curves (Figure S5, Supporting Information) and the calculation method followed previous reports (Montilla et al., 2004). The calculated Rf values of series of electrodes are shown in Fig. 6a. It could be found that the 2D Ti/ IrO2-Ta2O5 had an obviously higher surface roughness than 2D Ti/ Sb-SnO2, and all the MAEs’ Rf values were obviously higher than those of 2D electrodes. It indicated that the AEs indeed increased the surface roughness of the electrode and introduced considerable real surface area to 2D Ti/ IrO2-Ta2O5 electrode. The maximum Rf value of MAE was achieved by loading a small amount of AEs coatings (e.g., 0.05 g·cm⁻²). Further increased loading amount would decrease the roughness of MAE, which may be due to the stacking effect (or aggregation effect) of AEs particles.

3.3.2. Voltammetric charge (q*)

The voltammetric charge (q*) obtained from the narrow CV curves (Figure S5) could reflect the information of effective active sites (Montilla et al., 2004), where q* (q_a) obtained at fast scan rate reflects the outer active sites and q* (q_p) obtained at very slow potential scan rate corresponds to the total active sites. The difference between the above to q* values reflects the less accessible (or inner) active sites, called q_r (Zeradjanin et al., 2014). From Fig. 6b it could be noticed that q_r values of MAEs were much higher than those of 2D electrode, suggesting that loading AEs could introduce massive inner active sites. This phenomenon was in good accordance with our previous studies (Shao et al., 2018), but the improvement of both q_r and q_p in this study was more significant. It indicated that the Sb-SnO2 AEs indeed participated in the electrochemical functionalities of the MAE, and Sb-SnO2 may play an important role in the following EO degradation of organics.

3.3.3. OER activity

Loading AEs on the 2D electrode would not only modify the original electrode surface roughness, but also change the composition of electrode surface coating. Because the Fe3O4/Sb-SnO2 AEs and Ti/IrO2-Ta2O5 ME exhibit different OER activities, it is keen to know OER activity of the assembled MAE. Fig. 6c and d illustrates the CV curves and Tafel plots, respectively. It could be found that at current density of 0.01 A cm⁻², the OEP values of 2D Ti/IrO2-Ta2O5 and 2D Ti/Sb-SnO2 were around 1.39 V and 2.26 V (vs. SCE), respectively. These two 2D electrodes’ response current densities in OER region were also different in the two figures. After assembly, the OER activity of MAEs decreased with the increased amount of AEs. It indicated that the Fe3O4/Sb-SnO2 AEs covered certain part of ME and participated in the OER process, making the whole electrode’s OER activity move closer to that of the 2D Ti/Sb-SnO2. But high AEs loaded MAE (e.g., IrO2/SnO2(0.3 g)) still had much higher OER activity than Ti/Sb-SnO2. In addition, result of control experiment carried out in media containing saturated terephthalic acid (TPA, trapping agent) and 0.5 M Na2SO4 (Figure S6) shows that the trapping agent did not change the OER activity, indicating that in this MAE, IrO2-Ta2O5 provided main contribution to OER, because the higher oxide (the OER intermediate on IrO2-Ta2O5) would not interact with TPA.

3.3.4. Electrochemical impedance

From our previous studies, the ohmic drop of electrode would be increased after loading excessive AEs as the loaded AEs could inevitably...
hinder the contact between the ME and the bulk solution, increasing cell voltage and making the EO process high energy consuming. The impedance of the MAE was therefore studied. As the Nyquist plots of the electrodes (equilibrium potential 0 V (vs. SCE), in 0.5 M Na2SO4, frequency range 0.1 to 10^5 Hz) illustrated in Fig. 7a, the impedance in the low frequency rage decreased with the increased loading amount of AEs, indicating the positive effect of the enlarged real surface area. The high impedance data of the 2D IrO2-Ta2O5 indicated the poor intrinsic conductivity of IrO2-Ta2O5. However, thanks to the IrO2-Ta2O5, the charge transfer across the interface between AEs and the ME was good. Consequently, the AEs were well polarized, which could release the AEs’ EO ability and save the electric energy. The Nyquist plots at equilibrium potential of 1.2 V (vs. SCE) (Fig. 7b) shows that the impedance at low frequency range decreased significantly for Ti/IrO2-Ta2O5 and all MAEs, demonstrating the OER occurred at this potential for these anodes. However, for 2D Ti/Sb-SnO2, this potential was not positive enough for the occurrence of OER. This result was another proof for that the MAE’s electrochemical behavior were more like IrO2, not Sb-SnO2.

3.4. Synergetic mechanism of ME and AEs

The general rules in terms of the functionality of ME and AEs, effect of AEs loading amount, effect of type of target pollutant on participation of active sites, have been discussed in our previous study (Shao et al., 2018). Comparing the above inspiring organic degradation results with other 2D anodes and MAEs that were previously investigated by the authors (Supporting Information, Figure S7), we can see that the new MAE (IrO2/SnO2) not only exceeded the level of high OEP 2D anodes (2D Ti/Sb-SnO2 and 2D Ti/PbO2), but also exceeded the level of the combination of high OEP ME and high OEP AEs (SnO2/SnO2 and PbO2/SnO2). Therefore, it can be deduced that Ti/IrO2-Ta2O5 may have its unique additional synergism with Sb-SnO2 coated particles, not only the simple expansion of electrode area offered by the well dispersed AEs. The above electrochemical characterization results also indicated that the whole MAE’s characteristics (e.g., OER activity) were closer to that of IrO2-Ta2O5, which inspired us that the undesired relatively high OER activity brought by IrO2-Ta2O5 may play a crucial and positive part in the synergy. This specific synergism may include but not limit to the following three terms:

(i) The introduction of electrochemical combustion

IrO2 is a typical “active anode” and its EO power originates from the selective oxidation via direct charge transfer from organics to the so-called higher oxide (MOx+1) on the anode surface. While Sb-SnO2 could accumulate physical adsorbed hydroxyl radicals (·OHads), and more effective combustion occurs with this material at the surface of which ·OHads are accumulated (Comninellis, 1994). Since AEs are closer to the bulk solution than ME, the organic pollutant would reach to the vicinity of AEs more easily and be fast oxidized by the ·OHads.

(ii) The redistribution of anodic current

The AEs bring additional projecting parts on the electrode surface. Due to the tip effect, the current distribution on the relatively flat ME was weakened. The AEs also introduce many defects on the AEs/ME interface and these defects mainly located on the inner surface of the electrode and provide massive active sites (Section 3.3.2). The amount of original active sites on the IrO2-Ta2O5 was much less than the newly introduced active sites. In addition, some original active sites on the IrO2-Ta2O5 are covered by the AEs, but the OER side reaction still basically happened on the ME. The integrated effect of the above reasons may optimize the current distribution. During organic oxidation, the current distributed to the side reaction (OER) on IrO2-Ta2O5 could be minimized.

(iii) The released functionality of AEs

In the assembled MAE, as AEs is indirectly polarized through the ME, the polarization degree on the AEs is strongly dependent on the nature of ME. The OER on IrO2-Ta2O5 is very active, leading to the decrease of charge transfer impedance (Fig. 7) during the electrolysis. Consequently, a lower ohmic drop (or an expedite electron tunnel) could polarize the AEs more strongly. In other words, the capability of the AEs could be well released by the high OER activity of IrO2-Ta2O5.

All above three terms of the synergy and its illustration in Scheme 1 are the complement of the operating mechanism of the MAE. The first two terms could be regarded as the contributions of Sb-SnO2 coated AEs. But what is more encouraging is that the last one term of synergy mechanism corresponding to the excellent OER activity of Ti/IrO2-Ta2O5. Therefore, we replaced Ti/IrO2-Ta2O5 with a more powerful anode material graphite to verify the key impact of OER activity of ME.

3.5. Graphite as ME

Generally, graphite is more applicable than Ti/IrO2-Ta2O5 as anode in EO treatment of organic wastewater. Its higher OEP value and higher conductivity are the good qualities to inhibit side reaction and polarize the AEs, respectively. We estimated that graphite-based MAE may perform better than IrO2-Ta2O5-based MAE under similar condition. However, the result was contrary to the expectation. The material characterization result of graphite used in this study is shown in Figure S8. In EO degradation experiment, Fig. 8a–c shows that under similar condition, the graphite-based MAE exhibited lower organic removal efficiency than previous IrO2-Ta2O5-based MAE, although 2D graphite showed a higher efficiency than 2D Ti/IrO2-Ta2O5. In addition, the graphite-based MAE with higher AEs loading amount, e.g., Gr/
SnO₂(0.3 g), did not compete with 2D Ti/Sb-SnO₂ under the condition of lower current density or destroying more refractory organic. This result indicated that the Sb-SnO₂ coated AEs loaded on graphite was not as competitive as these loaded on 2D Ti/IrO₂-Ta₂O₅ (compared with the performances in Figs. 4 and 5). From Fig. 8d–h we could see that the graphite had higher conductivity and inferior OER activity with a more positive OEP value compared with 2D Ti/IrO₂-Ta₂O₅, and graphite-based MAE had similar surface roughness and even more active sites compared with the IrO₂-Ta₂O₅-based MAE (shown in Fig. 6). But at higher anodic potential (e.g., Fig. 8i), the charge transfer impedance of graphite was similar to that of 2D Ti/Sb-SnO₂, which was far beyond that of 2D Ti/IrO₂-Ta₂O₅, making the charge transfer on graphite-based MAE was not as good as that on IrO₂-Ta₂O₅-based MAE (shown in Fig. 7).

As a consequence, using more conductive and more powerful EO material could not gain the same good results, verifying the contribution of relative excellent OER activity of ME to the activation of the AEs. This conclusion was instructive to select other more novel OER material as ME to assemble more effective MAE.

3.6. Electrode stability and recyclability

Due to the reported excellent stability of Ti/IrO₂-Ta₂O₅ based electrode (Mráz and Krýsa, 1994), the lifetime of the MAE in this study was expected to be long enough in routine electrolysis (anodic current density of 20 mA·cm⁻² in 0.5 M Na₂SO₄ solution). During the routine electrolysis, the cell voltage remained well during three months of routine electrolysis, and the EO power of MAE (e.g., IrO₂/SnO₂(0.2 g)) only decreased by ~10% to ~20% after three months of routine electrolysis (Fig. 9a). The photos of the vertical state of MAE after 15

![Scheme 1. Schematic illustration of the terms in the synergetic mechanism of IrO₂ and Sb-SnO₂ on ME and AEs, respectively.](image)

![Fig. 8. Degradation performance and electrochemical characterization of graphite-based MAEs after just replacing Ti/IrO₂-Ta₂O₅ to graphite.](image)
days of routine electrolysis are shown in Figure S9. We can see that during the mild routine electrolysis (20 mA·cm$^{-2}$), the AEs were not found to be corroded and they were still attracted on the ME firmly. Therefore, the exact value of electrode lifetime was uncertain because of the limited test time. The accelerated lifetime test is a time-saving approach to reflect the electrode lifetime, where the anodic current density (200 mA·cm$^{-2}$) is 10 times large. However, during the 120 h of the accelerated lifetime test, the cell voltage was still quite stable (Fig. 9b), indicating the anode was still active and its main function was well retained even after the long-time and harsh electrolysis. However, the harsh condition would decrease of electrode's performance more obviously. From Fig. 9c it could be found that the anode's EO efficiency in destroying the three functional groups of ARG (azo linkage, naphthalene and benzene) first decreased significantly during the initial 24 h, and then basically maintained well during the rest period. Among the three functional groups of ARG, the decrease of electrode’s efficiency remaining in destroying azo linkage was the least. Thus, we deduced that the functionality of AEs had lost after the initial 24 h because the 2D Ti/IrO$_2$-Ta$_2$O$_5$ ME was quite stable and the AEs made the main contribution to the EO power of the whole MAE. The appearance of the ME and AEs was firstly checked (Fig. 9d). It could be found that the ME retained very well but the AEs' color became brownish red. Moreover, the AEs' conductivity under the SEM measurements was not as good as the fresh AEs and their morphologies were also damaged and became rougher (Fig. 9e, compared with Fig. 3). Furthermore, Fig. 9f illustrates the variation of voltammetric charge ($q^*$) of the electrode versus potential scan rate during the accelerated lifetime test. It could be found the $q_T$ and $q_i$ firstly went up by 2 times and then fell back to its original level. Therefore, it can be deduced that the outer surface of the electrode was stable and the AEs' distribution on the ME was basically unchanged, but the status of the inner surface varied continuously. In
In this study, when the 2D Ti/IrO₂-Ta₂O₅ was loaded by a small amount of Fe₃O₄/Sb-SnO₂ particles (0.2 g·cm⁻² or 0.3 g·cm⁻²), the assembled new MAE was not only superior to the original 2D Ti/IrO₂-Ta₂O₅, but also exceeded the levels of 2D Ti/Sb-SnO₂ and other MAEs investigated earlier. The typical OER material IrO₂-Ta₂O₅ was proved to destroy and the Fe₃O₄ core, which was partly oxidized to Fe₂O₃, was still magnetic.

Apparently, since the 2D Ti/IrO₂-Ta₂O₅ ME’s EO power was insufficient, if AEs were damaged, although the ME retained very well, the whole electrode’s high EO capability would not be ensured. Fortunately, for MAE, recycling the damaged AEs on time can ensure the sustainability of the electrode’s EO power without replacing the anodes and interrupting of the whole EO system. After 24 h of accelerated lifetime test, the AEs were dispersed in the bulk solution by removing magnetism, which can be collected and recycled by another magnet. After a short time, fresh AEs could be loaded on the previous ME when the magnetic field behind ME was reboot. It is delighted to see that after recycling for 5 times (24 h × 5) during the accelerated lifetime test, the EO ability of each MAE still could retain 95 % (Fig. 10), indicating the excellent recyclability of the MAE. This result inspired us to utilize Sb-SnO₂-coated anode in practical programs in the near future.

4. Conclusion

In this study, when the 2D Ti/IrO₂-Ta₂O₅ was loaded by a small amount of Fe₃O₄/Sb-SnO₂ particles (0.2 g·cm⁻² or 0.3 g·cm⁻²), the assembled new MAE was not only superior to the original 2D Ti/IrO₂-Ta₂O₅, but also exceeded the levels of 2D Ti/Sb-SnO₂ and other MAEs investigated earlier. The typical OER material IrO₂-Ta₂O₅ was proved to be an eligible ME material for MAE in energy-efficient organics degradation, which was beyond expectation. There was a specific synergy between IrO₂-Ta₂O₅ and AEs as follows:

(i) Sb-SnO₂ coated AEs introduced the effect of electrochemical combustion.
(ii) The anodic current distribution was optimized from IrO₂-Ta₂O₅ to the massive inner active sites along the ME/AEs interface.
(iii) The active OER behavior of the IrO₂-Ta₂O₅ facilitated the underlayer charge transfer and thereby released the functionality of AEs.

The relatively high OER activity (compared with PbO₂ or Sb-SnO₂) of IrO₂-Ta₂O₅ played an important and positive part in the synergy. Graphite as control ME material further verified this point. In addition, the good recyclability endowed this new MAE with sustainable and high EO efficiency, which was expected to save the destiny of Sb-SnO₂-coated anode in future EO wastewater treatment.

CRediT authorship contribution statement

Dan Shao: Conceptualization, Methodology, Validation, Resources, Investigation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition. Yuanyuan Zhang: Investigation, Visualization, Writing - original draft. Wei Lyu: Visualization, Writing - review & editing. Xinlei Zhang: Investigation. Guoqiang Tan: Resources, Supervision. Hao Xu: Writing - review & editing. Wei Yan: Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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