

Electrosynthesized TiO₂ and WO₃ coatings for photoelectrocatalytic destruction of pollutants

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Abstract. WO₃ and bilayer WO₃/TiO₂ coatings have been electrosynthesized on stainless steel (SS) 304 substrates from acidic aqueous solutions by potentiostatic cathodic deposition. The resulting WO₃/SS and WO₃/TiO₂/SS photoelectrodes have been screened for their photoresponse under ultraviolet (UV) and visible (VIS) light illumination by photovoltammetry and photoamperometry in sulfate solutions in the absence and presence of model organic pollutants. They were also evaluated for bulk photooxidation of oxalate, malachite green and 4-Chlorophenol under constant potential in the range determined on the basis of the photoelectrochemical tests. It was found that the photoelectrocatalytic activity of bilayer TiO₂/WO₃/SS is higher than that of plain WO₃/SS photoelectrodes under both UV and VIS light illumination. The enhancement of the UV and VIS photocatalytic activity of bilayer WO₃/TiO₂ is interpreted by efficient separation of photogenerated electron-hole pairs and reduced recombination rates.

1. Introduction

Photocatalytic processes are a promising class of advanced oxidation technologies used for environmental remediation. A suitable conductive support for TiO₂ and WO₃ allows obtaining electrodes with enhanced photocatalytic activity by a positive potential bias. These materials are potentially effective as photoelectrochemical catalysts for water treatment. Recently, electrosynthesis of TiO₂ and WO₃ coatings deposited on a cheap substrate of stainless steel has been proposed as an alternative, low-cost route for production of these catalysts tested in photoelectrocatalysis [1-3]. WO₃, in contrast to TiO₂, can be excited by illumination with VIS light. Bilayer WO₃/TiO₂ materials have shown superior UV and VIS photoelectrocatalytic activity with respect to their plain component analogues, which was explained by the favourable charge transfer and reduced rate of electron-hole recombination in this semiconductor combination [1,3].

In this work the objectives were first to apply the electrosynthesis from acidic aqueous solutions for preparation of WO_3/SS and bilayer $\text{TiO}_2/\text{WO}_3/\text{SS}$ electrodes with dimensions appropriate for bulk photoelectrocatalysis. The second task was the screening of the catalysts by evaluation of their photoelectrochemical activity and then to evaluate the performance of samples with large dimensions for bulk photooxidation of oxalate, MG and 4-chlorophenol under UV and VIS light illumination.

2. Experimental

2.1. Preparation and photoelectrochemical characterization of WO_3 and bilayer TiO_2/WO_3 coatings

All coatings were prepared in a three-electrode cell on SS plate specimens, using Pt as a counter electrode and a mercurous sulfate electrode (MSE) as a reference electrode.

WO_3 was deposited in a direct cathodic deposition step at -1.0 V vs. MSE from acidic aqueous solution of peroxytungstate. The deposit was heated in air at 350 °C for 30 min to obtain crystalline WO_3 .

Bilayer TiO_2/WO_3 coatings were electrosynthesized in a subsequent electrodeposition of TiO_2 onto WO_3/SS electrodes at -2.0 V vs. MSE from acidic aqueous solution of titanium oxosulfate. The deposited gel film was heated in air at 400 °C for 1 hour for TiO_2 crystallization.

Photovoltammetry and photoamperometry were carried out to assess the electric field enhancement of the photocatalytic activity of WO_3 and bilayer TiO_2/WO_3 deposits towards organics oxidation. Photoelectrochemical characterization of small photoelectrodes was performed in a three-electrode cell under UV and VIS light illumination. A saturated calomel electrode (SCE) was used as a reference electrode and a Pt foil as a counter electrode. The experiments were performed in 0.1 M K_2SO_4 solutions in the absence and presence of model organic pollutants. The photoelectrochemical tests served as a basis to determine the potential range appropriate for photoelectrocatalysis.

2.2. Photoelectrolysis experiments

To evaluate the catalytic activity of the $\text{TiO}_2/\text{WO}_3/\text{SS}$ and WO_3/SS photoelectrodes towards the photooxidation of oxalate, malachite green (MG) and 4-Chlorophenol, long-term constant potential bulk photo-

oxidation experiments were carried out, using 30 cm^2 electrodes. The experiments were performed in a 500 ml cylindrical cell with a removable cap. The UV or VIS light lamp, placed in a cylindrical sleeve, was introduced in the middle of the cell, leaving a solution available volume of 250 ml of $0.1 \text{ M K}_2\text{SO}_4$ aqueous solutions + 10^{-3} M oxalate, 10^{-5} M MG or 10^{-3} M 4-Chlorophenol. The potential was kept constant at $+0.4 \text{ V}$ vs. SCE for oxalate and MG and $+0.5 \text{ V}$ vs. SCE for 4-Chlorophenol.

The variation of oxalate concentration was determined by permanganate titration. The MG degradation was monitored by spectrophotometry ($\lambda_{\text{max}} = 617 \text{ nm}$) and by Total Organic Carbon (TOC) analysis in the case of 4-Chlorophenol degradation.

At bilayer TiO_2/WO_3 photoelectrodes after 2 h of UV (or VIS) illumination 21.4% (or 19.8%) removal of oxalate and 85.4% (or 66.8%) degradation of MG (Ref. [3]) was observed. After 5 h of UV (or VIS) irradiation 16% (or 12.8%) removal of 4-Chlorophenol was observed. The variation of the concentration of organic pollutants with time under UV and VIS light illumination is presented in Figs. 1-6.

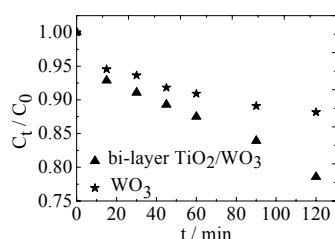


Fig. 1. Variation of oxalate concentration with time under UV light illumination.

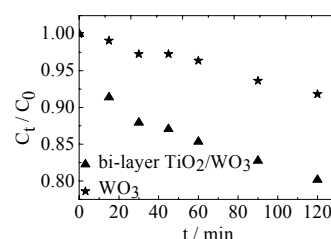


Fig. 2. Variation of oxalate concentration with time under VIS light illumination.

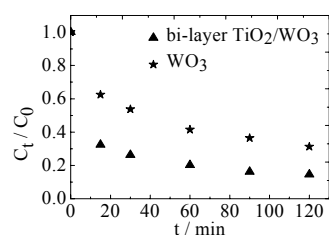


Fig. 3. Variation of MG concentration with time under UV light illumination.

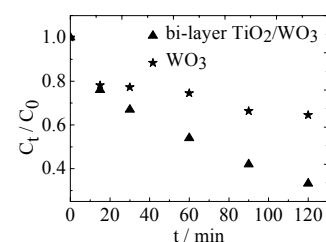


Fig. 4. Variation of MG concentration with time under VIS light illumination.

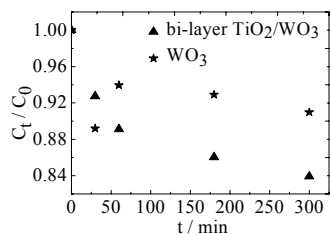


Fig. 5. Variation of 4-Chlorophenol concentration with time under UV light illumination.

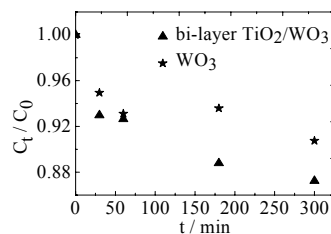


Fig. 6. Variation of 4-Chlorophenol concentration with time under VIS light illumination.

3. Conclusions

1. The efficiency of bilayer TiO₂/WO₃ coatings for photoelectrocatalytic destruction of all tested pollutants is higher than that of WO₃ under both UV and VIS irradiation.
2. The photo-degradation rate of 4-Chlorophenol is the lowest due to the high number of intermediate degradation products.

Acknowledgements

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References

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