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纳米**TiO_2**膜修饰电极异相电催化还原马来酸

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摘要 通过电化学合成前驱体和溶胶-凝胶法在Ti表面修饰一层纳米TiO_2膜，SEM，XRD测试表明晶型为锐钛矿型，晶粒平均尺寸为25 nm。采用循环伏安法、循环方波伏安法和电解合成法研究了纳米TiO_2膜电极在硫酸介质中的氧化还原行为以及对 马来酸（maleic acid）还原的电催化活性。结果表明，纳米TiO_2膜电极在阴极扫 描时有两对可逆氧化还原峰，可逆半波电位E_(1/2)~r分别为-0.53 V和-0.92 V（ sv. SCE，扫描速度0.05 V·s~(-1)），对应于TiO_2/Ti_2O_3和TiO_2/Ti(OH)_3两个氧化还原电对的可逆电极过程。其中TiO_2/Ti_2O_3电对对马来酸具有异相电催 化还原活性，纳米TiO_2膜中的Ti~(IV)/Ti~(III)氧化还原电对作为媒质间接电还 原马来酸为丁二酸（butane diacid），反应机理为电化学偶联随后化学催化反应 （EC'）机理。

关键词 纳米相材料 二氧化钛 电催化 循环伏安法 马来酸 丁二酸 扫描电子显微镜 X射线衍射分析

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Heterogeneous Electrocatalytic Reduction of Maleic Acid on Nanocrystalline TiO_2 Film Modified Ti Electrode

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Abstract The precursor Ti(OEt)_4 was prepared by anodic dissolution of metallic titanium in absolute ethanol and direct hydrolysis to prepare nanocrystalline TiO_2 film on titanium electrode (Ti/nano-TiO_2) by a sol-gel process. SEM and XRD were used to characterize the structure of nanocrystalline TiO2 film (anatase, 25 nm) . Redox behavior and electrocatalytic activities of the Ti/nano-TiO_2 electrode were investigated by cyclic voltainmetry (CV) and cyclic osteryoung square wave voltammetry (COV) and bulk electrolysis. The results indicate that there are two pairs of well-defined redox peaks for Ti/nano-TiO_2 film electrode in 1 mol/L H_2SO_4 with E_(1/2)~r of - 0.53 V and - 0. 92 V (vs. SCE) at 0.05 V·s~(-1) in correspondence with TiO_2/Ti_2O_3 and TiO_2/Ti(OH)_3 reversible electrode process and the heterogeneous electrocatalytic reduction activities of TiO_2/Ti_2O_3 redox in the electrode for maleic acid. It is found that the indirect electroreduction of maleic acid to butane diacid was achieved by Ti~ (IV)/Ti~(III) redox system on the nanocrystalline TiO2 film surface, the electrode reaction mechanism is the called catalytic (EC) mechanism.

Key words NANOPHASE MATERIALS TITANIUM DIOXIDE ELECTRO-CATALYSIS CYCLOVOLTAMGRAPH maleic acid butane diacid SEM XRD

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