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Preparation of Nano-crystalline Tungsten Carbide Thin Film by Magnetron Sputtering and Their Electrocatalytic Property for PNP Reduction

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Abstract: Nano-crystalline tungsten carbide thin films were deposited on Ni substrates by magnetron sputtering using WC as target material. The crystal structure and morphology of the thin films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrochemical investigations showed that the electrode of the thin film exhibited higher electrocatalytic activity in the reaction of *p*-nitrophenol (PNP) reduction. FT-IR analysis indicated that *p*-aminophenol (PAP) was synthesized after two step reduction of PNP on nano-crystalline tungsten carbide thin film electrode.

Keywords: Tungsten carbide, nano-crystalline, electrocatalyst, *p*-nitrophenol.

PAP is an important intermediate in the preparation of several analgesic and antipyretic drugs. Conventionally, PAP is manufactured by iron-acid reduction of PNP[1]. The major disadvantage of iron-acid reduction is the generation of large amount of Fe/FeO sludge. One of the most efficient and greener routes for PAP preparation is direct electrocatalytic reduction of PNP by noble metal (such as Pt), because it is a single step process. However the disadvantage of noble metal catalyst is its high price. Recently, there has been an extensive effort to look for a new catalyst material. Tungsten carbide is a promising alternative material to platinum and platinum-group metal electrocatalysts for its Pt-like surface electronic structure, lower costs and plenty of W and C natural resources. Although, no report about electroreduction of PNP on tungsten carbide thin film electrode was found, several papers have been published to study the electrocatalytic activity of tungsten carbides in alkane reforming, alkane isomerization and fuel cell electrodes [2-4]. But compared with Pt and Pt-group metal, the electrocatalytic activity of tungsten carbide is relatively lower. One of the possible approaches to improve the electrocatalytic activity of tungsten carbide is to nano-crystallize its thin film. B. H. Kear *et al.*'s investigation showed that the surface area and catalytic activity of tungsten carbide thin film composed of nano-crystalline were relative higher than that of common tungsten carbide thin film[5].

In this paper, nano-crystalline tungsten carbide thin films were successfully

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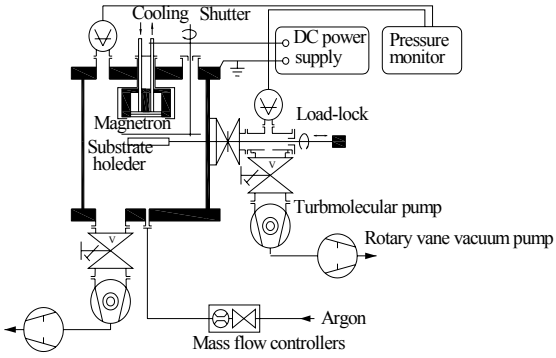
fabricated by magnetron sputtering. The morphology, crystal phase and chemical components of the thin film were characterized by SEM and XRD, and the catalytic activities of the films for PNP direct electrocatalytic reduction were investigated.

Experimental

Figure 1 Schematic of magnetron sputtering system



Nano-crystalline tungsten carbide thin films were deposited by DC magnetron sputtering technique using a commercial sintered WC(99.8%) target. Argon (99.99%) was used as a working gas and controlled by mass flow controller. Ni foil (0.1mm in thickness) was used as substrate which was ultrasonically cleaned in alcohol for at least 30 min. The target and substrate were separately pre-sputtered in Ar atmosphere for 10 min before deposition to clean and activate both surfaces. The base pressure of the system was 4.8×10^{-4} Pa and the working pressure was 5 Pa. The Ar flow rate was 100 sccm. The deposition power was 0.25 W/cm^2 and carried out at room temperature. The schematic of magnetron sputtering system was shown in **Figure 1**.

An X-Ray diffractometer (Rigakv D/max-Ⅲ) using Cu kα radiation was used to investigate the crystalline structure. The morphology of the thin film was determined by scan electron microscopy (Hitachi S-4700). The mechanism of catalytic reaction was analysis by FT-IR (Nicolet 670).

The cyclic voltammograms experiments were performed with a CHI660A electrochemical working station (CHI, USA) in a standard three electrode cell. A saturated calomel electrode (SCE) was used as a reference electrode and platinum gauze was used as a counter electrode. Tungsten carbide thin film deposited on Ni substrate was used as a working electrode with geometric area of 1 cm^2. There were two kinds of solution for the electrolytes which were made from analytical grade reagent and distilled water, one was 50% ethanol + saturated KCl, the other was 50% ethanol + 0.1 mol/L PNP + saturated KCl. The results presented in this article were the potential against the SCE. In each measurement, the fresh electrolyte was agitated and deaerated with high purity nitrogen gas (99.999%) for at least 30 min before and throughout the test to remove trapped air. The electrolyte resistance was compensated by positive feedback technique.

Results and Discussion

The X-ray diffraction pattern of the tungsten carbide thin film was shown in **Figure 2**. Five peaks that with a value of 2θ around 36.70˚, 41.77˚, 61.75˚, 73.82˚and 78.22˚ can be assigned to (111), (200), (220), (311), and (222) planes of WC_{1-x}, respectively. The XRD result indicated that WC_{1-x} was the main component of the thin film.

SEM morphologies of nano-crystalline tungsten carbide thin film were shown in **Figure 3**(a) (b). From the images, the thin film with thickness about 360 nm was completely overcoat the Ni substrate after 30 min deposition. The thin film has a crystalline structure formed by uniform dispersive well rounded grains about 35 nm in diameter, almost no congregation on outermost surface of the thin film was observed. There is no rift on the surface of the thin film. **Figure 3**(b) shows the cross-section morphology of the WC_{1-x} thin film, on which disordered grains are formed initially near the substrate zone of the thin film. The columnar structure has been grown after nano-crystalline tungsten carbide is nucleated on Ni substrate.

Figure 4 shows the cyclic voltammograms on tungsten carbide thin film electrode which were carried out in 50% ethonal+0.1 mol/L PNP + saturated KCl solution, along with the background curves in 50% ethanol + saturated KCl solution. The cyclic voltammagrams were performed at 25℃ with a scanning rate 50 mV/s in both electrolytes. In50% ethanol + saturated KCl solution, no cyclic voltammograms peaks were observed within -0.2 to -1.1V, indicating that there was no reaction occurred on the

Figure 2 XRD pattern of the obtained tungsten carbide thin film by magnetron sputtering

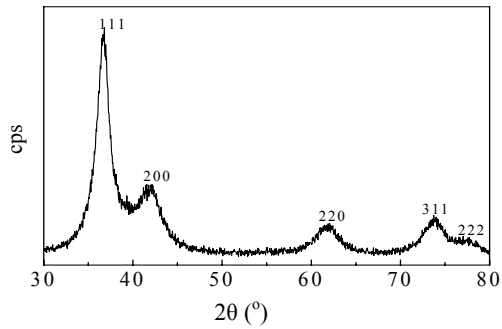
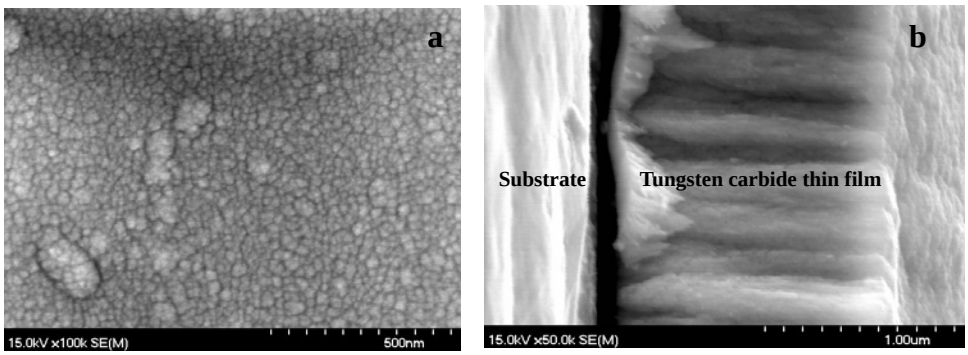


Figure 3 SEM morphologies of the tungsten carbide thin film



(a) The surface morphology of the thin film (b) The cross-section morphology of thin film

tungsten carbide thin film electrode. In the case of 0.1 mol/L PNP was added into electrolyte as shown in curve (2). Two significant cathodic current peaks A and B were found which caused by PNP electrocatalytic reduction. The cathodic current peaks A of the thin film catalyst is 0.86 mA/cm^2 at -0.73V, and the cathodic current peaks B is 6.0 mA/cm^2 at -0.93V. Long time electrolytic reaction process was investigated by using FT-IR spectroscopy *in situ*. The result suggested that the electrocatalytic reduction of *p*-nitrophenol by tungsten carbide catalyst can be described by the reduction equations (a) and (b) as demonstrated below. The current peak A in **Figure 4** was the response of reaction (a) and the current peak B is the response of reaction of (b). The investigated results indicated that nano-crystalline tungsten carbide catalyst showed a good electrocatalytic activity for PNP reduction, PNP was reduced into PAP in two steps reaction on tungsten carbide thin film electrode. Therefore, as an efficient PNP electroreduction catalyst, nano-crystalline tungsten carbide thin film will be a promising catalyst for PAP industry manufacture.

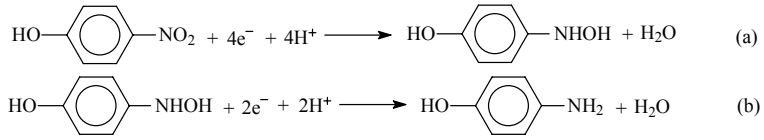
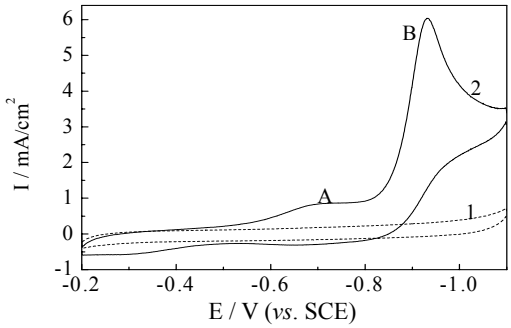


Figure 4 Cyclic voltammograms on the tungsten carbide thin film electrode



Electrolytes: 1-50% ethanol + saturated KCl; 2-50% ethonal+0.1 mol/L PNP +saturated KCl

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