



# Tungsten carbide nanowalls as electrocatalyst for hydrogen evolution reaction: New approach to durability issue



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## ABSTRACT

We report a new approach to the durability issue in tungsten carbide electrocatalyst for hydrogen evolution reaction (HER), in a form radically differing from that of the conventional nanoparticle approach: the WC nanowalls, bottom-up grown by a plasma-assisted deposition on Si wafer. The pristine nanowall was highly crystalline and its surface was smooth in atomic scale, which enabled a superior durability in HER environment: no oxidation occurred at prolonged cycling (10,000 cycles) in the HER environment, even without additional functionalization or modification. The electrochemical activity, as presented by Tafel slope and turnover frequency (TOF), was as excellent as those of the best data in the literature.

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## 1. Introduction

Molecular hydrogen has been actively studied since 70s, as post-hydrocarbon energy carrier owing to its numerous benefits: the largest energy density per unit mass, clean byproduct (water), in contrast to the hydrocarbon fuel with CO<sub>2</sub> byproducts [1], and global abundance. On the other hand, the hydrogen usually exists as compounds, from which the hydrogen should be isolated. The most widely adopted isolation process is the steam reforming process, but it relies on the fossil fuels, which suffers the CO<sub>2</sub> generation [2]. Among the clean, renewable and CO<sub>2</sub>-free hydrogen generation processes, one of the most promising processes is the water electrolysis [3], which employs the two half-cell reactions for electrochemical water splitting, *i.e.* the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [4]. The strongest catalyst for HER is Platinum, but its global resource is limited, which acutely falls short of the global energy demand. Consequently a strong demand is put on the alternative catalyst derived from the earth-abundant element, but it should satisfy (1) the electrochemical activity *i.e.* low overpotential, and (2) the durability in operating condition.

Tungsten carbide has been actively investigated [4–6], due to its Pt-like d-band DOS (density of states) [7–9], cost-effectiveness [7,10], mechanical strength as well as good conductivity [10]. But it still suffers some critical drawbacks: majority of studies employed nanoparticles form, which suffered sintering during synthesis, consequent coarsening, and eventual loss of activities when used in pristine form [7,11]. Moreover, such nanoparticle-based processes suffered oxide-passivation in HER environment, again with undesirable loss in the electrocatalytic activities and hence the poor durability [10]. Efforts were made, *e.g.* by adopting SiO<sub>2</sub> template to prevent sintering [7], surface modification or heteroatom hybridization to prevent oxidation [12,13]. However, such approaches still relied on the nanoparticles, of which the extreme-curvature surface is inherently defective and unstable [14], unless they are modified, *e.g.* by aforementioned means. Even for the nanoparticles with superior performances, some performance degradation still persisted at the prolonged exposure to the HER environment [7], probably due to oxide passivation. Thus, the oxide-passivation issue still hampers the successful progress of the tungsten carbide electrocatalyst.

Here we report a simple but radically differing approach to this issue. Instead of modifying the nanoparticles, we adopted tungsten carbide *nanowalls* which we have recently reported [15], synthesized by a plasma-assisted deposition, which is now in commercial scale [16]. It was important that the nanowalls were highly crystalline and were smooth in atomic scale on their surfaces [15],

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in contrast to the highly disordered pristine surface of the conventional tungsten carbide nanoparticles, as will be further shown here; it might accordingly enhance the electrocatalytic stability or durability. A further motivating observation was that the nanowalls collectively formed a nanoporous network [15], which might allow effective access of the HER solution. However, relevant studies were not reported so far. Here we investigated such possibilities, as a comparative study on the two contrasting types of tungsten carbide thin films, comprised of nanowalls and nanocrystalline grains, respectively, grown on nanodiamond-coated Si wafer substrates [15], which will highlight the origin of the superior HER performances of the former in its pristine form, as comparable to some best data in the literatures of the conventional tungsten carbide nanoparticles with additional surface modifications.

## 2. Experimental

### 2.1. Preparation of WC/NCD film

The tungsten carbide nanowall film was synthesized on the NCD-coated Si wafer by the direct current plasma assisted CVD (DC-PACVD) using surface-carburized tungsten cathode [15]. The substrate was exposed to the hydrogen plasma in the CVD chamber. The total hydrogen gas flow rate and the chamber pressure were 150 SCCM and 100 Torr, respectively. Details of the synthesis procedure, growth mechanisms, and preliminary characterizations were reported elsewhere [15].

### 2.2. Physical characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM, FEI Co., Titan 300 kV) were employed to observe structure of synthesized WC. The surface morphology of the WC/NCDs was analyzed by scanning electron microscope (SEM, FEI Co., Nova 200 NanoSEM) at an acceleration voltage of 10 kV. The distribution of the oxide phase was analyzed by the Fourier-masked scanning TEM [17]. The surface chemistry of WC was characterized by the x-ray photoelectron spectroscopy (XPS, Ulvac Co., PHI 5000 Versaprobe). Wide angle X-ray diffraction (XRD, Rigaku Co., D/MAX-2500H) was used to examine the crystal structure and identify the nature of carbide and oxides. The roughness of WC surface was analyzed by non-tapping mode atomic force microscope (Park system Co., XE-100).

### 2.3. Electrochemical analysis and durability test

All electrochemical measurements were performed with a VSP Potentiostat/Galvanostat (Bio-logic Co., France). The experiment was performed in a three-compartment electrochemical cell in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode and graphite rod were used as the reference electrode and the counter electrode, respectively. It was calibrated with respect to reversible hydrogen electrode (RHE), in the high purity H<sub>2</sub>-saturated electrolyte with a Pt wire as the working electrode. CVs were run at a scan rate of 1 mV/s, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions, i.e. in 0.5 M H<sub>2</sub>SO<sub>4</sub>, E (RHE) = E (SCE) + 0.702 V. All the potentials reported in the present study are against RHE.

The electrochemical activation was carried out employing the cyclic voltammetry of 4000 cycle from -0.3 V to 0 V (RHE) with 10 mV/s scan rate. The linear sweep voltammetry was carried out with 5 mV/s scan rate. The durability test was carried out using cyclic voltammetry of 10,000 cycle from -0.5 V to 0.2 V (RHE) with 10 mV/s scan rate. The electrochemical impedance spectroscopy was carried out at open circuit voltage from 10<sup>5</sup> Hz down to 10<sup>-2</sup> Hz with 10 mV AC amplitude. In order to estimate the effective surface

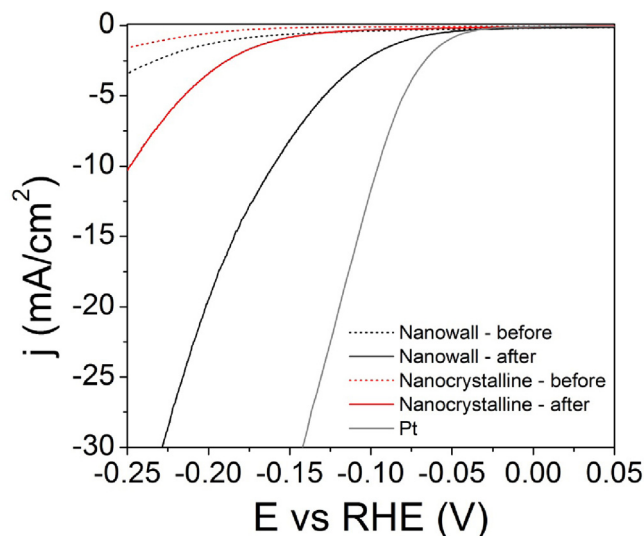


Fig. 1. Polarization curves of HER for WC nanowall and WC nanocrystalline films, before and after the initial cyclic cleaning.

Table 1

HER activity comparison of WC nanowall and WC nanocrystalline films.

Material	Onset potential (V)	Overpotential @ 10 mA/cm <sup>2</sup> (mV)	Current density @ 0.25 V (mA/cm <sup>2</sup> )
WC nanocrystalline	-0.102	248	-10.31
WC nanowall	-0.052	160	-40.10
Pt	-0.005	95	-83.85

area of the samples, the double-layer capacitance ( $C_{dl}$ ) was analyzed by cyclic voltammetry in a potential range of 0.1–0.2 V with various scan rates (20, 40, 60, 80, and 100 mV/s).

## 3. Results and discussion

Fig. 1 shows the LSV (Linear Sweep Voltage) curve [corrected of the ohmic potential drop ( $iR$ )] of the WC nanowall sample at its HER, before and after the 4000 cycles of the initial cyclic cleaning (ohmic potential correction details: Statement S1 and Fig. S1). While the cleaning enhanced the activities for both samples, the enhancement was much stronger for the nanowall sample: the results were summarized in Table 1. The onset potential and the current density of the nanowall sample were superior to those of nanocrystalline sample: the overpotential ( $\eta$ ) of the former at the cathodic current density around 10 mA/cm<sup>2</sup> was 88 mV lower than that of the latter. Origin of such strongly differing HER response to the initial cleaning could be inferred from the W 4f XPS spectra (Fig. 2). While tungsten oxide peaks were drastically reduced for the nanowall sample by the cleaning (Fig. 2a, b), the peaks persisted to a substantial extent for the nanocrystalline sample (Fig. 2c, d). The carbide peaks changed little (Fig. 2a, b) in accord with previous reports [18,19]. The corresponding responses of the carbon peaks strongly differed also (Fig. 3: C 1s XPS analyses). While the graphitic carbon peak drastically dropped after cleaning for the nanowall sample (Fig. 3a, b), it changed little for the nanocrystalline sample (Fig. 3c, d). Such graphitic carbon layer was reported to damage the electrochemical activity [20]. While the enhanced HER activities should be attributed to such removal of oxide and carbon layer, which was reported to be caused by the dissolving action of the sulfuric acid in the initial cycling, microscopic observations revealed further details of the cleaning-induced changes: SEM (Fig. 4, S2), HR-TEM (Fig. S3: nanowall; Figs. S5, S6 and S8: nanocrystalline) and corresponding Fourier-masked HR-TEM (Fig. S4: nanowall; Figs. S7,

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