

Supporting Information

For

# **Morphology Dependent Oxygen Reduction Activity of Titanium Carbide: Bulk vs. Nanowires**

*Vankayala Kiran,<sup>a</sup> Srinivasu Kancharlapalli,<sup>b</sup> and Srinivasan Sampath<sup>a,\*</sup>*

*Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore -560012*

## **Contents**

- 1. STEM-EDS mapping of TiC-NW**
- 2. Electrical properties of TiC-NW**
- 3. SEM images of hydrothermally treated TiC (a) in 0.5 M HCl and (b) in NaCl (pH~7)**
- 4. N<sub>2</sub> adsorption-desorption isotherms**
- 5. Deconvoluted O-1s spectrum of TiC-NW**
- 6. Raman spectra of (a) bulk TiC particles and (b) 1D TiC-NW**
- 7. Effect of peak current on square root of scan rate for ORR using TiC-NW**
- 8. Effect of loading ORR kinetic parameters**
- 9. Methanol tolerance studies**

## STEM-EDS mapping of TiC-NW

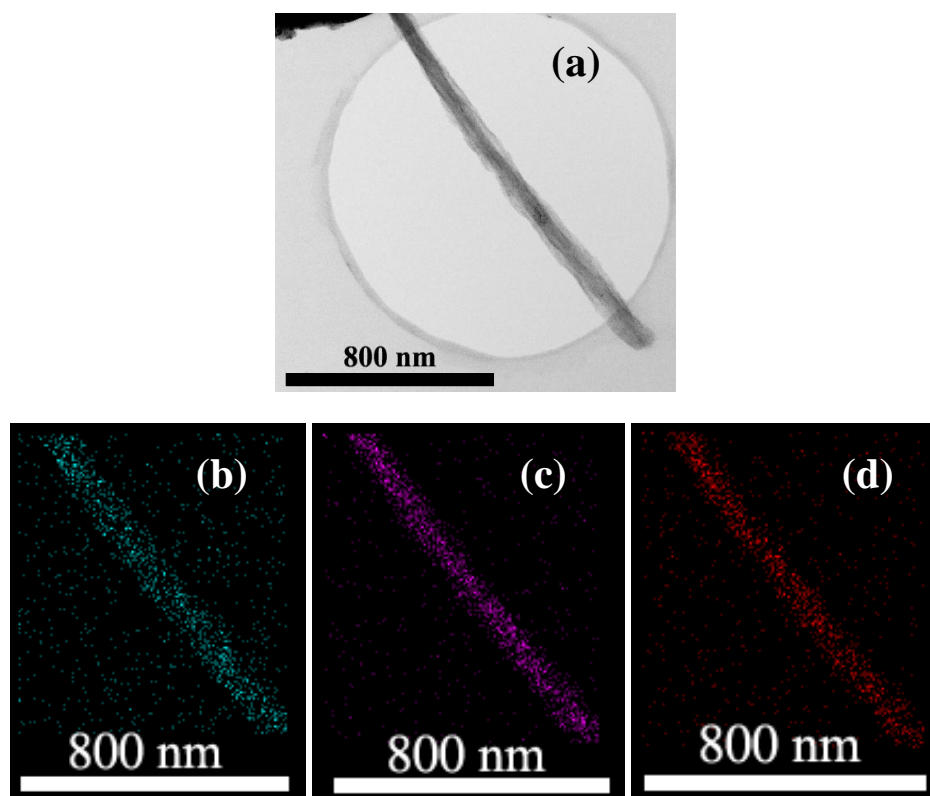


Figure S1. STEM (a) B F image of TiC-NW and corresponding X-ray maps (b) C-map, (c) Ti-map and (d) O- map.

## Electrical properties of TiC-NW

To depict the electrical properties, preliminary studies are carried out on as-obtained TiC-NW. Devices are fabricated on Si/SiO<sub>2</sub> substrate using dielectrophoresis. Device was fabricated as follows. Pre-defined patterns are fabricated onto pre cleaned Si/SiO<sub>2</sub> substrates using optical lithography with Au (50nm) as contact material deposited on selective regions using RF sputtering, followed by lift-off procedure. Individual and well-separated TiC-NW dispersed in dichloro ethane are aligned in respective regions using AC dielectrophoresis with  $V_{p-p}$  of 10 V and a frequency of 5 MHz. AC dielectrophoresis result in the alignment of TiC-NW between fingers of the device (figure S2). *I-V* characteristics represent a linear response to voltage suggesting typical ohmic behaviour (figure S3). Effect of gate voltage on *I-V* characteristics of TiC-NW displayed no effect of gating, suggesting metallic nature of TiC-NW.

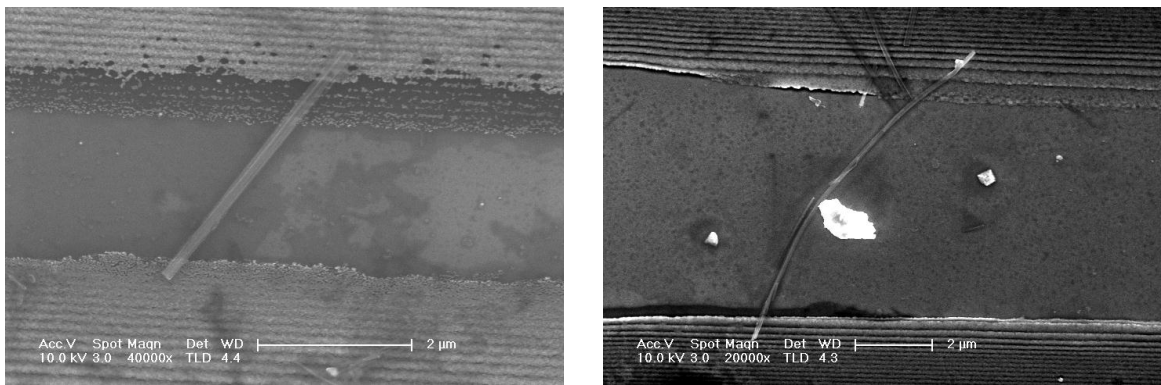


Figure S2. SEM images of TiC-NW based device after dielectrophoresis

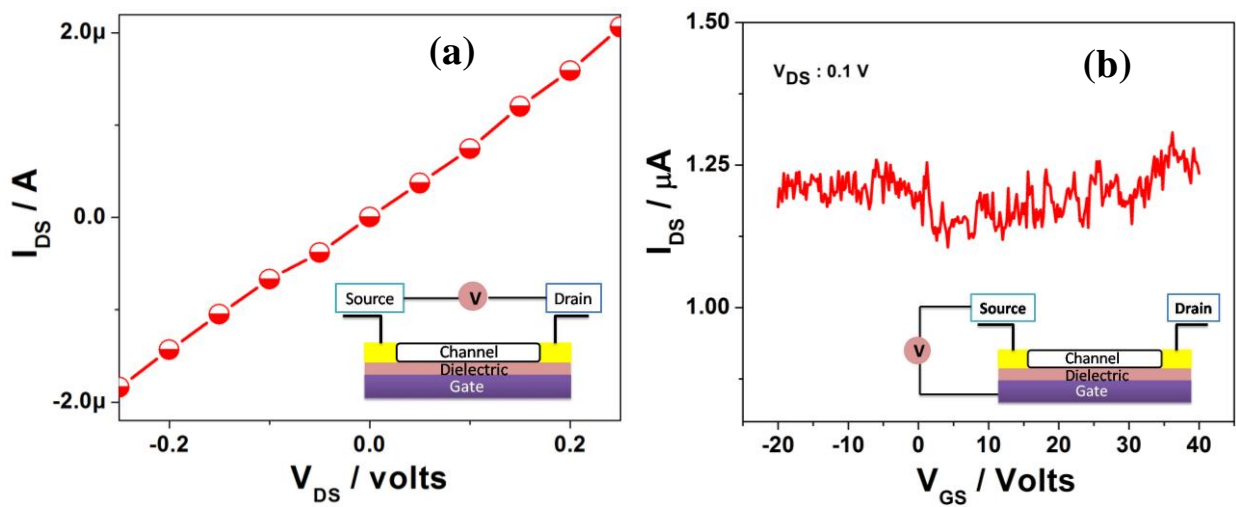


Figure S3. I-V characteristics of TiC-NW based device. (a) Plot of  $I_{DS}$ - $V_{DS}$  at  $V_{GS}=0$  V; (b) plot of  $I_{DS}$ - $V_{GS}$  at  $V_{DS}=0.1$  V. (DS represents source-drain and GS represents gate-source). Inset shows configuration of the device used.

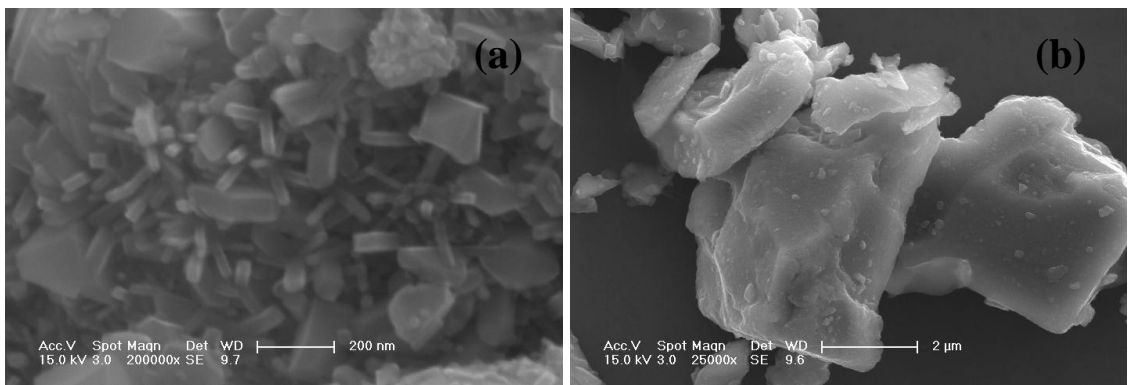


Figure S4. SEM images of hydrothermally treated TiC in (a) 0.5 M HCl and (b) NaCl (pH~7)

## N<sub>2</sub> adsorption-desorption isotherms

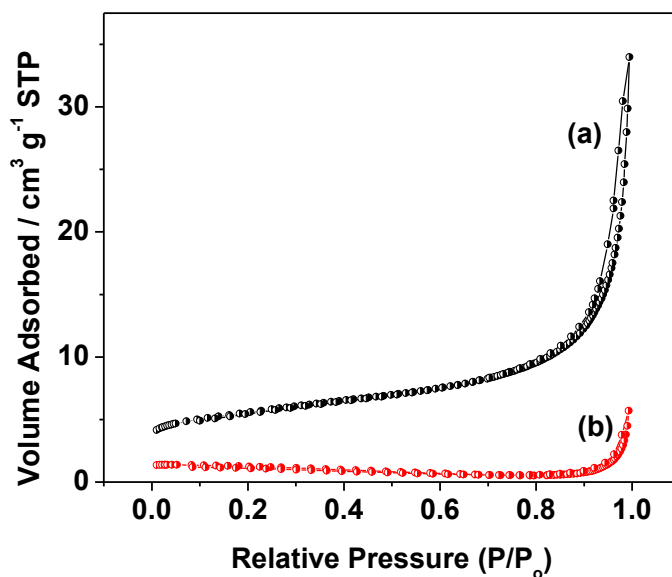


Figure S5. Nitrogen adsorption-desorption isotherms corresponding to (a) TiC-NW and (b) bulk TiC particles

## Deconvoluted O-1s spectrum of TiC-NW

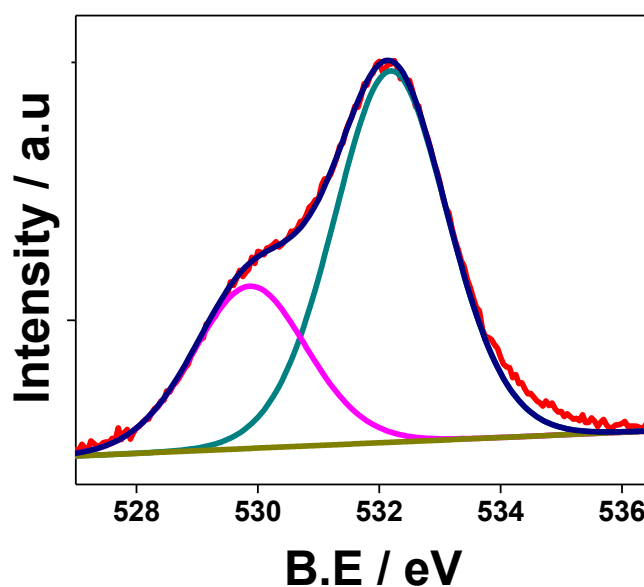


Figure S6. Deconvoluted O-1s spectrum of TiC-NW

The deconvoluted O-1s region of TiC-NW shown in figure S5 consists of two peaks located at binding energy (B.E) values 529.9 eV and 532.2 eV. The appearance of former peak reveals the presence of titanium oxides<sup>1,2</sup> whereas the latter peak is attributed to the

presence of adsorbed water.<sup>2</sup> It has been reported that the latter peak can be eliminated by Ar<sup>+</sup> ion etching.

### Raman spectrum of TiC-NW

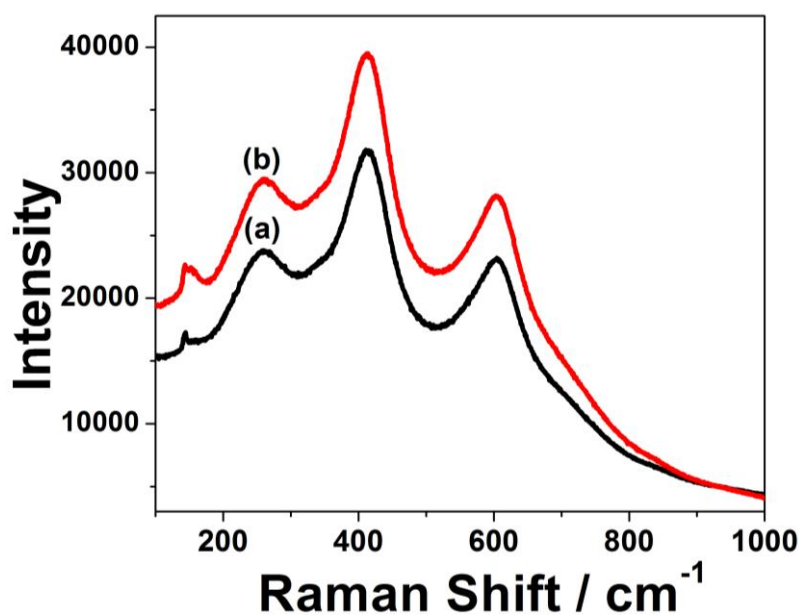


Figure S7. Raman spectra of (a) bulk TiC particles and (b) 1D TiC-NW

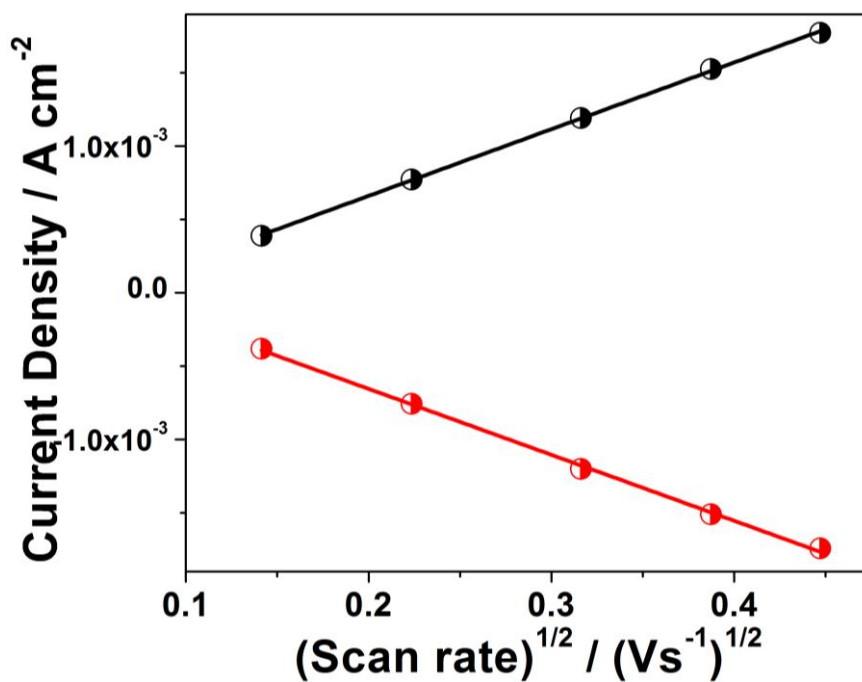


Figure S8. Variation of forward (black) and reverse (red) currents as a function of square root of scan rate using TiC-NW. Electrolyte used is 0.001 M [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> in 0.5 M phosphate buffer (pH~7)

## Effect of loading of TiC-NW on ORR

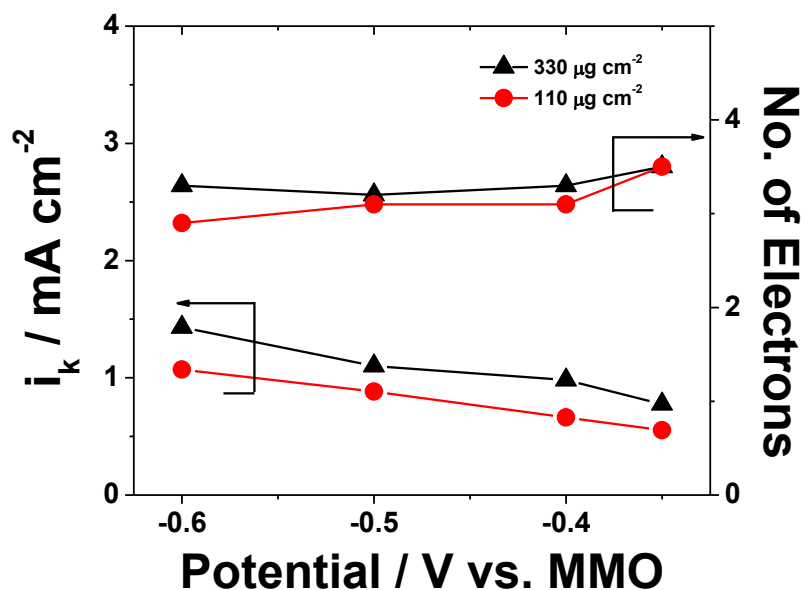


Figure S9. Effect of loading on kinetic current density and number electrons transferred during ORR on TiC-NW modified electrode.

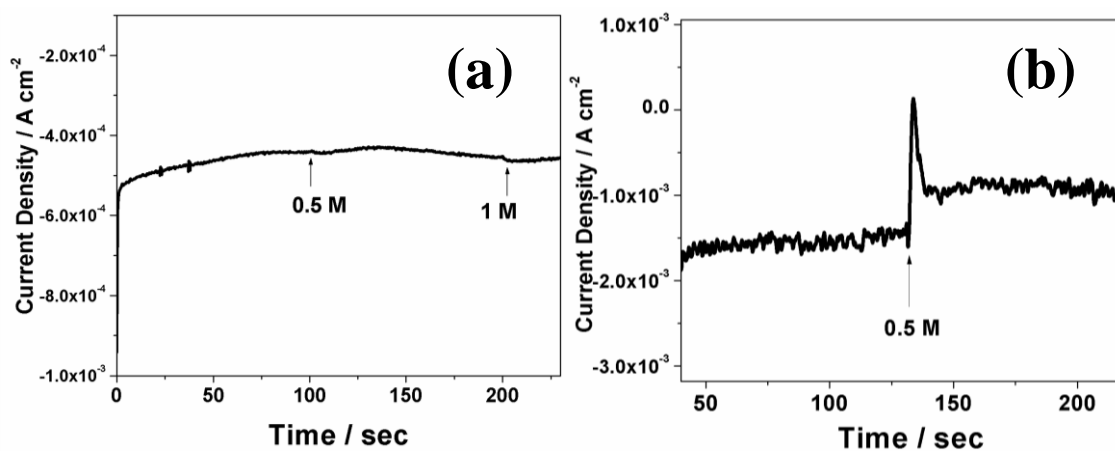


Figure S10. I-t transients recorded at -0.35 V vs. MMO in O<sub>2</sub> saturated 0.5 M KOH on (a) TiC-NW and (b) 40 wt% Pt/C. The addition of methanol is shown in figure. Loading of Pt/C used is 44  $\mu\text{g/cm}^2$

## References

1. Robinson, K. S.; Sherwood, P. M. A. *Surf. Interface Anal.* **1984**, *6*, 261.
2. Bertoncello, R.; Casagrande, A.; Casarin, M.; Glisenti, A.; Lanzoni, E.; Mirengi, L.; Tondello, E. *Surf. Interface Anal.* **1992**, *18*, 525.