Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

2D single- or double-layered vanadium oxide nanosheets assembled 3D microflowers: controlled synthesis, growth mechanism, and applications

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Evolution of F-VO over reaction time

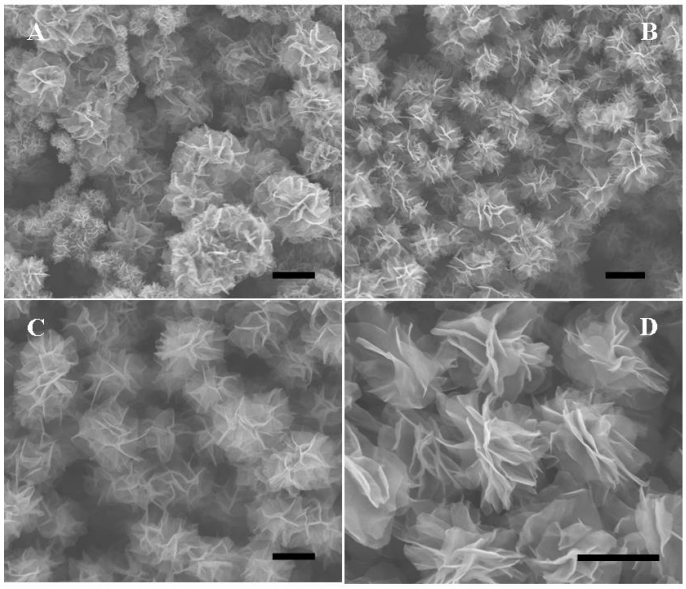

Fig. S1. SEM images taken after different reaction time: 2 h (A), 5 h (B), 10 h (C), and 24 h (D). Scale bars = 1 μm.

XRD patterns of YS-VO and B-VO are distinct to that of F-VO

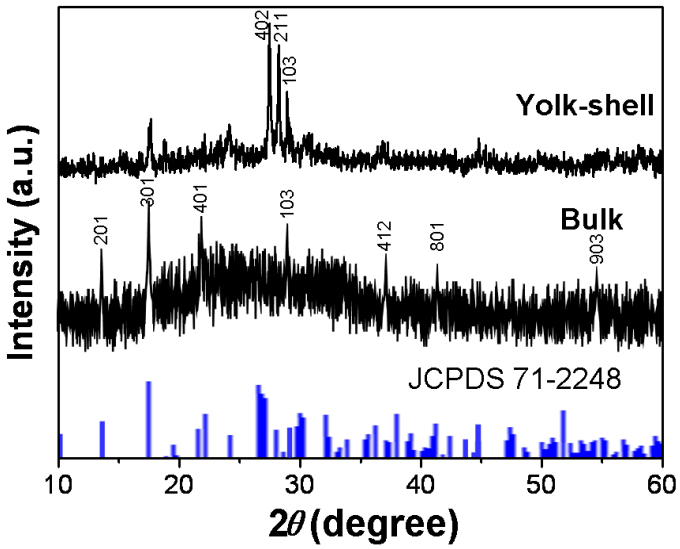

Fig. S2. XRD patterns of yolk-shell and bulk V_4O_9.

Methanol Detection

Methanol is an important organic solvent with widespread applications. But it is highly toxic and there is a growing concern on its contamination in drinking water. Therefore, it is important to detect techniques to detect methanol at low levels. Currently, most methanol sensors are based on electrochemical detection using noble metal nanoparticles as the catalyst.[1,2] But noble metal is not only expensive but also easily poisoned by the generated CO intermediates from methanol oxidation.

Herein, we demonstrate that F-VO coated glassy carbon electrode can electrochemically detect methanol with high sensitivity. At the holding voltage of -0.34V and in 1.5 M KOH solution, a typical amperometric current in response to successive addition of methanol is shown in Fig. S3A. As seen, amperometric response to 60 μM methanol can be clearly resolved (S/N = 24). We propose that the detection is due to oxidation of methanol catalyzed by reduction of V^{5+} to V^{4+} in V_4O_9. This is supported by the cyclic voltammetry (CV) measurements. As shown in Figure S4, the CV of F-VO electrode exhibits a pair of redox peaks: the oxidative peak corresponding to V^{4+} to V^{5+} conversion while the reductive peak corresponding to V^{5+} to V^{4+} conversion. The reductive peak increases with the increasing concentration of methanol because electron donated from methanol oxidation facilitates the reduction of V^{5+} to V^{4+}. Furthermore, it is observed that the sensitivity of amperometric detection of methanol by YS-VO or B-VO coated electrode is inferior to F-VO electrode (Fig. S3B and C).

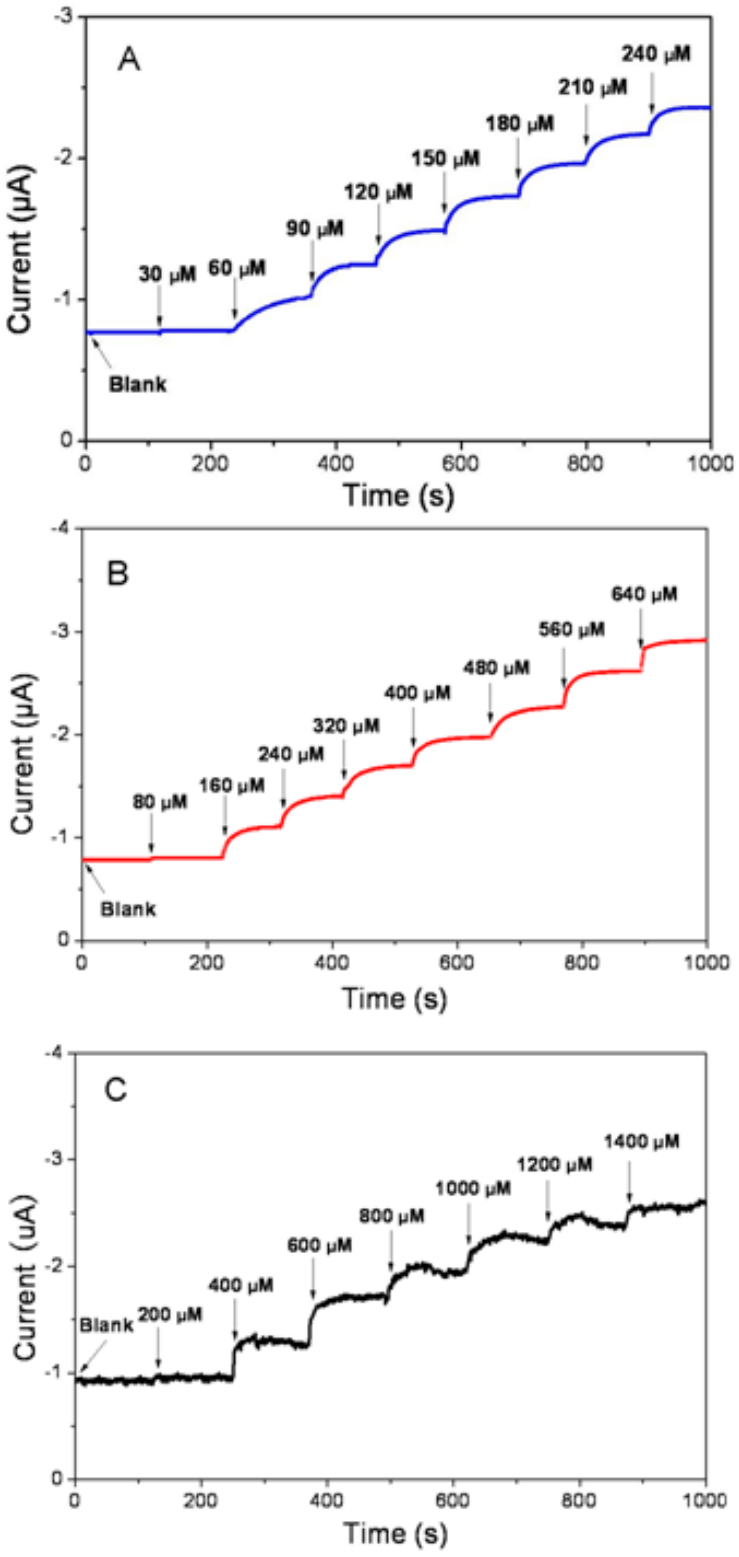

Fig. S3. Detection of methanol in 1.5 M KOH solution using different morphological vanadium oxides. Amperometric response of the as-prepared F-VO (A), YS-VO (B) and B-VO (C) electrodes (holding at -0.35 V) upon addition of methanol to increasing concentrations.

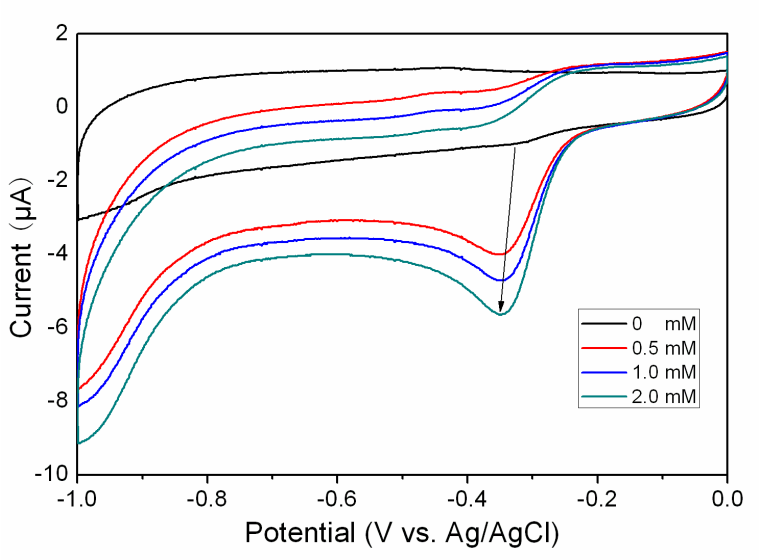

Fig. S4. CV curves without methanol (black) and with methanol at different concentrations (0.5 mM (red), 1.0 mM (blue) and 2.0 mM (green) of F-VO coated on glassy electrode.

Reference

1. Choi, Y.; Gu, M.; Park, J.; Song, H. K.; Kim, B. S. Graphene Multilayer Supported Gold Nanoparticles for Effi cient Electrocatalysts Toward Methanol Oxidation. *Adv. Energy Mater*. **2012**, *2*, 1510–1518.

2. Cui, C. H.; Li, H. H.; Yu, S. H. Large scale restructuring of porous Pt-Ni nanoparticle tubes for methanol oxidation: A highly reactive, stable, and restorable fuel cell catalyst. *Chem. Sci*. **2011**, *2*, 1611-1614.

3. Romanyshyn, Y.; Guimond, S.; Kuhlenbeck, H.; Kaya, S.; Blum, R. P.; Niehus, H.; Shaikhutdinov, S.; Simic-Milosevic, V.; Nilius, N.; Freund, H. J.; Ganduglia-Pirovano, M. V.; Fortrie, R.; Dobler, J.; Sauer, J. Selectivity in Methanol Oxidation as Studied on Model Systems Involving Vanadium Oxides. *Top Catal.*, **2008**, *50*,106–115.