Supplementary Information

Economical Hafnium Oxygen Nitride Binary/Ternary Nanocomposite Counter Electrode Catalysts for High-Efficiency Dye-Sensitized Solar Cells

Sining Yun,[a]* Huawei Zhou,[b] Liang Wang,[b] Hong Zhang,[b] and Tingli Ma[b]*

[a.] School of Materials & Mineral Resources, Xi'an University of Architecture and Technology, Xi'an 710055, China.

Fax: +86-29-85535724; Tel: +86-29-82202022 ; E-mail: alexsyun1974@yahoo.com.cn

[b.] State Key laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China.

Fax: +86-0411-39893820; Tel: +86-0411-39893820; E-mail: tinglima@dlut.edu.cn

*** Corresponding authors: Dr. Sining Yun and Prof. Tingli Ma**

X-ray diffraction peak assignments of the as-synthesized nanocomposites

X-ray diffraction peak assignments of the as-synthesized Hf-R0-U, Hf-R5-B and Hf-R12-T samples were as follows: for HfO_2 (JCPDS:65-1142, PDF-2 Database), the diffraction peaks at 17.52°, 24.18°, 24.58°, 28.34°, 31.64°, 34.30°, 34.66°, 35.52°, 36.06°, 38.84°, 40.98°, 45.10°, 45.80°, 49.60°, 50.48°, 50.88°, 51.56°, 54.42°, 56.32°, 57.56°, 58.28°, 60.30°, 61.72°, 62.26°, 63.24°, 64.68°, 66.12°, 69.42°, 71.68°, 73.22°, 75.76°, 76.96° and 78.06° are assigned to the crystal planes (100), (011), (110), $(\bar{1}11)$,

(111), (002), (020), (200), ($\bar{1}$02), (021), ($\bar{2}$11), (112), ($\bar{2}$02), (022), (220), ($\bar{1}$22), ($\bar{2}$21), (300), (130), (310), ($\bar{1}$31), (131), (113), ($\bar{2}$13), (311), ($\bar{1}$23), (222), (132), ($\bar{3}$22), (040), (041), ($\bar{4}$11), and ($\bar{1}$33), respectively. The diffraction peaks at 30.30°, 35.50°, 50.84°, 60.38° and 63.24° for $Hf_7O_8N_4$(JCPDS:50-1173, PDF-2 Database) are assigned to the crystal planes (003), ($\bar{3}$22),(214), ($\bar{3}$25) and (006), respectively. The crystallite size of all samples can be estimated from the strongest diffraction peaks using the Scherrer equation

$$D = 0.89\lambda/(\beta \times \cos\theta) \quad \text{(S1)}$$

where D is the crystallite size, λ is the wavelength of the incident X-ray (λ = 0.154056 nm), θ is the Bragg angle of the diffraction line, and β is FWHM in radians.

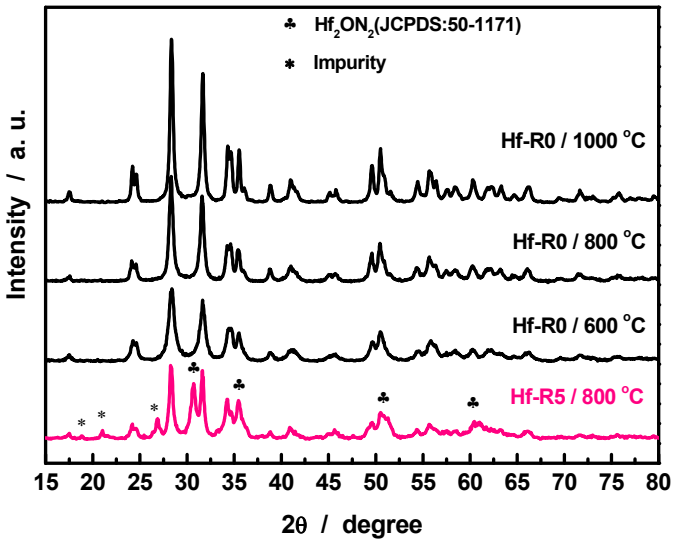

Fig.S1 XRD patterns of the as-synthesized Hf-R0 and Hf-R5 at different heating treatment temperature. The diffraction peaks are well-matched to the corresponding JCPDS card data (JCPDS:65-1142) even though the Hf-R0 samples were heated at different sintering temperature. For Hf-R5 sample, the mixed species were obtained through calcination at 800 ^{o}C for 3 h under nitrogen, and the main diffraction peaks can be indexed to HfO_2 (JCPDS:65-1142) and Hf_2ON_2 (JCPDS:50-1171). Note that there are several diffraction peaks due to the impurity are unknown, as indicated by the asterisk.

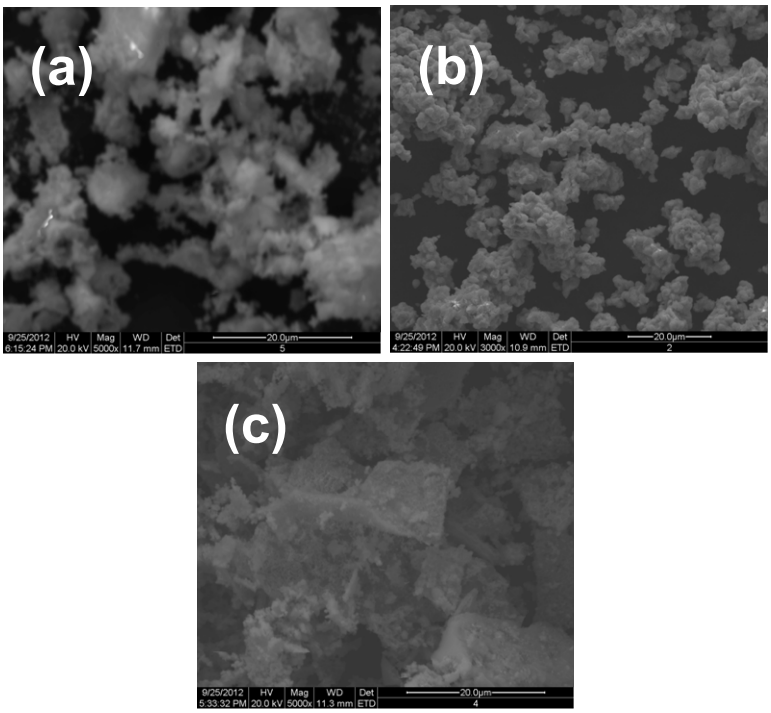

Fig.S2 SEM images for samples at various urea-metal molar ratio. (a) Hf-R0-U, (b) Hf-R5-B and (c) Hf-R12-T (scale bar 20 μm).

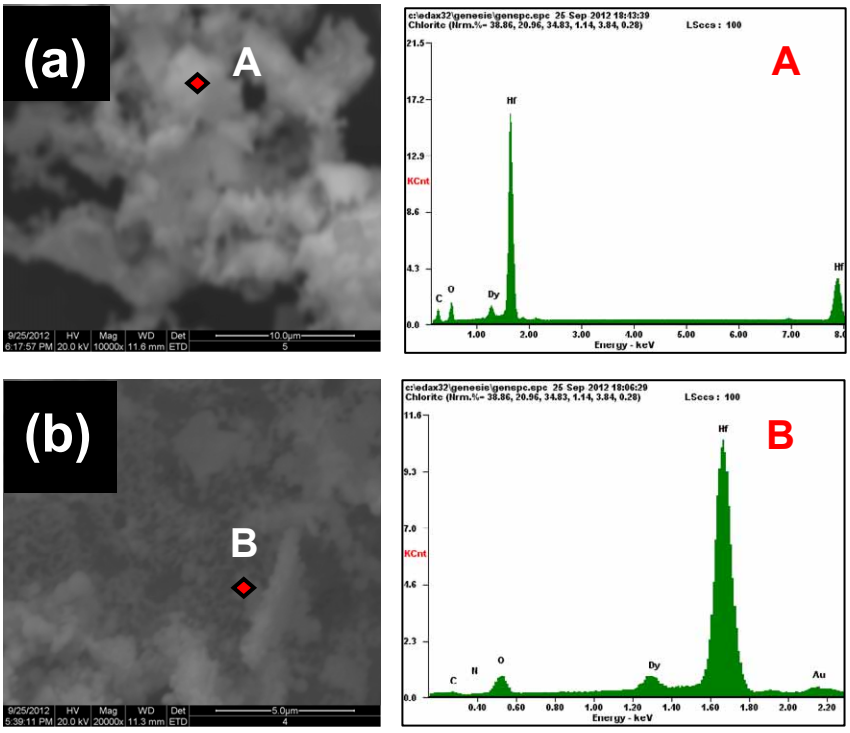

Fig.S3 Local magnified SEM images and the corresponding EDS spectra of the spots A and B for binary composites Hf-R5-B (a) and ternary composites Hf-R12-T (b), respectively.

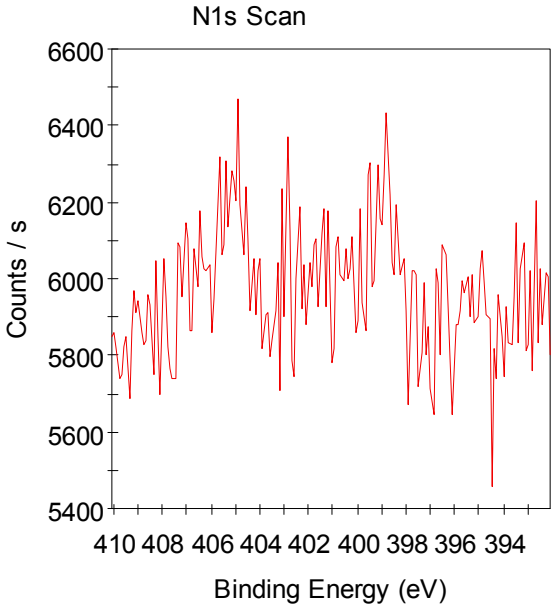

Fig. S4 N 1s XPS spectra of ternary composites Hf-R12-T sample prepared using a urea-metal route.

The equivalent circuit of the symmetrical cells

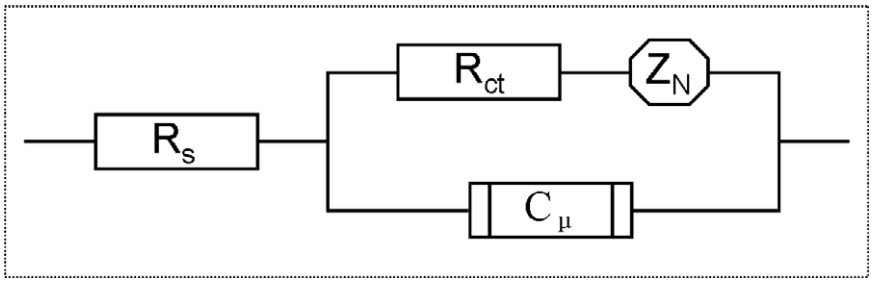

Fig. S5 The equivalent circuit of the symmetrical cells. R_s: series resistance; R_{ct}: charge-transfer resistance; C_μ: double layer capacitance; Z_N: Nernst diffusion impedance of the redox couple in the electrolyte.