Multiple synergistic effects of Zr-alloying on the phase stability and photostability of black niobium oxide nanotubes as efficient photoelectrodes for solar hydrogen production

Kholoud E. Salem, Nageh K. Allam

Energy Materials Laboratory (EML), School of Sciences and Engineering, The American University in Cairo, New Cairo, 11835, Egypt

Background

Hydrogen is a promising alternative to fossil fuels. Its superior properties such as light weight, high energy density, and sustainability make it the ideal candidate for our future energy resources.

Most hydrogen production processes produce undesirable by-products such as CO_2.

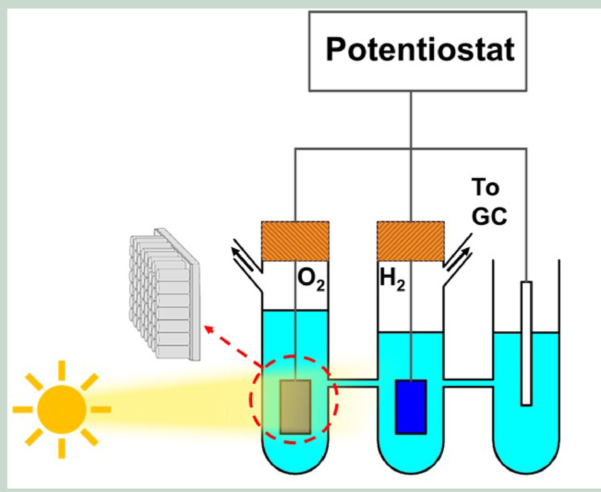
Solar Hydrogen production through photoelectrochemical water splitting holds a great potential as a clean, renewable and sustainable energy source.

Niobium oxide-based photocatalysts are the most efficient to catalyze and convert water into molecular hydrogen, however their photocatalytic performance is prevented by stability issues.

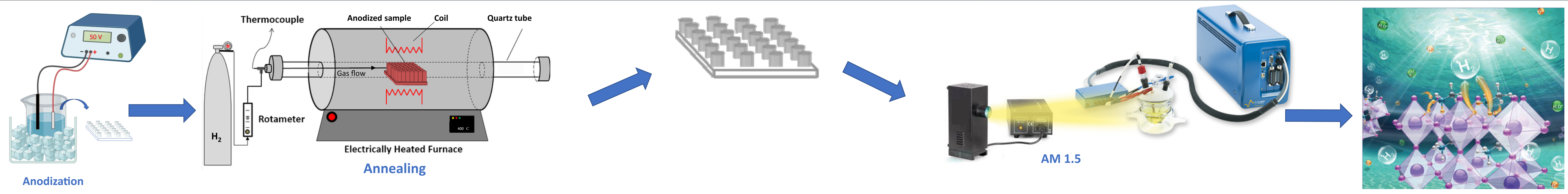
Several niobium oxide polymorphs have gained enormous attention for their widespread in plethora of applications, with the orthorhombic one (T-Nb_2O_5) showed promising photocatalytic characteristics.

Bandgap engineering via doping as well as hydrogen treatment strategy are becoming an active area of research due to their unique influence on the catalytic activity of the material.

In this work, a novel single reduced composite of Zr- doped Nb_2O_5 nanotubes were synthesized via anodization followed by hydrogen annealing at various temperatures for comparison.



Method



Results

Characterization (SEM &TEM)

SEM images of the anodized sample (Fig. 1 a,b) displays well-ordered nanotubes, with the fast transport of charge carriers associated to the short nanotubes formation .

HR-TEM characterization of the fabricated sample (Fig. 1 c,d) displays tubular morphology, with clear spots are characterized by the 0.39 nm spacing, as expected for crystalline T-Nb_2O_5 [1]

The substrate sheet completely covered by Nb-Zr mixed oxide nanotubes, mainly indicates their homogeneous distribution on the surface.

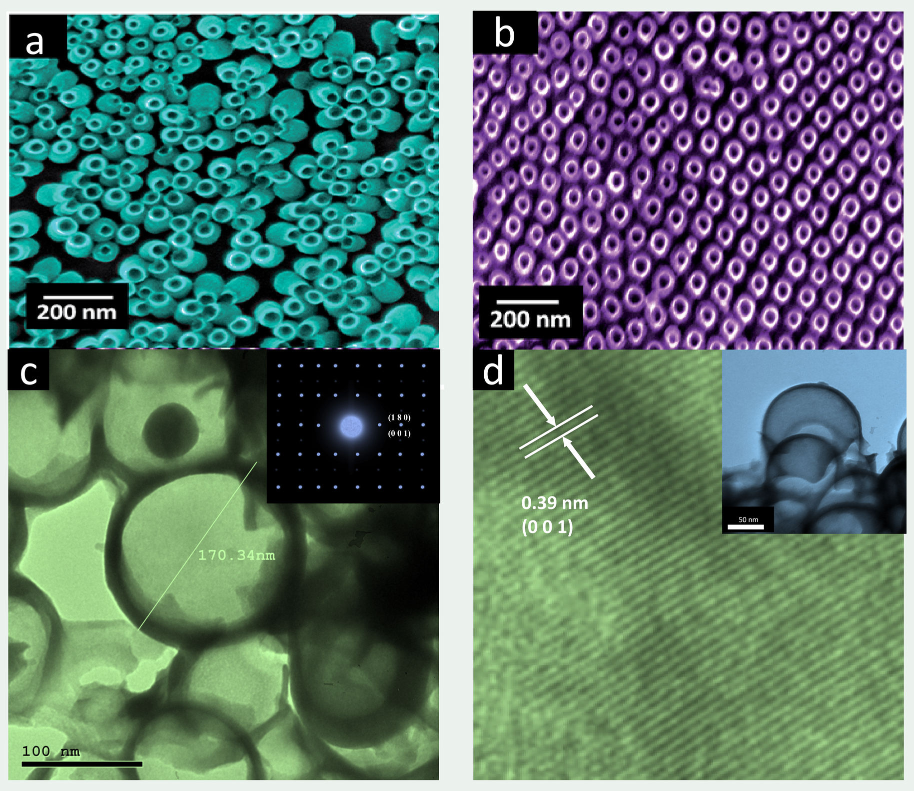


Fig. 1 a,b) SEM and c,d) HR-TEM micrographs of Nb-Zr mixed oxide NTs.

Photoelectrochemical chacterzaction, Mott-Schottky & Impedance

Mott- Schottky &Impedance, are alternative ways to have insights on the nature of the surface trap states and the charge dynamics characteristics of the photocatalyst.

Reduced Nb-Zr-O photocatalyst exhibited lower charge transfer resistance as compared to the air- atmosphere, which is a clear indication of the fast electron transfer at the solution electrode interfaces, leading to the higher current density.

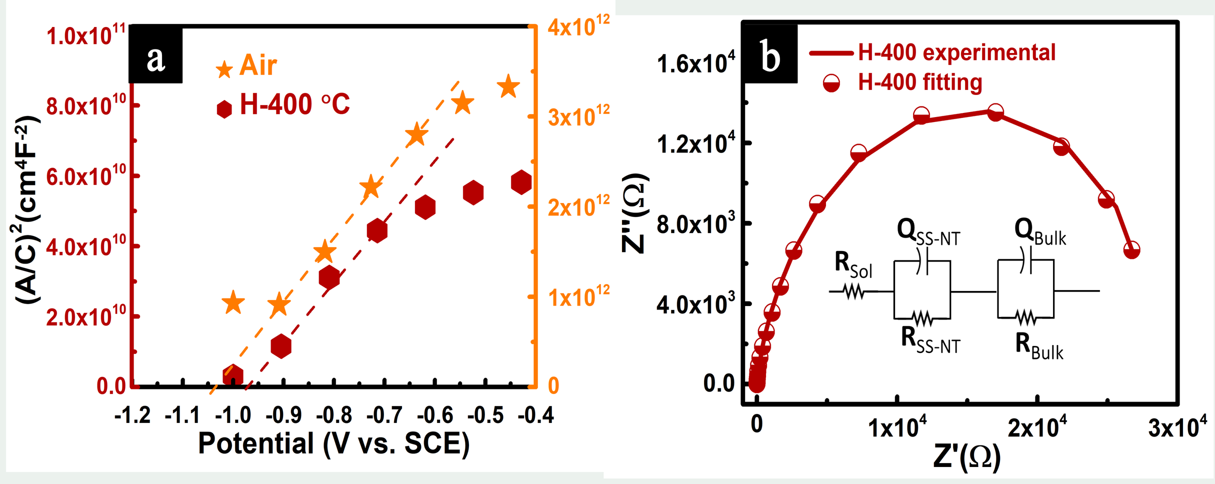
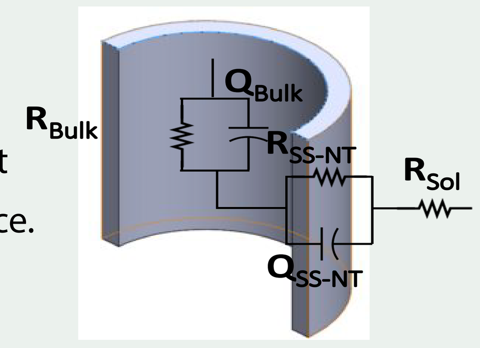


Fig. 5. a) Mott- Schottky, and b) Nyquist plots of the H_2-and air-annealed sample.

Schematic of the equivalent circuit model for the interfacial impedance.



Characterization (XRD & XPS)

The diffraction peaks at around 22.5⁰ and 50.11⁰ correspond to the (001) and (0160) planes of orthorhombic Nb_2O_5 [1].

No charachterstic peaks of $ZrO_2$was obtained, in agreement with other studies [2].

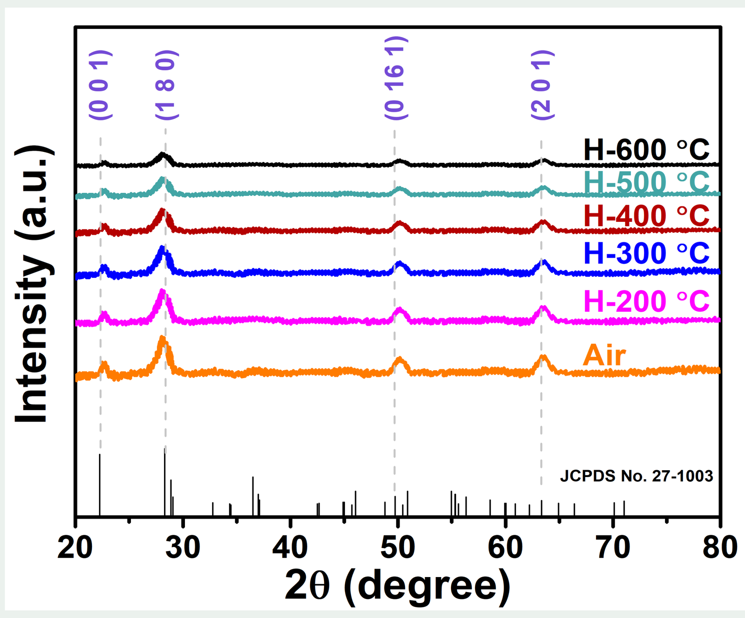


Fig. 3. XRD patterns at various T for the air- and hydrogen treated NTs samples.

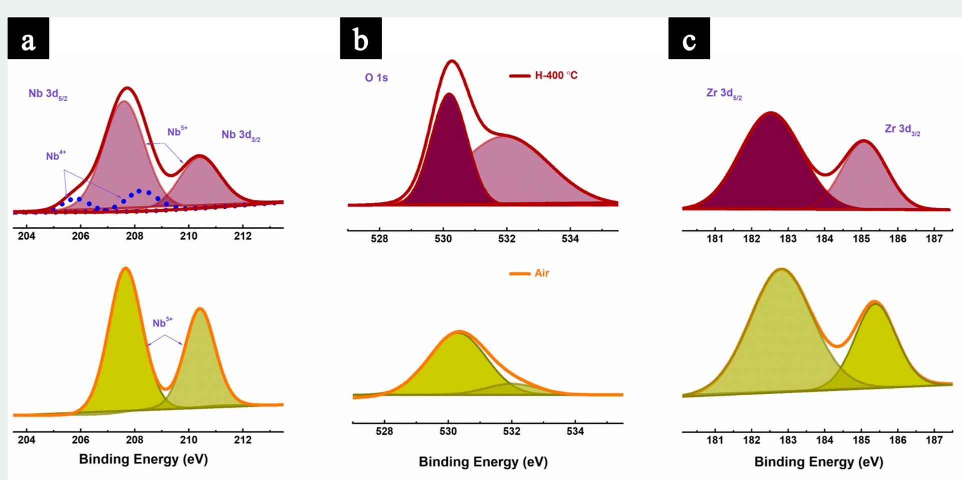


Fig. 2. (a) XPS spectra of the air- and H_2-treated samples at 400 °C.

The XPS analysis could further relate the influence of the reduction process on the presence of suboxides that are associated with increased oxygen defects within the lattice

Photolectrochemical chacterzaction, Hydrogen production & Sustainability

The steady rate during the whole cycling tests could infer the continuous stability of the reduced electrodes that retained their photocatalytic performance along with three successive cycles.

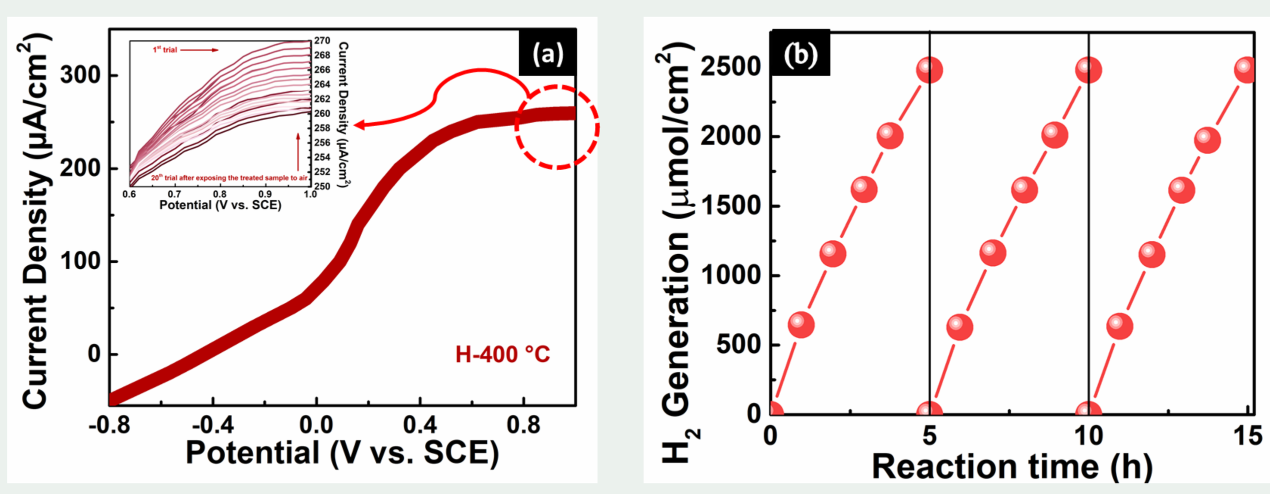
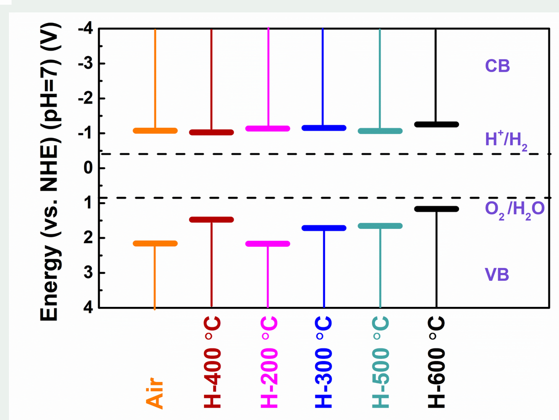


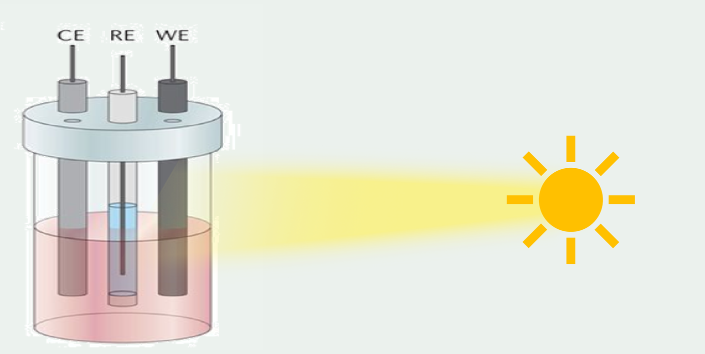
Fig. 6. a) Sustainability test, and b) measured solar hydrogen evolution activity obtained from H_2-annealed photoelectrode.

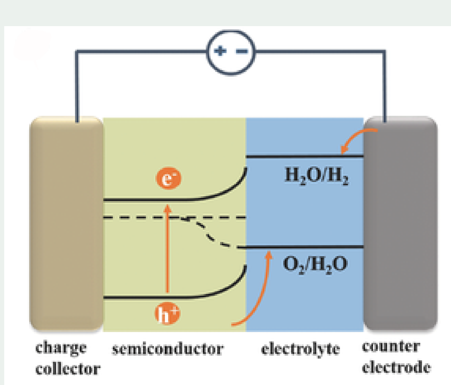
The energy diagram of all annealed samples relative to the water oxidation/ reduction potentials, confirming that all samples could appropriately straddle the two redox potentials of water.



Phtolectrochemical characterization, IV & Chronoamperometry

- Reduced fabricated electrodes (Zr-doped Nb2O5)
- SCE (Sat. KCl),
- Platinum foil.





Possible hydrogen production mechanisms in alkaline electrolytic conditions under illumination.

A remarkable enhancement in the photocurrent of the reduced sample with superior continuing stability without decay for 48h, could evidence the favorable photoactivity.

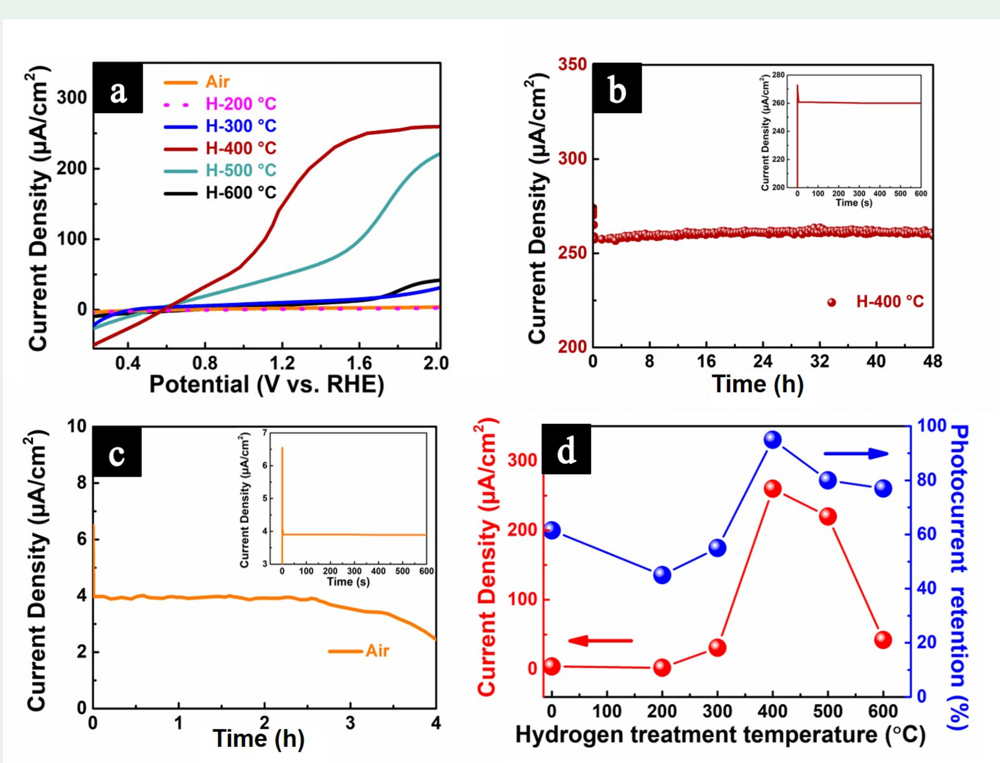


Fig. 4. a) Polarization curves, b,c) stability tests, and d) photo current retention of Zr-doped Nb_2O_5 photoelectrodes.

Conclusions

- The influence of Zr doping promotes photocatalytic activities, dramatically contributing to the PEC hydrogen production systems.
- In addition to the doping strategy, the superior performance is due to the influence of the hydrogen reducing atmosphere , which is responsible for the superior superconducting properties.
- The large enhancement for the performance of anodized sample is due to the synergistic electronic and photostability effects including the abundant charge carriers.
- Generally, these findings will open strategy to enhance semiconductors photocatalytic performance via synergetic effect.
- We hope those results will inspire researchers to investigate more materials for PEC.

Acknowledgement

The authors acknowledge the financial support from the American university in Cairo under grant for Energy Materials Laboratory.

Referances

[1] K.G. Kanade, J.O.K. Baeg, B.B. Kale, S. Mi Lee, S.J. Moon, K. jeong KongRose-red color oxynitride Nb2Zr6O17-x Nx: a visible light photocatalyst to hydrogen production. Int. J. Hydrogen Energy, 32 (2007), pp. 4678-4684.

[2] K.E. Salem, A.M. Mokhtar, A. Abdelhafiz, N.K. Allam. Niobium–zirconium oxynitride nanotube arrays for photoelectrochemical water splitting. ACS Appl. Nano Mater., 3 (2020), pp. 6078-6088,.