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Gold-Silver@TiO_2 Nanocomposite-Modified Plasmonic Photoanode for Higher Efficiency Dye-Sensitized Solar Cells

Su Pei Lim,[1,2]* Yee Seng Lim,[2] Alagarsamy Pandikumar, [2] Hong Ngee Lim, [3,4]*, Yun Hau Ng, [5] Ramasamy Ramaraj, [2,6] Daniel Chia Sheng Bien[7] , Osama K. Abou-Zied[8]* and Nay Ming Huang[2]*

[1] School of Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Selangor Darul Ehsan.
[2] Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[3] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[4]Functional Device Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[5]Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales, Sydney NSW 2052, Australia
[6]Department of Physical Chemistry, Centre for Photoelectrochemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India.
[7]Nanoelectronics Cluster, MIMOS Berhad, Technology Park Malaysia, Kuala Lumpur 57000, Malaysia
[8] Department of Chemistry, Faculty of Science, Sultan Qaboos University, P.O. Box 36, Postal Code 123, Muscat, Sultanate of Oman
*Corresponding authors: supei529@gmail.com (Lim S.P), huangnayming@um.edu.my (Huang N.M.), janet_limhn@science.upm.edu.my (Lim H.N.), and abouzied@squ.edu.om (Abou-Zied O.K.)

Supplementary information

Femtosecond Time-Resolved Absorption Measurements:

The ultrafast transient absorption measurements were performed using a femtosecond laser source (Libra, Co-herent) that contains a diode-pumped, mode-locked Ti:Sapphire oscillator (Vitesse. Fundamental 800 nm), amplified by a diode-pumped intracavity doubled Nd:YLF laser (Evolution). The Libra generates compressed laser pulses (90 fs pulse width) with output of 4.26 W at a repetition rate of 5 kHz. The output beam was split into two parts. A small portion was used as the gate pulse (vide infra), while the major portion of the output pulse was used to pump a Coherent OPerA Solo (Light Conversion Ltd.) optical parametric amplifier to generate spectrally tunable light spanning the range 240−2600 nm and is used as the pump beam.

For optical detection, a Helios transient absorption spectrometer (Ultrafast Systems LLC) was used. The source for the pump and probe pulses was derived from the output of Libra. The small portion of the output pulse was focused on a sapphire crystal to generate a white light continuum in the range 430-800 nm which is used as the gate pulse. The probe light was measured by a fiber optic that is coupled to a multichannel spectrometer with a CMOS sensor in the range 350-850 nm. The sensor has a 1.5 nm intrinsic resolution. The repetition rate of the laser was reduced to 1 kHz in order to match the working parameters of the Helios. A chopper was used to block every other pump pulse (~3 mm diameter), thus generating 500 Hz sync signals.

Rotational contribution to the overall excited state decay kinetics was removed by depolarizing the pump beam using a depolarizer (DPU-25, Thorlabs). In this way, the excited molecules' absorption is isotropic and therefore any dipole-dipole interactions between the excited molecules and the probe light are cancelled out. The pump pulse was attenuated to

~150–200 nJ in order to avoid multiphoton excitation and to ensure a one-photon absorption process.[1-3]

The pump and probe pulses were focused on the sample which was placed in a cylindrical cell with a path length of 2 mm. The relative temporal delay between pump and probe pulses was varied in 20 fs steps or longer, using a computer-controlled linear stage (retro reflector in double pass setup). Kinetic traces at appropriate wave-lengths were assembled from the time-resolved spectral data. Surface Xplorer software (supplied by Ultrafast Systems) was used for data analysis. The wavelength dependence of the coherent artifact signal from the pure solvent was used to correct time-zero of the time-resolved absorption data and to determine the instrument response. The latter was estimated to be ~ 150 fs. The steady-state absorption spectra of the samples were compared before and after the experiments and no change were observed in the absorbance and the spectral shape, indicating no photodegradation effect due to the laser pulses.

References:

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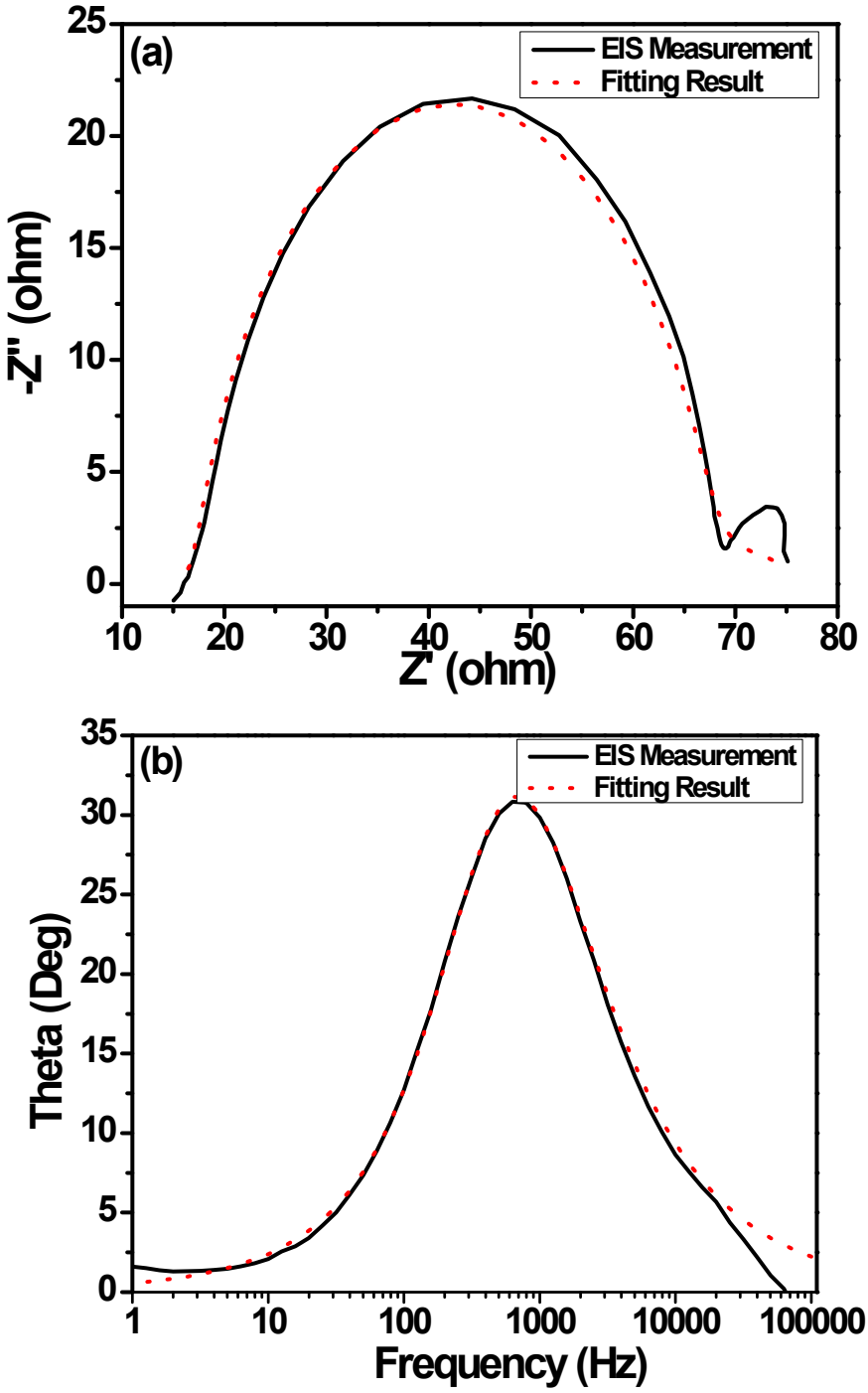

Figure S1 Fitting results obtained for Nyquist plot and **(c)** Bode phase plots obtained for Au-Ag/TiO_2 nanocomposite (Au_{75}:Ag_{25})