The Nanoporous Metallisation of Insulating Substrates through Semiconductor Photocatalysis

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A significant property of semiconductor materials lies in the ability of photogenerated charge carriers to interact chemically with local species at the semiconductor-electrolyte interface. We present on a novel exploitation of this facility for the metallisation of insulating surfaces sensitised with semiconductor-based materials and the in-process formation of nano-structured porosity within this metal.

In the process of Photocatalytically Initiated Electroless Deposition (PIED) we have developed a one-step metal deposition process which utilises photocatalysis to directly metallise mesoporous and/or nanoparticulate TiO_2 sensitised insulating substrate surfaces. Metallisation is initiated by photocatalytic means at the semiconductor surface and subsequently spreads / extends by auto-catalytic means to generate a coherent metal layer at the semiconductor sensitised insulator surface. PIED has been successfully utilised to produce electrically conductive layers of various metals including Ag and Pd on glass, quartz and polymer substrates. The process is spatially selective and offers several advantages over traditional, non-photocatalytic techniques such as enhanced controllability and purity of the deposit as well as reduced operational costs and environmental impact.

PIED can also be used to fabricate thin metal films with highly ordered porosity on the nano-scale with the addition of a hexagonally close-packed polystyrene microsphere template to the substrate prior to metal deposition. As the self-assembly of such a microsphere template is reliant on the substrate surface being sufficiently hydrophilic we have exploited the fact that TiO_2 coated surfaces exhibit super-hydrophilicity upon irradiation with UV light [1] to optimise the formation of ordered microsphere arrays. With a template in place, metallisation occurs directly onto the TiO_2 sensitised substrate through the interstitial spacing in the microsphere array, Fig.1 (ii) which is subsequently removed by dissolution, producing a conductive, nanoporous metal film, Fig.1 (iii-v). The thickness of the deposited metal is readily controlled by deposition time allowing the selective metallisation of substrates with single or multi-layer porosity, Fig.1 (vi).

The fabrication of nanoporous metal by this novel method adds a conductive and permeable metallic structure of high surface area to an otherwise electrically insulating surface. Such metallised insulating materials have potentially wide applications in membrane and separation technology, desalination, electrode/solid electrolyte composites for fuel cells, energy storage and sensors – especially surface enhanced resonance Raman spectroscopy (SERRS).

References:

[1] J.C. Yu, J. Yu, W. Ho, J. Zhao, Journal of Photochemistry and Photobiology A: Chemistry, 148 (2001) 331-339

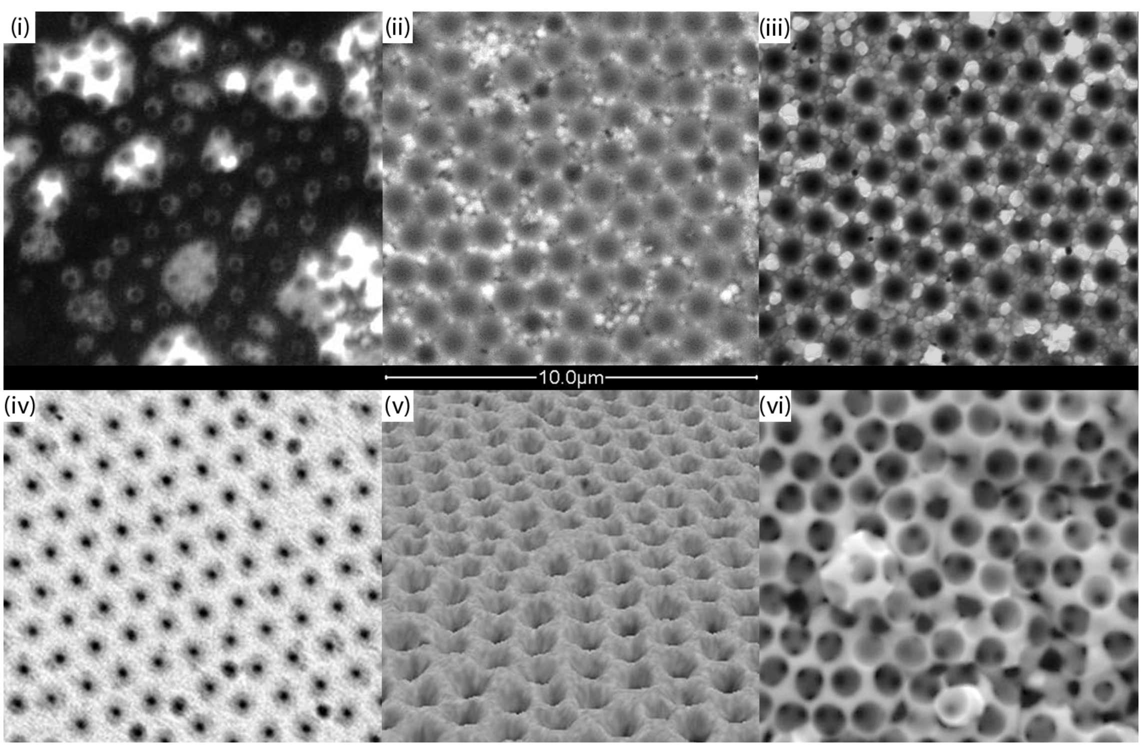

Fig.1 SEM images of **(i)** Photo-generated Ag nucleation; **(ii)** PIED generated Ag layer with 1µm microsphere template still present, deposition time = 60 min; **(iii)** same deposit after template removal **(iv)** nanoporous Pd deposit on glass after template removal, deposition time = 60 min; **(v)** 3D 'shape from shading' surface reconstruction of same Pd deposit; **(vi)** multi-layer porosity in Pd