Photothermal Characterization of Ordered Metallic Structures Template On Opals

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Synthetic opals represent new materials where the heat flow is drastically reduced due to the huge numbers of internal interfaces and thermal barriers. The study of the heat transport in such materials is here performed by applying photothermal techniques. Photothermal radiometry is here used to localize the internal heat sources where the light is absorbed and to measure the sample effective thermal diffusivity and the porosity of the opal. In this work we discuss the results obtained on Ni and Pd metallic opals of different thicknesses prepared by electrochemical deposition.

The metallic opals were prepared according to the following procedure:a) ordered arrays of monodisperse PS spheres supported onto gold or indium tin oxide (ITO) substrates were used as templates. Figure 1 shows the schemas of a template structure. PS spheres were prepared by emulsion polymerization in aqueous media, according to a procedure described in the literature. Two types of substrates, gold sputtered microscope slides and commercially available ITO covered slides (Präzision Glas&Optik GmBH) were used to grow opals. Before growing the opal or monolayer templates the substrates were subject to a hydrophilization pretreatment by oxygen plasma etching. PS artificial opals were grown by vertical deposition method, and as a result, highly ordered fcc structures with controlled thickness were obtained. The typical sample thickness used for metal deposition ranges from 100 nm to 4-5 μm. Inverse opals were obtained dissolving the polystyrene on cyclohexane and ethanol. b) Nickel (or Palladium) was infiltrated potentiostatically at a constant potential. Electrochemical experiments were carried out in a conventional three electrode electrochemical cell and controlled using an Autolab PGSTAT30 potentiostat-galvanostat. The active area of monolayers, about 1 cm^2, was delimited by a mask of transparent nail varnish. An Ag/AgCl electrode was used as reference electrode. The electrical circuit was closed with a counter electrode, CE, consisting in a platinum sheet of 4cm^2 area used to close the electrical circuit. All experiments were performed at room temperature. The amount of electrodeposited metal (or the thickness of the metal layer) infiltrated was proportional to the time of the infiltration, so this parameter was used in order to control the electrodeposition process. To obtain the new configuration the PS spheres were chemically activated by $SnCl_2$ and $PdCl_4$. This activation allowed the selective deposition of the metal on the surface of the spheres.

The optothermal characterization has been performed by using photothermal radiometry. The sample is here heated by a Ar laser @ 488 nm modulated by an acousto-optical modulator at a frequency ranging from 1 Hz up to 100 kHz so to change the penetration (i.e. the resolution) of the induced thermal waves from 100nm to 1mm. The modulated infrared emission from the surface is collected by a Germanium lens and focused onto an infrared detector HgCdTe. The signal allows the measurement of the effective thermal diffusivity and the porosity of the whole structure. The porosity obtained by photothermal radiometry is reported in the table below for all the investigated Ni and Pd opals.

Note that the porosity reported in the tables is about 50-60 % for PS spheres of 320 nm, while reaches 60-70 % for PS spheres of 457 nm. These values of "thermal" porosity (obtained with photothermal measurements) well fit with the "geometrical" porosity of the opaline structure. Nevertheless for some particular opal samples no reduction of the effective thermal diffusivity is observed and the calculated porosity tends to zero as if in the opal the heat could diffuse only through the metal (percolation effect). This demonstrates how photothermal radiometry may be applied to detect the "thermal" porosity and the effective thermal diffusivity in these structures.

Nickel opal structures					Palladium opal structures				
Sample	Opal type	PS diameter	Thickness	Porosity	Sample	Opal type	PS diameter	Thickness	Porosity
NiIt-2	(fig.1a)	320 nm	600 nm	52 %	PdIt-2	(fig.1b)	457 nm	370 nm	0 %
NiIt-3	(fig.1a)	320 nm	1100 nm	49 %	PdIt-3	(fig.1b)	457 nm	3200 nm	66 %
NiIt-4	(fig.1a)	320 nm	1600 nm	59 %	PdIt-4	(fig.1b)	457 nm	1200 nm	0 %
NiIt-5	(fig.1a)	457 nm	2000 nm	71 %	PdIt-5	(fig.1b)	457 nm	2400 nm	4 %
NiIt-6	(fig.1a)	457 nm	180 nm	0 %	PdIt-6	(fig.1b)	676 nm	4900 nm	57 %
NiIt-7	(fig.1a)	457 nm	3900 nm	0 %	PdIt-7	(fig.1a)	320 nm	370 nm	misfit

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