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Opal and inverse opal photonic crystals: Fabrication and characterization

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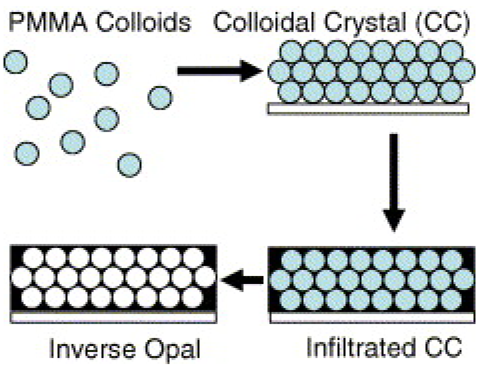
Abstract

Three-dimensional photonic crystals made of close-packed polymethylmethacrylate (PMMA) spheres or air spheres in silica, titania and ceria matrices have been fabricated and characterized using SEM, XRD, Raman spectroscopy and UV–Vis transmittance measurements. The PMMA colloidal crystals (opals) were grown by self-assembly from aqueous suspensions of monodisperse PMMA spheres with diameters between 280 and 415 nm. SEM confirmed the PMMA spheres crystallized uniformly in a face-centred cubic (fcc) array, and UV–Vis measurements show that the colloidal crystals possess pseudo photonic band gaps in the visible and near-IR regions. Inverse opals were prepared by depositing silica (SiO_2), titania (TiO_2) or ceria (CeO_2) in the voids of the PMMA colloidal crystals using sol-gel procedures, then calcining the resulting structure at 550 °C to remove the polymer template. The resulting macroporous materials showed fcc ordering of air spheres separated by thin frameworks of amorphous silica, nanocrystalline titania or nanocrystalline ceria particles, respectively. Optical measurements confirmed the photonic nature of the inverse opal arrays. UV–Vis data collected for the opals and inverse opals obeyed a modified Bragg's law expression that considers both diffraction and refraction of light by the photonic crystal architectures. The versatility of the colloidal crystal template approach for the fabrication of macroporous oxide structures is demonstrated.

Graphical abstract

PMMA colloidal crystals have been fabricated and used as templates for the preparation of SiO_2, TiO_2 and CeO_2 photonic crystals with inverse opal structures.



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Introduction

Photonic crystals are highly ordered materials that possess a periodically modulated dielectric constant, with periods on the scale of visible light wavelengths (380–750nm). Periodicity affects the propagation of electromagnetic waves in the material due to Bragg reflections on lattice planes. The result is a photonic band gap (PBG or stop band), a band of frequencies where light propagation in the photonic crystal is forbidden (the optical analogue of electronic band gaps in semiconductors). A complete photonic band gap occurs when a range of wavelengths is forbidden for every state of polarization and propagation direction [1]. Ever since Yablonovitch [2] and John [3] first demonstrated the possibility of a photonic band gap in such periodic structures, there has been determined effort from the scientific community to develop materials with complete photonic band gaps in various optical regimes and in particular in the visible region [4]. Complete photonic band gap materials could potentially be used to produce waveguides, laser resonant cavities, or to inhibit spontaneous emission [5]. Before their full potential can be realized, improved methods for the fabrication of highly ordered three-dimensional photonic crystals must be developed.

Experimentalists have traditionally used two approaches to fabricate photonic crystals: nanolithography and self-assembly of colloidal crystals. Engineers have used nanolithography (the so-called "top-down" approach) to etch successively smaller features into various solid substrates with remarkable precision [6], [7]. However, this method is expensive, slow and capable only of producing materials of a few structural layers thickness. The self-assembly of colloidal crystals (the so-called "bottom-up" approach) is the more preferred route as it is simpler, inexpensive and can yield crystalline samples of a few to several hundred structural layers thickness [8], [9]. This approach involves the crystallization of a colloidal dispersion of monodisperse spheres of silica, polystyrene or polymethylmethacrylate (PMMA) to form a material with a three-dimensional periodic structure in which 24% of the volume is air (a colloidal crystal or opal). Natural opal is an example of such a periodic colloidal crystal, and is composed of face-centred cubic (fcc) arrays of monodisperse amorphous silica spheres with average diameter in the range 15–900 nm. Theoretical [2], [3], [10], [11], [12], [13] and experimental [8], [9] studies have shown that a pseudo photonic band gap exists in the [1 1 1] direction for fcc arrangements of silica or polymer spheres. These opals do not possess a complete photonic band gap, since the band gap position, and hence frequencies of light allowed to propagate within the crystal, vary with the angle of incidence of incoming photons. Most of the technological applications envisaged for photonic crystals require materials that possess a complete photonic band gap. Theoretical requirements to achieve a complete band gap in opaline structures include a refractive index contrast higher than 2.9 and long range three-dimensional crystalline order (see above). The refractive index ratios for colloidal crystals of silica (n_{silica}/n_{air}=1.45), polystyrene (n_{PS}/n_{air}=1.59) and PMMA (n_{PMMA}/n_{air}=1.492) are all well below the value of 2.9 needed for the realization of a full gap, thus they exhibit only pseudo photonic band gaps. A complete PBG is more easily achievable in materials with inverse opal structures, comprising fcc arrays of air spheres in materials with high refractive indices (e.g. Si n=3.5 or Ge n=4.5). The filling fraction of the dielectric in such structures is around 26%. A silicon inverse opal with a complete three-dimensional PBG at 1460 nm has been demonstrated [14]. Inverse opal structures can readily be fabricated from colloidal crystal (opal) templates, by filling the voids in the opal with a dielectric material, and then removing the original opal template by wet chemical etching in the case of SiO_2 or calcination in the case of polymer spheres [9]. The failure to date of researchers to realize a complete PBG in systems other than silicon is due to experimental difficulties in fabricating inverse opals with a large enough refractive index contrast and the required degree of crystalline order.

Macroporous oxides fabricated using the colloidal crystal template approach may also prove useful in other areas of materials science. Recently, dye-sensitized solar cells of the Grätzel type, based on inverse opal TiO_2 films, have been developed [15], [16], [17]. The cells show improved power conversion efficiency under simulated solar light compared to Grätzel cells prepared by conventional methods using nanocrystalline titania particles. The improved performance is attributed to the inherent uniformity and macroporosity of inverse opal TiO_2 architectures. Efficiencies could be further improved if technical difficulties related to the fabrication of inverse opal TiO_2 films with uniform thickness and large area could be overcome. The combination of high surface area and macroporosity (hence facile gas flux) suggest that inverse opal structures may also be useful in the field of heterogeneous catalysis [18], [19], [20]. It is envisaged that the colloidal crystal template approach could be used to fabricate highly efficient TiO_2 photocatalysts or CeO_2-based catalysts for CO oxidation, the water-gas shift reaction (WGS), the reforming of hydrocarbons and the partial oxidation of methane. To our knowledge, only one previous study of inverse opal ceria has appeared in the literature [21] justifying further research in this area.

In view of the discussion above, we have commenced a comprehensive programme aimed at the fabrication opal and inverse opal thin films with ordered structure extending over large areas. Here we describe the synthesis and characterization of PMMA colloidal crystals (opals) with long range three-dimensional order, and then show how the colloidal crystals can be used as templates for the fabrication of macroporous SiO_2, TiO_2 and CeO_2 structures (inverse opals) possessing comparable order and strong photonic behaviour in the visible and near-IR regions.

Section snippets

General

Methyl methacrylate (MMA, 99%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (97%), tetraethylorthosilicate (TEOS, 98%), titanium (IV) isopropoxide (97%), concentrated HCl (37% in water), $Ce(NO_3)_3 \cdot 6H_2O$ (99%), hexamethylenetetramine (99%), TiO_2 powder (99%, anatase form) and CeO_2 powder (99.9%, <5 μm) were all obtained from Aldrich and used without further purification. CeO_2 nanoparticles were prepared from $Ce(NO_3)_3 \cdot 6H_2O$ and hexamethylenetetramine using a literature procedure [22]. The CeO_2…

Synthesis of monodisperse PMMA spheres

The optical quality of colloidal crystals (opals) and their inverted structures is highly dependent on the size uniformity of the spheres used to fabricate the colloidal crystal. In this study, uniformly sized PMMA spheres where fabricated by the free radical induced polymerization of MMA in water. Table 1 shows the effect of synthesis conditions on the size and polydispersity of the PMMA spheres obtained by this method.

Results show that the reaction parameters can be adjusted to produce PMMA…

Conclusions

The fabrication of well-ordered photonic crystals with opal and inverse opal structures has been demonstrated. These materials have intrinsically interesting optical properties (such as photonic band gaps) that may be exploited in applications such as solar energy conversion or light-emitting devices. We are currently developing conducting polymer and piezoelectric oxides with inverse opal structures. In general, the well-ordered colloidal crystal templates provide an excellent route for the…

Acknowledgements

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References (29)

P.R. Somani *et al.*
Sol. Energy Mater. Sol. Cell. (2005)

Q. Fu *et al.*
Chem. Eng. J. (2003)

J.D. Joannopoulos *et al.*
Photonic Crystals: Molding the Flow of Light
(1995)

E. Yablonovitch
Phys. Rev. Lett. (1987)

S. John
Phys. Rev. Lett. (1987)

V.L. Colvin
MRS Bull. (2001)

L. Bechger *et al.*
J. Phys. Chem. B (2005)

S. Noda *et al.*
Science (2000)

M. Qi *et al.*
Nature (2004)

P. Jiang *et al.*
J. Am. Chem. Soc. (1999)

R.C. Schroden *et al.*
Chem. Mater. (2002)

K. Busch *et al.*
Phys. Rev. E (1998)

R. Biswas *et al.*
Phys. Rev. B (1998)

R. Biswas *et al.*
Phys. Rev. B (2000)

There are more references available in the full text version of this article.

Cited by (282)

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