Photonic Crystals

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Electrodeposition of 3D Ordered Macroporous Germanium from Ionic Liquids: A Feasible Method to Make Photonic Crystals with a High Dielectric Constant**

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Three-dimensionally ordered macroporous (3DOM) nanostructures have been intensively studied in recent years because of their intriguing properties and potential applications. Much effort has been devoted to the synthesis of various 3DOM nanostructured materials, such as semiconductors,[1,2] metals,[3,4] metal oxides,[5–7] ternary oxides,[8] and polymers.[9] Routes for the synthesis of 3DOM nanoarchitectures with close-packed colloidal crystal templates (CCT) include chemical vapor deposition (CVD),[10] electrodeposition,[11] chemical (bath) deposition,[12] sol–gel techniques,[13] and atomic layer deposition.[14] Template-assisted electrochemical deposition has been used to synthesize 3DOM structures of nickel, CdS, CdSe, and conductive polymers.[15–19] This method ensures a high density of the deposited materials, as the deposition occurs in the space between the template spheres filling from the bottom of the electrode up rather than on the surface of the template spheres as for other methods, which lead to filling of only the top few layers.

Three-dimensional macroporous dielectric structures are of great interest for optical applications. The periodic modulation of the refractive index in all three dimensions of such structures gives rise to a strong coherent multiple scattering of the electromagnetic waves within the material, which produces a band structure for photons. These 3DOM materials are commonly referred to as inverse opal structural photonic crystals. The templating method by colloidal crystals is quite promising for the fabrication of a high-dielectric-contrast inverse opal with a visible and near infrared full photonic band gap (PBG). A typical procedure includes three steps: self-assembly of the template, infiltration of the template with the desired materials, and removal of the template.

While the initial concept of producing a full PBG material by forming an inverse opal was straightforward, the reality of forming such structures has proven to be more difficult. The main requirement for the formation of an inverse opal with a complete PBG in the visible spectral region is the proper choice of the material used to fill the voids of the template. This material needs to have both a high refractive index and a negligible absorption at optical wavelengths. It has proven to be extremely challenging to find materials that fulfill both criteria.

Germanium is a major material in the optoelectronics industry. Of all materials that are transparent in the near infrared regime ($\lambda > 1850$ nm), it has the highest dielectric constant ($\varepsilon = 16$).[18] It also has a very high refractive index ($n = 4.12$ at $\lambda = 2$ μm), making it a very promising candidate for photonic applications in the IR spectral range. As the width of the photonic band gap increases with the dielectric contrast, 3DOM germanium will deliver wider gaps than silicon, which makes it the best material to produce a high-contrast PBG. Van Vugt et al. made random macroporous germanium with a dried suspension of silica spheres.[20] Míguez et al. reported the preparation of a macroporous lattice of hollow spheres in a germanium medium by a three-step approach involving the hydrolysis of tetramethoxygermane in a crystalline silica template; results on the synthesis of a germanium inverse opal made from digermane by CVD have also been reported.[21] Shimmin et al. employed an evaporation-driven infiltration technique to fill polystyrene synthetic opals with germanium nanoparticles. An interstitial volume of the polystyrene template with Ge nanoparticles was calculated to reach a value of 49 vol% by the Maxwell–Garnett model of dielectric mixing.[22]

However, most of these techniques have low degrees of infiltration, because lower layers cannot be reached starting from the surface. Electrodeposition is a feasible method for the production of 3DOM materials, because it allows for complete infilling of the vacancies of the matrix from the bottom up to the top layers of the template. Unfortunately, germanium can hardly be obtained in aqueous solutions, as its deposition in water is always accompanied by hydrogen evolution.[23] In organic solvents such as poly(ethelene glycol)

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the current efficiencies are also low, and hydrogen evolution remains a problem. However, germanium can quite easily be electrodeposited in ionic liquids.[24] Herein we report for the first time on the synthesis of 3DOM germanium by direct electrodeposition at room temperature within polystyrene colloidal crystal templates from the ionic liquids 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm]FAP) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf_2N) containing $GeCl_4$ as precursor. Our method is quite promising, because these types of ionic liquids are chemically and electrochemically stable enough to deposit germanium, they are aprotic, and they can be dried quite easily.[25] Moreover, there is no need to add supporting electrolytes that are needed when organic solvents are used.[20] The PS template has the advantage of being easily removed by simple dissolution in THF without damage to the Ge macroporous structure. The only restriction to this method is that the experiments must be performed under inert gas owing to the water-sensitive nature of $GeCl_4$.

Figure 1 shows the cyclic voltammogram of 0.1 mol L^{-1} $GeCl_4$ in [HMIm]FAP at room temperature on an ITO substrate covered with a polystyrene (PS) template. The first

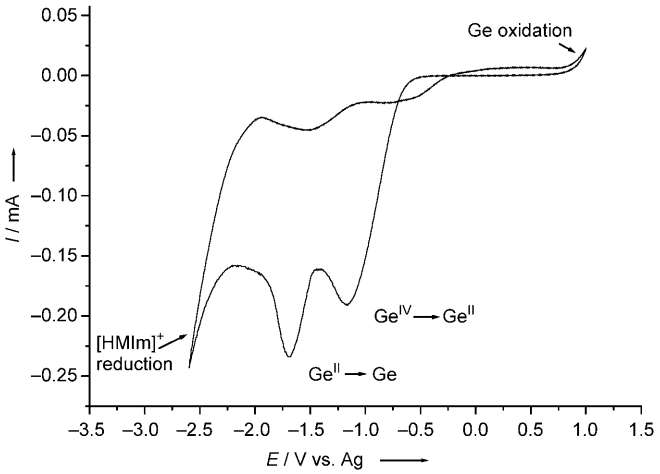

Figure 1. Cyclic voltammogram of 0.1 mol L^{-1} $GeCl_4$ in [HMIm]FAP on the indium tin oxide (ITO) substrate covered with a PS template acquired at a scan rate of 10 mV s^{-1} at room temperature.

reduction peak at −1.1 V corresponds to the reduction of Ge^{IV} to Ge^{II}. The second peak at approximately −1.7 V is correlated with the bulk deposition of elemental germanium, as confirmed by energy-dispersive X-ray spectroscopy (EDX; see the Supporting Information) and X-ray photoelectron spectroscopy (XPS, Figure 3). The rising current at about −2.25 V is due to the reduction of the organic cation. The oxidation peak in the reverse scan is partly due to the electrochemical oxidation of Ge. The electrochemical behavior of $GeCl_4$ on PS-modified ITO in Figure 1 is quite similar to that obtained on a bare gold electrode and to the electrochemical behavior of the PS-modified ITO in [EMIm]Tf_2N/$GeCl_4$. It is evident that the ionic liquid with $GeCl_4$ easily permeates the interstices in the close-packed structure of the polystyrene colloidal crystal template to access the ITO surface. This good penetration is due to the low surface tension of ionic liquids, leading to a good wetting of polystyrene.

Figure 2 shows scanning electron microscopy (SEM) images for a 3DOM Ge layer with a thickness of 1.5 μm obtained after applying a constant electrode potential of

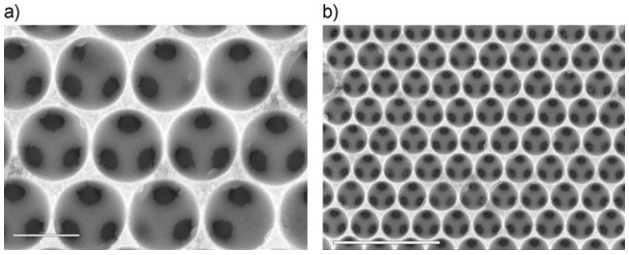

Figure 2. High-resolution SEM images of 3DOM Ge obtained after applying a constant potential of −1.9 V (vs. Ag quasi-reference electrode) for 3 h at room temperature. Scale bars: a) 500 nm, b) 2 μm.

−1.9 V (vs. Ag quasi-reference electrode) for 3 h at room temperature after removal of the PS spheres with THF. The deposited germanium has a well-ordered macroporous nanoarchitecture consisting of uniform close-packed spherical pores. The holes into the layer below are clearly visible, indicating the three-dimensional ordering of the structure. The average center-to-center distance between the pores is (555 ± 10) nm, indicating that no shrinkage occurs with the electrodeposition method. The smooth surface morphology in Figure 2a clearly shows that germanium grows uniformly into the interstices of the PS colloidal crystal template, and the structure is well-ordered even on the $4 \times 4\ \mu m^2$ scale (Figure 2b).

XPS analysis of the surface of the 3DOM Ge showed that the sample contains only Ge, O, and trace amounts of carbon owing to surface contaminations (see the Supporting Information). The Ge 3d XPS spectrum of the core level (Figure 3) indicates that germanium is partially oxidized. The peak at 32.5 eV corresponds to GeO_2, and the prominent peak at 30.8 eV is attributed to GeO. The peak at 29.3 eV is, as expected, a contribution from Ge. In our experience, electrodeposited germanium is subject only to surface oxidation

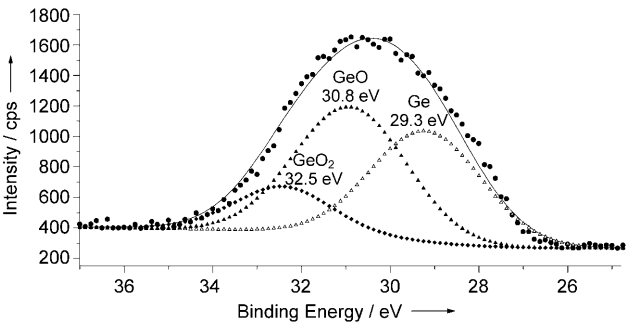

Figure 3. Ge 3d XPS spectrum with fitted components after 2 min Ar^+ ion sputtering of the 3DOM Ge surface.

from exposure to air. Quite recently we showed that ionic liquids even allow the deposition of luminescent semiconducting Si_xGe_{1-x} with direct band gaps between 1.5 and 3.2 eV.[27] Thus, electrodeposition from ionic liquids delivers extremely pure materials, provided ultrapure ionic liquids are used.

Figure 4 shows photos of the whole 3DOM Ge sample made in [HMIm]FAP. When the incident angle between the substrate and artificial white light is changed, the 3DOM Ge

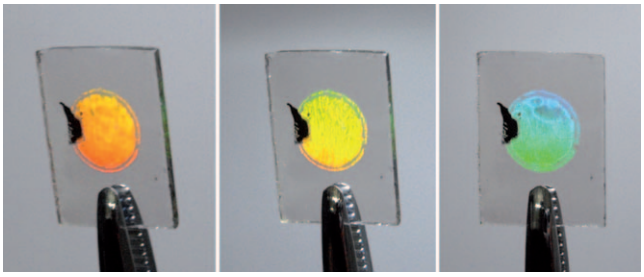

Figure 4. Photographs of 3DOM Ge showing the color change that occurs with a slight change in the angle of incident white light. The black area is a conductive gel used to carry out SEM.

turns blue, yellow, and orange owing to light reflection. The light emission of the surface of 3DOM Ge can be simply explained by Bragg's law, $2d\sin\theta = n\lambda$ (λ is the wavelength, θ is the scattering angle, n is integer representing the order of the diffraction peak, and d is the interplanar distance (center-to-center distance of air spheres)). When the wavelength of the light, the interplanar spacing of the crystal, and the incidence angle satisfy the Bragg condition, the incident light is reflected and displays different colors depending on θ.

With our method, the thickness, the quality, and the pore size of 3DOM materials can be improved by simply changing some parameters, such as the ionic liquid used, the template, the concentration of $GeCl_4$, the applied potential, and the reaction temperature. As an example, we used a PS colloidal crystal with a smaller average pore size of approximately 370 nm as a template and the ionic liquid $[EMIm]Tf_2N$ as a solvent with the same concentration of $GeCl_4$ (0.1 mol L^{-1}) and the same other reaction conditions. The ionic liquid $[EMIm]Tf_2N$ was chosen because it has a lower viscosity than [HMIm]FAP and thus a higher mobility of the electroactive species and a higher deposition rate of Ge. These properties give rise to a thicker deposit at a shorter deposition time. Figure 5a shows an SEM picture of 3DOM Ge obtained from the mentioned system after applying a constant potential of −2 V (vs. Ag quasi-reference electrode) for only 30 min. The uniform 3D macroporous structure is clearly observed over a wide area. To get more information about the thickness of the 3DOM Ge structure, an SEM image of a cross-section of the sample before dissolution of the PS template was taken (Figure 5b). At least seven successive macroporous Ge layers (Figure 5b) can be clearly observed, which corresponds to a thickness of at least 2 μm (after only 30 min). Figure 6 shows optical photographs of the whole 3DOM Ge sample, which has a surface area of 0.3 cm^2, with a wider range of colors (orange, yellow, green, and blue) indicating a wider PBG.

Electrodeposition in ionic liquids provides a novel route for the formation of 3DOM germanium. Our results show

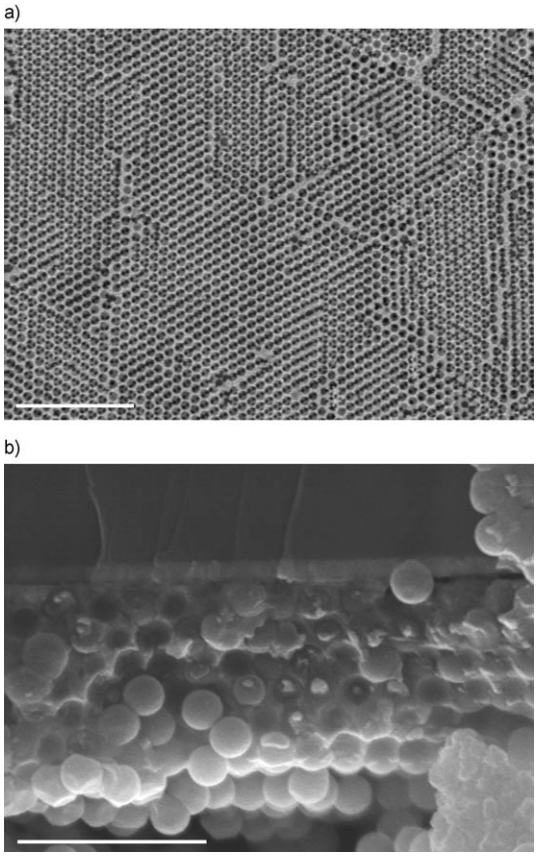

Figure 5. SEM images of: a) 3DOM Ge (after removing the PS matrix) obtained after applying a constant potential of −2 V (vs. Ag quasi-reference electrode) for 30 min (pore size ca. 370 nm); scale bar: 5 μm. b) A cross-section of the same sample before the dissolution of the PS spheres; scale bar: 2 μm.

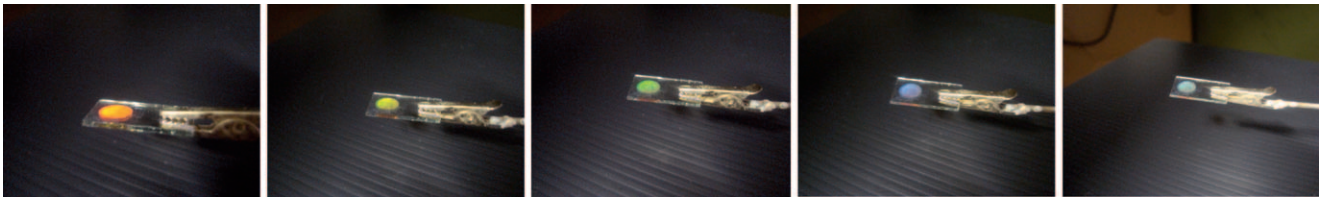

Figure 6. Optical photographs of the deposited Ge photonic crystal (pore size ca. 370 nm) on the ITO glass substrate showing a color change when the angle of incident white light is changed. The deposit was obtained after potentiostatic polarization at −2 V (vs. Ag quasi-reference electrode) for 30 min in $[EMIm]Tf_2N$.

that direct template-assisted electrodeposition in ionic liquids is a well-suited technique for the creation of 3DOM materials. In particular, many high-refractive-index materials, such as semiconductors, can be electrodeposited as 3DOM materials, which are very difficult to synthesize by traditional techniques. Electrodeposition in ionic liquids has an unprecedented potential in the fabrication of photonic crystals, as many reactive elements, for example, aluminum, selenium, tantalum, and many others, as well as conducting polymers can be made without the disturbing effect of hydrogen evolution. Our results might be of considerable interest to improve the efficiency of solar cells.

Experimental Section

The ionic liquids [HMIm]FAP and [EMIm]Tf_2N were purchased in the highest available (ultrapure) quality from Merck KGaA and Io-Li-Tec (Germany) and were used after drying under vacuum at 100 °C to a water content below 1 ppm. $GeCl_4$ (99.9999 %, Alfa Aesar) was used as delivered. Monodisperse PS spheres with an average diameter of 560 or 370 nm (± 10 nm) were obtained using an emulsifier-free emulsion polymerization technique.[26] Polystyrene colloidal crystals were grown on indium tin oxide (ITO)-coated glass. The preparation process was as follows: The ITO glass substrate was placed into a cylindrical vessel, and an aqueous suspension of PS spheres (0.1 vol %) was added. The vessel was then placed into an incubator at 55 °C until complete growth was achieved. A well-ordered multilayer PS colloidal crystal was obtained on the ITO substrate and used as the template.

Germanium(IV) chloride was added to [HMIm]FAP or [EMIm]Tf_2N to a concentration of 0.1 mol L^{-1} in an argon-filled glovebox (OMNI-LAB, Vacuum Atmospheres). All of the electrochemical experiments were performed inside the glovebox. ITO-coated glass with a polystyrene colloidal crystal on top of it was used as a working electrode (WE). A silver wire was used as a quasi-reference electrode (RE), which gives, especially in the presence of $GeCl_4$, a sufficiently stable potential. A Pt ring was used as a counterelectrode (CE). The electrochemical cell was made of polytetrafluoroethylene (teflon) and clamped onto the template with a teflon-covered O-ring (Viton), yielding a geometric surface area of 0.3 cm^2. The size of the photonic crystal to be made is only limited by the size of the sample and of the electrochemical cell.

The electrochemical measurements were performed by using a VersaStat II (Princeton Applied Research) potentiostat/galvanostat controlled by powerCV software. The electrodeposition of Ge was achieved by applying a constant potential of −1.9 V for 3 h and −2 V for 30 min in the ionic liquids [HMIm]FAP and [EMIm]Tf_2N, respectively. The deposit was then removed from the glovebox and rinsed quickly with isopropyl alcohol to avoid the possible chemical attack of $GeCl_4$ on deposited Ge. The polystyrene template was removed with THF to give the macroporous germanium structure. Figure 7 shows a schematic procedure for the fabrication of 3DOM germanium.

The deposits were characterized using a high-resolution scanning electron microscope (HR-SEM, Carl Zeiss DSM 982 Gemini), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS, Perkin–Elmer PHI5700 ESCA system with $Al_{K\alpha}$ source).

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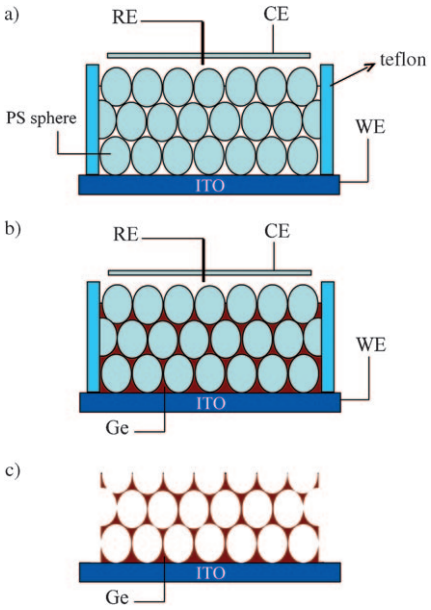

Figure 7. Schematic illustration of the electrodeposition of 3DOM Ge: a) Electrochemical cell, which is then filled with 0.1 mol L^{-1} $GeCl_4$. b) Electrodeposition of Ge. c) Removal of PS colloidal crystal by THF.

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