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研究課題名(英文) Fast-Recharge, high energy density hybrid supercapacitors using sol-gel transformation block copolymer templates

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研究成果の概要(和文)：取扱容易な薄膜物質を用いたスーパーキャパシタや高効率光起電発電は持続可能なエネルギーを低コストで実現する上で望ましい。いずれの技術も多孔質電極を活用しており当研究ではこれらに適用可能なメソポーラスTiO₂層の作成手法を開発してきた。ペロブスカイト型の光発電においてPMMAを鋳型としたゾルゲル法を用いて細孔を制御し、ひいてはデバイス特性の制御に成功した。当手法で作成したTiO₂を用いた光電池において12.6%のデバイス効率を実現し対照試料の2.8倍の効率を得た。高分子材を用いた容易なゾルゲル法はエネルギー貯蔵や光発電に用いる低価格なメソポーラス電極の開発に大きく貢献する可能性があると考えられる。

研究成果の概要(英文)：Supercapacitors and high-efficiency photovoltaics based on solution-processable thin film materials are desirable for sustainable energy at reduced cost of material and fabrication. Both of these applications make use of highly porous electrode surfaces. In this research, we have developed some unique methodologies to obtain mesoporous TiO₂ layer which have application in both of these applications. In the case of perovskite solar cells, using a facile sol gel technique loading a general polymer PMMA as a templating agent, we were able to control porosity and the resulting effect on device performance. The perovskite solar cells based on PMMA-mediated mesoporous TiO₂ achieved a device efficiency of 12.6%, which is 2.8 times higher than a control sample. We believe this facile sol gel technique with a simple polymer additive has the great potential to contribute significantly toward the development of low-cost mesoporous electrodes for energy storage and generation from sunlight.

研究分野：高分子物理学

キーワード：Battery Supercapacitor High Porosity Electrodes

1. 研究開始当初の背景

There has been significant research investment into alternative methods of energy production that reduce our dependence on fossil fuels. With the exception of nuclear or neo-fossil fuels (e.g. biofuels), these resources (e.g. solar, wind) are neither generated nor converted into useful forms of energy (electric or mechanical) at the 'point of use' or 'on-demand' and require storage and a substantial delivery network. Battery technology will be an intrinsic part of the development of alternative energy strategies. However battery technology, whilst boasting large storage capability, is an essentially electrochemical process, and requires significant charging-up times. Therefore one cannot currently recharge electric car batteries as quickly as filling up a car with petrol. Equally, low capacity and high recharge-times of batteries in mobile devices (lap-tops, mobile phones) limits their ability to contain more functionality. It is obvious that the next breakthrough technology in mobile devices will be in their power packs.

Supercapacitors are strong contenders to provide both high capacity and fast storage/release of energy. Capacitors, as every science student is aware, can store charge between two electrodes separated by an insulator (the dielectric). Releasing this charge through a mechanical or electric load is a way to usefully harness the stored potential. The key difference in supercapacitors is that the dielectric is an inherent part of each electrode, and charge is stored within nanoporous pathways within the dielectric. Discarding the distinct dielectric in supercapacitors allows composite wafer-thin sandwiches of cells to be made yielding a high density storage device. Storage is dictated by density. The ability to store a lot in as little space as possible is energy efficient.

2. 研究の目的

In this proposal, we use a radical new technology to generate dielectrics with high surface area densities. This is accomplished by introducing highly interconnected nanoscale pores into the materials in a controlled, reliably repeatable way. Certainly making nanoporous materials is not a new idea in itself. However existing methods are either expensive, or too unreliable. Our technique uses cheap materials, fast process-times and good reproducibility. This will be important in

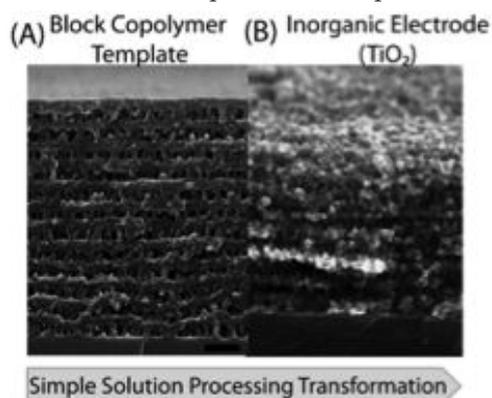
the future when taking such supercapacitor technology, from a proven state in our laboratory towards commercialization.

3. 研究の方法

Mesoporous TiO₂ – method 1. A recent discovery, called *Collective Osmotic Shock* (COS), published by us in *Nature Materials* and patented, is able to generate a unique polymer structure that has several industrially important aspects:

- It is made from low-cost styrenic materials. **The COS-processed nanoporous polystyrene scaffolds (figure 1a) are inert and have advantages as separator membranes.**
- Using simple, industrially relevant, sol-gel transformations, **multilayer metal oxide (e.g. titania) structures are generated; figure 1b.**
- Our nanoscale layers in electrode interfaces **provide spatial control vertically from the surface and/or laterally across the electrode surface.**

Figure 1(a) Original block copolymer template produced by COS process. (b) The transformed nanoporous state produced by



sol-gel replacement of void spaces.

The fabrication of polymeric templates was performed using commercially available BCPs from Polymer Source Inc. made of PS-*b*-PMMA with a PMMA weight fraction (ϕ_{PMMA}) between $0.14 < \phi_{PMMA} < 0.16$. Different film thicknesses between 300nm and 1µm were made by spin coating technique. Based on previous work, it is known that the number of internal layers after COS phenomenon is directly proportional to the initial thickness of the BCP film before treatment. Beside the traditional thin film coating techniques, other coating methods can also be used, such as the industrial technique of roll-blade coating and spray coating. Films

produced were self-assembled into the spherical phase using thermo-solvent conditions under toluene/N₂ atmospheres.

The use of thermo-solvent conditions not only reduces processing time, but also helps in the control of pore formation on the surface of the films. The use of pure N₂ annealing produced reduced pore sizes (~1nm), in contrast to the surface pore formation using thermo-solvent annealing which produced ~20nm pores. Pore control is very important because the opening in the pores helps in the infiltration of the solutions needed in nanostructure fabrication.

The next step is the film curing by UV radiation (254nm). The samples are treated with doses between 4.5J/cm² for silicon wafers or aluminum foil and 7.5J/cm² for glass or plasticized substrates; this is for films cured in pure O₂ at 40°C and 300nm thickness. The difference in UV dose is due to differing optical reflection and absorption properties. Following curing, the last step in COS development is the sequential soaking in glacial acetic acid at room temperature. The acetic acid induces the required osmotic shock due to the selective solvation of the degraded PMMA, leading to the structure formation and removal of the PMMA oligomers. Additional treatment with methanol improved the diffusion of the compounds used in the following steps needed to transform the templates into metal or metal oxides.

The sol-gel method is a well-understood nano-fabrication technique ease of scale-up and control. Normally this technique has been used alongside BCP templates, mainly in the elaboration of 2D nanostructures or 3D ones based on the gyrioid phase. Using COS structures, we attempted to produce metal oxide COS nanostructures by sol-gel. The samples were filled with the sol and left to age in order to induce gelation of the sol. These structures are usually an amorphous conformation of the desired metal oxide. Finally, the samples were thermally treated to determine the crystallographic composition. In the case of TiO₂ nanostructures, a modification of a protocol proposed by Lancelle-Beltran et al. was used, with precursors based on TiCl₄ solutions in absolute ethanol. The use of absolute ethanol instead of water in the solutions improved the sol infiltration into the COS structure, most likely due to the hydrophobic nature of the PS walls. The

final structures were treated in a pre-heated oven at 500°C for 3hr in air, causing the TiO₂ to crystallize into anatase phase, although other crystallographic phase could be achieved by controlling the temperature during the heat treatment. The heat treatment employed aids in the calcination of the polymer template, uncovering the metal oxide nanostructure. A particular quality of the transformed COS structure is its mesoporosity and the ability to separate the multilayer architecture into mesoporous monolayers.

Mesoporous TiO₂ – method 2. A second approach, was also used to generate the mesoporous TiO₂ layers for the generation of solar cells. High-efficiency photovoltaics based on solution-processable thin film materials are desirable to sustainable energy at reduced cost of material and fabrication compared to established crystalline silicon solar cells. Recently, methylammonium lead halide perovskites (CH₃NH₃PbX₃, X = halogen) have offered the promise of a breakthrough for such next-generation photovoltaic devices. Since they were first used in the dye-sensitized solar cell as a sensitizer with a power conversion efficiency (PCE) of 3.81%, mesoscopic perovskite-based solar cells have reached the PCE more than 16%, owing to the advantageous characteristics of perovskite materials: excellent light-harvesting ability in the visible-light region, ambipolar charge transport, and long charge transport lengths. A typical perovskite solar cell contains a mesoporous TiO₂ (mpTiO₂) layer where the perovskite materials are deposited. The mpTiO₂ are prepared by spin-coating a paste containing TiO₂ nanoparticles to form TiO₂ films with high surface area. However, the procedure for preparation of the TiO₂ nanoparticle pastes is complicated, thereby inhibiting the advantages of cost-effective perovskite solar cells. Furthermore, perovskite crystallization in the mesoporous scaffolds by solution procedures often causes incomplete crystalline formation, depending on the employed TiO₂ nanoparticle size. Therefore, a quest for simple methodology to fabricate the mpTiO₂ layer with desirable morphology, porosity, and pore size is crucially important for the further improvement of PCE and reduction of fabrication cost in perovskite solar cells. Herein, we examine the effects of

polymeric additions into sol-gel precursors on the resulting structures of TiO₂ films prepared by sol-gel reactions.

TiO₂ films were prepared by spin coating the precursor solution on silicon wafers or fluorine-doped tin oxide (FTO)/compact TiO₂ (cTiO₂) and subsequent calcination. The precursor solution included 3.1 % titanium(IV) isopropoxide, 1.6 % titanium(IV) chloride, and 0 or 1 % polymer (PMMA or polystyrene (PS)) in chloroform. It is assumed that all of the titanium sources are converted to TiO₂, the final weight ratio of TiO₂ : PMMA is 60 : 40 with an initial concentration of 1 % PMMA fed in the chloroform precursor solution. Thus, we denote it as TiO₂(40wt%-PMMA). The TiO₂(40wt%-PMMA) film showed crack-free mesoporous structure, where nanoparticles with sizes of 20 – 30 nm are interconnected seamlessly (Figure 2a), together with a few hundreds nm-sized plate-shaped TiO₂ on the surface (Figure 2d). The pores and TiO₂ domains have larger sizes and better-connected structures in comparison with the mpTiO₂ films made by the convectional method using TiO₂ nanoparticles. Although the mesoporous structure is ill-defined compared to mesoporous TiO₂ made by sol-gel methods with block copolymers, it is of great value that simple addition of a common polymer for the sol-gel procedure could create the mesoscopic structure. Figures 1b and 1e display the side and top views of the TiO₂ film prepared by the same sol-gel method with 1 % PS as a control polymer in the precursor chloroform solution (denoted as TiO₂(40wt%-PS)). The PS addition also provided TiO₂ nanoparticles with a diameter of ca. 20 nm, but the particles are closely packed without forming porous structures. In addition, the packed nanoparticles are covered with large TiO₂ discs with a thickness of ca. 20 nm and a diameter of several micrometers. As expected, the same sol-gel procedure without polymer additions (denoted as TiO₂(no-polymer)) yielded structureless cTiO₂ film (Figure 2c, 2f). These results corroborate the importance of additive polymer structures to assist the mesopore formation of TiO₂. PMMA has ester groups in the side chains, whereas PS consists of only hydrocarbon. The high polarity of the esters may improve the miscibility with titanium reagents and induce the meso-sized phase separation. It should be noted here that the wide-angle X-ray

diffraction (XRD) pattern indicated the formation of the crystalline anatase TiO₂ phase on FTO/cTiO₂ after calcination in all samples prepared by the sol-gel methods.

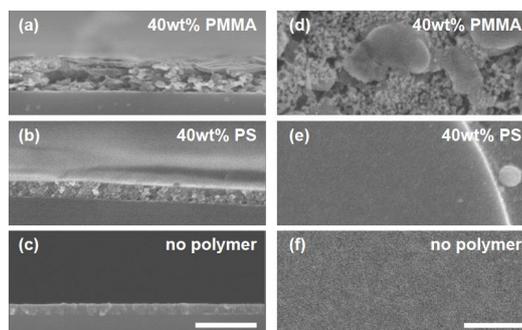


Figure 2. (a-c) Side and (d-f) top SEM images of (a,d) TiO₂(40wt%-PMMA), (b,e) TiO₂(40wt%-PS), and (c,f) TiO₂(no-polymer) on silicon wafers. Scale bars, 300 nm.

4 . 研究成果

We measured current density (J)-voltage (V) characteristics of the perovskite solar cells based on the TiO₂ films made by the sol-gel technique as well as by the conventional method using TiO₂ nanoparticle paste (denoted as TiO₂(nanoparticle)). Figure 3a depicts J - V curves of the best performing devices, and the best and average values of photovoltaic parameters made under the same conditions are summarized in Table 1. The important observation from the J - V curves is the significant improvement of the photovoltaic performance of the TiO₂(40wt%-PMMA)-based device (PCE=12.6%) relative to that of TiO₂(nanoparticle)-based one (PCE=10.8%). All the photovoltaic parameters, short-circuit current density (J_{sc} , 18.6 mA cm⁻²), open-circuit voltage (V_{oc} , 0.959 V), fill factor (FF, 0.705), of the TiO₂(40wt%-PMMA)-based device are higher than those of the TiO₂(nanoparticle)-based one (J_{sc} = 17.7 mA cm⁻², V_{oc} = 0.919 V, FF = 0.665). To confirm the enhancement of the photocurrent, we recorded incident photon-to-current efficiency (IPCE) spectra, as illustrated in Figure 2b. Overall IPCE values of the device with TiO₂(40wt%-PMMA) are higher than those with TiO₂(nanoparticle), and the shapes of both spectra reflected the absorbance of the perovskite layer. The convolution of the spectral response with the photon flux of the AM 1.5G spectrum provided the

estimated J_{SC} values of 17.7 mA cm^{-2} and 16.4 mA cm^{-2} , respectively, which are in good agreement with the corresponding measured values. On the other hand, it is not surprising that the devices based on $\text{TiO}_2(40\text{wt}\%-\text{PS})$ and $\text{TiO}_2(\text{no-polymer})$ revealed much lower photovoltaic performances with PCE values of 5.28 and 4.51%, respectively, and lower IPCE values (Figure 3b) due to the incomplete formation of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$.

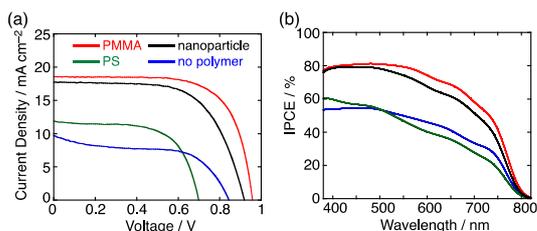


Figure 3. (a) Current density–voltage curves and (b) IPCE spectra of the best-performing solar cells based on $\text{TiO}_2(40\text{wt}\%-\text{PMMA})$ (red line), $\text{TiO}_2(40\text{wt}\%-\text{PS})$ (green line), $\text{TiO}_2(\text{no-polymer})$ (blue line), and $\text{TiO}_2(\text{nanoparticle})$ (black line).

In summary, we have established a unique methodology to obtain mesoporous TiO_2 electrode layers. The electrodes layer were prepared by a facile sol–gel technique loading a general polymer PMMA as a templating agent. Pore morphologies were controllable by varying the amount of PMMA and it was noted that the choice of polymer, based on its interactions with the sol–gel components can be critical.

Such electrode surfaces have application in energy storage as well as perovskite and dye-sensitized solar cells. The perovskite solar cells based on PMMA-mediated mesoporous TiO_2 achieved a PCE of 12.6%, which is 2.8 times higher than that using TiO_2 layer prepared without polymer addition (4.51%). Remarkably, it was superior to the conventional device with mesoporous TiO_2 prepared with nanoparticle paste (10.8%). The appropriate pore size and structure with no clear boundary may enhance the performance of the device with PMMA-mediated mesoporous TiO_2 . We believe that the mesostructure-tuned TiO_2 layers made by the facile sol–gel technique with a simple polymer additive has the great potential to contribute significantly toward the development of low-cost perovskite solar cells.

Although we had considerable success in the development of the TiO_2 mesoporous structures, the main success was in the application of these structures in the use for light harvesting TiO_2 electrodes. That research result is described here, though we continue our efforts to develop the materials for supercapacitor applications. A further difficulty in extending such metal oxide layers to energy storage electrodes is a requirement for thickness mesoporous layers; this also leads to cracking phenomena, and this is presently the challenge to developing that application.

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

〔雑誌論文〕(計1件)

Yue Y., Umeyama T., Kohara Y., Kashio H., Itoh M., Ito S., Sivaniah E., Imahori H. Polymer-Assisted Construction of Mesoporous TiO_2 Layers for Improving Perovskite Solar Cell Performance, 査読有, J.Phys.Chem.C, 119, 22847-22854 (2015), DOI 10.1021/acs.jpcc.5b07950

〔学会発表〕(計0件)

〔図書〕(計0件)

〔産業財産権〕

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取得状況 (計0件) Status of above

〔その他〕

ホームページ等

6. 研究組織

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