University of Groningen

Facile Fabrication, Structures, and Properties of Laser-Marked Polyacrylamide/Bi₂O₃ Hydrogels

Cao, Zheng; Hu, Yanchao; Yu, Qiang; Lu, Ying; Wu, Dun; Zhou, An; Ma, Wenzhong; Xia, Yanping; Liu, Chunlin; Loos, Katja

Published in:
Advanced materials

DOI:
[10.1002/adem.201600826](https://doi.org/10.1002/adem.201600826)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Cao, Z., Hu, Y., Yu, Q., Lu, Y., Wu, D., Zhou, A., Ma, W., Xia, Y., Liu, C., & Loos, K. (2017). Facile Fabrication, Structures, and Properties of Laser-Marked Polyacrylamide/Bi₂O₃ Hydrogels. *Advanced materials*, 19(5), [1600826]. <https://doi.org/10.1002/adem.201600826>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

DOI: 10.1002/adem.201600826

Facile Fabrication, Structures, and Properties of Laser-Marked Polyacrylamide/Bi₂O₃ Hydrogels**

By Zheng Cao, Yanchao Hu, Qiang Yu, Ying Lu, Dun Wu, An Zhou, Wenzhong Ma, Yanping Xia, Chunlin Liu* and Katja Loos

Laser marking of wet and soft polyacrylamide/bismuth oxide (PAM/Bi₂O₃) hydrogel materials can be achieved by simply embedding Bi₂O₃ particles inside PAM hydrogels and a subsequent laser treatment with a Nd: YAG laser beam at 1064 nm. In comparison with the pure hydrogel, the marking properties of the laser-marked PAM/Bi₂O₃ hydrogel samples vary as the Bi₂O₃ content increase from 0.17 to 3.0 wt% and as the laser power increase from 23.5 to 47.0 W. SEM, XPS, XRD, TGA, Raman spectroscopy, water contact angle and mechanical property tests are performed to characterize the laser-marked PAM/Bi₂O₃ hydrogels. The results herein indicate that the marking contrast and visual appearance on the surface of the PAM/Bi₂O₃ hydrogels after laser irradiation are mainly due to the decomposition of Bi₂O₃ to black bismuth metal.

1. Introduction

Hydrogels are three-dimensional network structures that have widely been used as scaffolds for tissue engineering,^[1] optics,^[2] microenvironments for cells,^[3] and drug delivery systems^[4,5] due to their hydrophilicity, biocompatible nature, responsiveness to environmental stimuli (e.g., pH, temperature, and ionic strength),^[6–11] and high water content. Recently, functional microstructures, patterns, and morphologies on the surface of hydrogels have become increasingly

important due to their diverse applications in nanotechnology,^[12] hydrogel electronics and devices,^[13] scaffolds for cell cultures,^[14,15] and microfluidic chips.^[16] Although the microstructures, configurations, and chemical and physical properties of patterned hydrogels have been extensively investigated, little attention has been paid to the marking and identification of these highly hydrophilic and soft materials. Identifying marks on hydrogel materials have proven to be useful for indicating serial numbers, production dates, and company logos. For specific applications, such as contact lenses and other commercial hydrogel products, identifying marks can also be used for recognizing the orientation with respect to the eye, the top or the bottom, or the back or the front surface of the product.

The commonly used methods for marking hydrogels are based on cutting and etching with symbols or letters. However, the etching or cutting methods for marking hydrogels usually involve damage to the surface, which results in poor performance in practical applications. Another proposed way is to use patterned metal or plastic inserts that can be transferred to the hydrogel surfaces during processing.^[17,18] However, these metal inserts are first marked with symbols and letters, which makes this method rather complicated and less flexible. In particular, the marks, including symbols and letters, are of low contrast and have poor visibility due to the excellent optical transparency of the hydrogel materials. Therefore, a versatile and facile method that is capable of making damage-free, high quality and high-contrast markings on the surfaces of hydrogels is still in high demand.

[*] Prof. C. Liu, Dr. Z. Cao, Y. Hu, Prof. Q. Yu, Y. Lu, D. Wu, A. Zhou, Dr. W. Ma, Y. Xia

School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, China

E-mail: chunlin301@hotmail.com

Prof. K. Loos

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

[**] Financial support provided for this project by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) is gratefully acknowledged. This work is also supported by the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 16KJB150003) and the Research Project of Changzhou University Science and Technology Plan (Grant No. ZMF15020064). (Supporting Information is available from Wiley Online Library or from the author).

The application of laser beams has been extensively reported in the hydrogel field, mainly including laser-ignited frontal polymerization,^[19] periodic patterning by laser lithography,^[20] and laser patterning of regular vertical pore arrays.^[21] To the best of our knowledge, few studies have been performed to demonstrate the marking and identification of hydrogels by laser technology without significantly damaging the network structures. Laser marking is an ideal method for marking various materials, including plastics,^[22–24] metals,^[25] and ceramics,^[26,27] and it has received considerable attention due to its fast speed, excellent durability, high contrast and environmental-friendliness. Generally, the permanent and damage-free markings with discoloration on the material surface are the result of the photothermal conversion of laser-sensitive particles in the polymers and the subsequent carbonization of the surface polymer chains induced by the laser beam. By controlling the operating parameters of the laser beam, such as the scanning speed, current, beam spot size, and line width,^[28,29] the marking contrast and quality on the material surface can be easily tailored, while preventing undesired damage to the materials.

However, the application of laser marking in hydrogels is still limited due to three main challenges. First, unlike plastic resins, the high water content of hydrogels significantly reduces the heating effect of laser beams on the hydrogel surfaces. Second, hydrogels in their wet state are light in color or transparent to laser beams, or they undergo negligible surface changes, which makes it difficult or impossible to mark hydrogels after laser irradiation. Third, the lack of high char (carbon) residue in the hydrogel is not beneficial to the formation of black carbonized materials. To enable laser marking for hydrogels, the strategy of adding laser-sensitive pigments to hydrogels will help to address these challenges. Laser-sensitive pigments such as mica, bismuth oxide (Bi₂O₃) and titanium dioxide (TiO₂), which are often dispersed in the polymer matrix, can absorb the laser energy and locally heat up the surrounding polymer chains, leading to black carbonized materials that are used for the laser marking.^[24,30–32] This means that the laser energy absorption of laser-sensitive pigments would not be significantly influenced by the wet state and the transparency of the hydrogel, which is helpful for addressing the three above-mentioned challenges. Bi₂O₃, an important non-ferrous semiconductor material,^[33–36] is one of the most attractive laser-sensitive additives that are used to fill plastics. In a previous study, it has been reported that the reduction of Bi₂O₃ into black bismuth metal occurs, which contributes to the formation of black markings on the polymer surface, accompanied with the carbonization of the polymer chains.^[24] It can be supposed that the blackening of Bi₂O₃ after exposure to laser irradiation would be significant enough to enable laser marking of hydrogels. Therefore, the carbonization of polymer chains favored by the high char residue in the hydrogel structure is not necessarily required to produce black marks. To the best of our knowledge, the details regarding the preparation and laser-marking properties of the hydrophilic and soft hydrogels with Bi₂O₃ additives have not yet been

reported in literature. A better understanding of the laser-marking process in hydrogels embedded with Bi₂O₃ and its optimization is essential for not only enhanced performance but also the extended utilization of hydrogel materials.

In the current study, Bi₂O₃ was used as a laser-marking additive to produce laser markings on commonly used polyacrylamide (PAM) hydrogels. PAM/Bi₂O₃ composite hydrogels were prepared by dispersing Bi₂O₃ in monomer solutions and then initiating the polymerization and cross-linking of AM. The PAM/Bi₂O₃ hydrogels were marked in the air by scanning the hydrogels with a controlled neodymium-doped yttrium aluminum garnet (Nd: YAG) pulsed laser beam at 1064 nm. The laser-marking properties of the PAM/Bi₂O₃ hydrogel materials were studied under various marking conditions. The laser-marked hydrogels were characterized using optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermogravimetry analysis (TGA), Raman spectroscopy, water contact angle measurements, and mechanical property tests. Finally, a mechanism for the laser-induced darkening of the PAM/Bi₂O₃ hydrogels has been proposed.

2. Results and Discussion

2.1. Fabrication of PAM/Bi₂O₃ Hydrogels

Figure 1 shows a schematic illustration of the design of the PAM/Bi₂O₃ hydrogels for the laser-marking tests. The general idea behind the fabrication method is to embed the laser-sensitive Bi₂O₃ particles inside the network structures of the soft and wet PAM hydrogels, which can be further investigated for their laser-marking properties. A series of PAM/Bi₂O₃ hydrogel samples with different Bi₂O₃ contents ranging from 0.17 to 3.0 wt% was prepared in two steps: that is, Bi₂O₃ was firstly modified with hydrophilic and water-soluble PEG chains, and the free radical polymerization of the AM monomers and the cross-linking reaction of PAM chains were then performed in aqueous solution, using KPS as the

Fig. 1. Schematic representation of the developed process for the preparation of the laser-marked PAM/Bi₂O₃ hydrogels.

initiator, TEMED as the accelerator, MBA as the cross-linker and the modified Bi₂O₃ as the laser-sensitive additive (Figure 1a). While the PAM/Bi₂O₃ hydrogels were treated in the air by a controlled Nd: YAG pulsed laser beam, Bi₂O₃ can undergo a photothermal conversion on the surface layer, but the hydrogel matrix will maintain their three-dimensional network structure, which results in the formation of black identifying marks of “hydrogel” on the surface (Figure 1b). The effects of the Bi₂O₃ loading content and the laser operating parameters on the marking quality, and the structures and properties of the laser-marked surfaces were studied to achieve excellent laser-marking properties and unravel the laser-marking mechanism of the PAM/Bi₂O₃ hydrogels.

2.2. Laser Marking of PAM/Bi₂O₃ Hydrogels

Figure 2 shows the visual appearance of the PAM hydrogels, PAM/Bi₂O₃ hydrogels, and Bi₂O₃ powder pellet samples before and after the laser treatment. Compared to the transparent PAM hydrogels, the PAM/Bi₂O₃ hydrogels show an increasingly enhanced yellow color when the Bi₂O₃ content is increased from 0.17 to 3.0 wt% (Figure 2a). As shown in Figure 2b, the Bi₂O₃ underwent a photothermal conversion after exposure to the laser beam at a laser power of 23.5 W, leading to a black square mark against the yellow-colored Bi₂O₃ on the surface. Note that a software application was used to design and create various markings on the surface of the materials. In industry, using the photothermal conversion feature of the Bi₂O₃ particles and the local carbonization of the polymer matrix induced by the laser beam, the laser-marking properties of commercial plastics, which are less sensitive to laser beams, can be dramatically improved for identification and decorative applications. In our research, various amounts of Bi₂O₃ particles were embedded inside the PAM hydrogel by the in situ free radical polymerization of AM and the cross-linking reactions of the PAM chains to improve the laser-marking properties of hydrogels. Figure 2c shows the effects of the laser operating power and Bi₂O₃ loading content on the laser-marking quality of the PAM/Bi₂O₃ hydrogels. No laser darkening was observed on the pure PAM hydrogel surface due to the transparency of the PAM hydrogel. At a lower Bi₂O₃ content of 0.17 and 0.33% and the same laser power, the laser-induced diamond markings on the PAM/Bi₂O₃ hydrogel surface are rather vague and light black-colored, which is not suitable for marking a hydrogel. Upon increasing the Bi₂O₃ content from 0.67 to 3.0%, a deep black color and high marking contrast were obtained due to the increased density of Bi₂O₃ particles embedded inside the PAM network structure, which is sufficient to form the black markings. In addition, the marking contrast and quality on PAM/Bi₂O₃ hydrogels with the same Bi₂O₃ content (0.17 or 0.33%) are enhanced when the laser power is increased from 23.5 to 47.0 W. The higher the laser power is, the greater the laser energy absorption for the same amount of Bi₂O₃ particles per unit area of the hydrogels. At the higher laser power of 47.0 W, both the blackness and marking quality of the

Fig. 2. Experimental results showing the visual appearance of samples. (a) The visual appearance of the pure PAM hydrogel and a series of PAM/Bi₂O₃ hydrogels with different Bi₂O₃ contents ranging from 0.17 to 3.0%. The addition of Bi₂O₃ with a particle size of 80–200 nm leads to yellow-colored and homogeneous hydrogels, which are different from the transparent pure PAM hydrogel. (b) The visual appearance of the surfaces of the Bi₂O₃ powder-pressed pellets before (left) and after (right) laser marking. The black square mark against the yellow-colored Bi₂O₃ was obtained due to the photothermal reaction of Bi₂O₃ induced by the laser beam. (c) The visual appearance of the diamond marking on the surfaces of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ contents ranging from 0.17 to 3.0% under the laser powers of 23.5, 35.3, and 47.0 W. (d) The visual appearance of the QR code markings on the surfaces of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ contents ranging from 0.17 to 3.0% under the same laser operating power of 35.3 W. (e) The visual appearance of the markings for the “hydrogel” characters on the surfaces of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ contents ranging from 0.17 to 3.0% under the same laser operating power of 35.3 W.

PAM/Bi₂O₃-1.0% and PAM/Bi₂O₃-3.0% samples decreased due to the generation of water vapor, which accompanies the more vigorous photothermal reaction of Bi₂O₃. In the surface layer, the water surrounding the Bi₂O₃ particles can be heated up to form water vapor, which influences the final appearance of the hydrogel surface. The results confirmed that the marking quality of the PAM/Bi₂O₃ hydrogel was determined by the laser power and the loading content of Bi₂O₃. It can be concluded that the appropriate laser power for marking PAM/Bi₂O₃ hydrogels containing 1, 2, and 3% Bi₂O₃ is 35.3 W.

As is shown in Figure 2d and e, various markings including the quick response (QR) codes and the “hydrogel” letters were written on the surfaces of PAM/Bi₂O₃ hydrogels with different Bi₂O₃ loading contents in the range from 0.17 to 3.0 wt% after exposure to the pulsed laser beam at the same laser power of 35.3 W. The unmarked PAM/Bi₂O₃ hydrogel showed the yellow color due to the addition of the yellow Bi₂O₃ pigments. In Figure 2d and e, it was noticeable that the color of the PAM/Bi₂O₃ hydrogels was changed from yellow to green. Figure 2d and e were both obtained using the same digital camera under different viewing conditions including different background and different lighting. It was clear that Figure 2d was taken under the bright background when the hydrogels were placed on the top of the white paper. However, the Figure 2e was achieved under the dark background, when the hydrogels were put on the black desk. The use of two different viewing conditions contributed to the color change of the PAM/Bi₂O₃ hydrogels from yellow to green, but the laser markings of high contrast on the surface of the PAM/Bi₂O₃ hydrogels were still observed. Among all the hydrogel samples, the PAM/Bi₂O₃-1.0% and PAM/Bi₂O₃-2.0% hydrogels showed the clearest markings and highest marking quality. However, the QR codes on both sample surfaces are still not easily identified by the QR scanning software because of their insufficiently high marking resolution. On the other hand, the word “hydrogel” can be visibly recognized with the naked eyes, indicating the potential of this facile method in the identification and decorative applications of hydrogel products. The surfaces and cross sections of the PAM/Bi₂O₃ hydrogels containing 1.0 and 2.0% Bi₂O₃ were further analyzed to obtain details on the dispersion of Bi₂O₃ particles in the hydrogel networks and the black markings on the hydrogel surface.

2.3. Morphological Analysis of the Unmarked and Laser-Marked PAM/Bi₂O₃ Hydrogels

Figure 3a shows the cross sections of the PAM/Bi₂O₃ hydrogels containing 0.33, 0.67, 2.0, and 3.0% Bi₂O₃, which were obtained using a microscope before laser marking was performed. The transparency and smooth cross sections of the hydrogels can be observed for samples with 0.33 and 0.67% Bi₂O₃ in Figure 3a. For a higher Bi₂O₃ content of 3.0%, aggregates of yellow Bi₂O₃ particles can be found in the hydrogels, which results in inhomogeneous structures and a low marking quality of the PAM/Bi₂O₃-3% hydrogels. After

the laser treatment, black markings were formed on the surface of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ loading contents of 0.33, 0.67, 2.0, and 3.0. The Bi₂O₃ particles in the hydrogel surface layer absorb the laser energy and heat up the surrounding water molecules, which leads to the evaporation of water from the hydrogel structures and is accompanied with the darkening of the hydrogels. Hole structures on the hydrogel surface were, therefore, formed after the vigorous thermal chemical reactions, as shown in Figure 3b. In addition, the number of holes on the surfaces gradually increased as the Bi₂O₃ loading increases. Figure 3c shows the metalloscope image of the cross section of the laser-marked PAM/Bi₂O₃-1% hydrogel. The depth of penetration by laser marking was estimated to be $\approx 372.4 \mu\text{m}$, which is comparable to the depth value of $400 \mu\text{m}$ of the laser-induced darkening on the TPU/Bi₂O₃ composite surface reported in the literature.^[24] Figure 3d and e show the microscope images of the laser-marked surfaces of the PAM/Bi₂O₃-1% hydrogel in the wet and dry state (drying was conducted in the vacuum oven), respectively. The dark laser-marked area is different from the yellow-colored background of the unmarked area, indicating high marking contrast on the surface.

The morphological information on the surface and cross sections of smaller areas can be determined by SEM. Figure 3f and g show the morphologies of the surfaces and cross sections of the PAM/Bi₂O₃-1% hydrogels before and after laser marking. Note that the laser-marked hydrogels were freeze-dried to prevent the collapse of hydrogel structures after water removal. It can be clearly observed that the unmarked sample has a rather smooth and slightly flat surface without significant damage. Contrastingly, the laser-marked sample exhibits network structures with a number of small holes on the surfaces. Furthermore, large holes similar to “volcanic eruptions” were observed on the surfaces and cross sections of the laser-marked hydrogel samples, as shown in Figure 3g. The size of such holes was estimated to be in a range of 40 to $110 \mu\text{m}$. The hydrogel surface became slightly rough and inhomogeneous due to the photothermal reactions of Bi₂O₃ and the subsequent heat-induced water evaporation. Compared to the laser-influenced surface layer, the deeper layers inside the hydrogel remained unchanged after laser marking, which is in line with the results on the depth of penetration by laser marking obtained using the metalloscope. All the results for the PAM/Bi₂O₃ hydrogels confirm that the addition of laser-sensitive Bi₂O₃ particles enabled the laser marking and structural changes on only the surface of the hydrophilic and wet PAM hydrogel.

2.4. The Surface Compositions and Structures of the Laser-Marked PAM/Bi₂O₃ Hydrogel

The surface composition, structure, thermal stabilities, and mechanical properties of the laser-marked hydrogels are important properties for potential applications and were therefore studied. The PAM/Bi₂O₃-1% hydrogel was selected

Fig. 3. Morphological observations of the PAM/Bi₂O₃ hydrogels. (a) The cross sections of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ loading contents of 0.33, 0.67, 2.0, and 3.0% using a microscope before laser marking was performed (scale bar 100 μ m). (b) The surfaces of the PAM/Bi₂O₃ hydrogels with different Bi₂O₃ loading contents of 0.33, 0.67, 2.0, and 3.0% using a microscope after laser marking was performed (scale bar 100 μ m). The number of small black holes on the surfaces gradually increases as the Bi₂O₃ loading content increases. (c) Metalloscope image of the cross sections of the PAM/Bi₂O₃-1% hydrogel after laser marking. The depth of penetration by laser marking is approximately 372.4 μ m (scale bar 100 μ m). (d) Microscope image of the laser-marked and unmarked area on the surface of the PAM/Bi₂O₃-1% hydrogel (scale bar 100 μ m). (e) Metalloscope image of the laser-marked and unmarked surface of the PAM/Bi₂O₃-1% hydrogel after drying was conducted in the vacuum oven (scale bar 600 μ m). (f) The SEM images of the surface of the freeze-dried PAM/Bi₂O₃-1% hydrogel before laser marking (scale bar 50, 10, and 5 μ m). (g) The SEM images of the laser-marked surfaces and cross sections of the PAM/Bi₂O₃-1% hydrogel. The laser-marked hydrogel was freeze-dried before the SEM tests. The large holes appear similar to "volcanic eruptions" on the surfaces and cross sections of the laser-marked hydrogel sample (scale bar 50, 10, 500, and 50 μ m).

for the complete analysis. XPS spectra of the PAM/Bi₂O₃-1% hydrogel before and after laser marking at the laser power of 35.3 W are shown in Figure 4a. The unmarked and laser-marked PAM/Bi₂O₃-1% hydrogel samples both showed the expected carbon, oxygen, and nitrogen contents. The details of the XPS spectra of the C 1s and O 1s core level regions of the PAM/Bi₂O₃-1% hydrogel and the Bi 4f core level region of the Bi₂O₃ particles before and after laser marking can be found in the supporting information (Figure S1, Figure S2, and Table S2). Figure S2 clearly shows that there is no observable change in the XPS spectra of the Bi₂O₃ particles before and after the laser treatment. In addition, the XPS spectra of the laser marked and unmarked Bi₂O₃ powders both showed two similar peaks at around 164.2 and 158.9 eV, which were close to the standard values 166.0 and 158.8 eV of Bi 4f_{5/2} and Bi

4f_{7/2} for Bi₂O₃ obtained from the website of the National Institute of Standards and Technology (NIST). Note that the standard values of Bi 4f_{5/2} and Bi 4f_{7/2} for elemental Bi are found to be 162.3 and 157.0 eV. Compared to the unmarked PAM/Bi₂O₃-1% hydrogel, the laser-marked sample shows two stronger broad peaks at around 164.3 and 159.0 eV ranging from 166 to 156 eV; these correspond to the Bi 4f component (Figure 4b). In addition, the elemental compositions of the surfaces, which are calculated from the XPS spectra, are listed in Table 1. The carbon content of the PAM/Bi₂O₃-1% hydrogel decreased from 74.59 to 72.83% after laser marking. However, the Bi content of the PAM/Bi₂O₃-1% hydrogel increased from 0.03 to 0.21% after laser marking. Generally, the Bi₂O₃ particles in the polymer matrix can absorb the laser energy and heat up, which locally carbonizes

Fig. 4. The properties and structures of the PAM/Bi₂O₃ hydrogels before and after laser marking. (a) High-resolution photoemission spectra of the PAM/Bi₂O₃-1% hydrogel before and after laser marking at the laser power of 35.3 W. (b) High-resolution photoemission spectra of the Bi 4f core level regions of the PAM/Bi₂O₃-1% hydrogel before and after laser marking at the laser power of 35.3 W. (c) X-ray diffraction patterns of the Bi₂O₃ powders in the 2θ range from 5° to 70° before and after laser marking at the laser power of 35.3 W. (d) X-ray diffraction patterns of the Bi₂O₃ powders in the 2θ range from 25° to 45° before and after laser marking at the laser power of 35.3 W. (e) X-ray diffraction patterns of the PAM/Bi₂O₃-1% hydrogels in the 2θ range from 5° to 70° before and after laser marking at the laser power of 35.3 W. (f) X-ray diffraction patterns of the PAM/Bi₂O₃-1% hydrogels in the 2θ range from 25° to 45° before and after laser marking at the laser power of 35.3 W.

the polymer matrix and leads to the formation of black markings. For the hydrogel system, in addition to the polymer chains, the water molecules were directly in contact with the Bi₂O₃ particles, and the molecules could be easily heated up and evaporated. The polymer pyrolysis and carbonization found in plastics were probably negligible in the high water

content and soft hydrogel system studied here. Poulia et al. reported the laser-induced reduction mechanisms of lead white pigments (basic lead carbonate, Pb(OH)₂PbCO₃),^[37] which was confirmed by XPS (the content of lead relative to oxygen increased after the laser treatment). They suggested that the formation of elemental lead on the surface led to the blackening of lead white after laser irradiation. In our research, although some changes could be observed in the XPS spectra of the laser marked and unmarked hydrogels, the results of XPS did not seem to provide sufficient evidence for the reduction of elemental bismuth. The possible mechanism of the laser marking on the surfaces of the PAM/Bi₂O₃-1% hydrogel should be verified in the following measurements.

XRD measurements were performed to study the structural changes in the Bi₂O₃ particles and PAM/Bi₂O₃ hydrogel before and after laser irradiation. Figure 4c shows X-ray diffraction patterns of the Bi₂O₃ powders in the 2θ range from 5° to 80° before and after laser marking at the laser power of 35.3 W. The unmarked Bi₂O₃ powders show four main reflections at approximately $2\theta = 27.8^\circ$, 31.6° – 32.7° , 45.9° – 48° , and 54° – 57.6° , which agree with the characteristics of Bi₂O₃ reported in literature.^[38] A zoom-in of the region between 25° and 45° is shown in Figure 4d. Compared to the unmarked Bi₂O₃ powders, the laser-marked Bi₂O₃ powders exhibit several new peaks at approximately $2\theta = 26.8^\circ$, 35.9° , and 37.5° , which are in agreement with the XRD characteristics of bismuth metal. Eom et al. found the same characteristic peaks in XRD patterns, which were attributed to Bi metal.^[38] Figure 4e and f show XRD patterns of the PAM/Bi₂O₃-1% hydrogels in the 2θ range from 5° to 70° and 25° to 45°, respectively, before and after laser marking at the laser power of 35.3 W. In

the spectrum of the unmarked PAM/Bi₂O₃ hydrogel, the characteristic peaks attributed to Bi₂O₃ can be found. In the spectra of the PAM/Bi₂O₃ hydrogel, besides the Bi₂O₃ peaks, new peaks appear at $\approx 27.0^\circ$ and 37.9° after laser irradiation; these correspond to the Bi metal. As the Bi₂O₃ content increased, both peaks intensified due to an increased amount of the produced Bi metal. Therefore, the mechanism for the laser-induced blackening of the PAM/Bi₂O₃ hydrogel is probably based on the formation of black Bi metal during laser irradiation. However, it is still necessary to determine if the polymer pyrolysis and carbonization caused by the thermal chemical reaction of Bi₂O₃ particles also contributed to the blackening of Bi₂O₃ hydrogels. TGA measurements were carried out to further explore the mechanism for the black markings.

Table 1. Characteristic XPS data for the PAM/Bi₂O₃ hydrogels before and after laser marking.

Samples	C 1s [%]	O 1s [%]	N 1s [%]	Bi 4f [%]
Before laser marking	74.59	21.22	4.16	0.03
After laser marking	72.83	22.49	4.48	0.21

Fig. 5. The structures and hydrophilic properties of the PAM/Bi₂O₃ hydrogel samples before and after laser treatment. (a) TGA and (b) DTG curves of the PAM/Bi₂O₃-1% hydrogel samples before and after laser marking. (c) Raman spectra of the Bi₂O₃ powder samples before and after laser marking. (d) Raman spectra of the PAM/Bi₂O₃ hydrogel samples before and after laser marking. (e) Water contact angles of the PAM hydrogels, the unmarked and laser-marked PAM/Bi₂O₃-1% hydrogels, and the unmarked and laser-marked PAM/Bi₂O₃-2% hydrogels (from left to right), which correspond to 28°, 40.5°, 63°, 52°, and 89.5°, respectively. The laser marking mentioned above for all samples was performed at the laser power of 35.3 W.

2.5. The Thermogravimetric and Raman Analysis, and Hydrophilic Properties of the PAM/Bi₂O₃ Hydrogel Samples before and after Laser Treatment

To verify the laser-induced pyrolysis of the PAM chains, the TGA and DTG curves (Figure 5a, b) of the PAM and PAM/Bi₂O₃-1% sample were measured in oxygen before and after laser marking at the laser power of 35.3 W. Note that the unmarked and laser-marked surface materials were obtained by cutting from the dry PAM/Bi₂O₃-1% hydrogel samples with a blade to test their thermal stability. Table 2 summarizes the characteristic TGA results of the PAM and PAM/Bi₂O₃-1% hydrogel samples before and after laser marking. In conjunction with the weight-loss temperatures recorded in Table 2, the PAM hydrogel sample showed a temperature for the five percent weight loss ($T_{5\%}$) and a temperature for the maximum decomposition rate ($T_{\max}$) at ≈ 112.9 and 415.4 °C, respectively. After Bi₂O₃ particles were embedded into the PAM networks, the $T_{5\%}$ and $T_{\max}$ of the PAM hydrogel both shifted to higher temperatures of ≈ 145.2 and 536.0 °C, respectively. This means that the addition of Bi₂O₃ can significantly improve the thermal stability of PAM hydrogels. However, the $T_{5\%}$ and $T_{\max}$ of the laser-marked PAM/Bi₂O₃-1.0% sample at the laser power of 35.3 W were found to be 124.1 and 520.5 °C, which were still higher than the above-mentioned values of the pure PAM hydrogel. The $T_{5\%}$ and $T_{\max}$ of the unmarked materials

were slightly higher than those of the laser-marked materials. This result indicates that the thermal stability of the PAM/Bi₂O₃-1.0% hydrogel decreased after laser marking, which is attributed to the previous pyrolysis of the surface PAM chains induced by laser irradiation, thus decreasing both the $T_{5\%}$ and $T_{\max}$ of the PAM hydrogel.

Raman spectroscopy can be used to determine the formation of the amorphous carbonized materials during the laser irradiation of plastics.^[24] In this research, Raman spectra of the Bi₂O₃ powder samples and the PAM/Bi₂O₃ hydrogels before and after laser marking are shown in Figure 5c and d, respectively. Note that the appearance of a broad diffusion band in the Raman spectral region from 1000 to 2000 cm^{-1} corresponds to the presence of amorphous carbon.^[39] The characteristic peaks of Bi₂O₃ at ≈ 310 and 426 cm^{-1} can be found in the spectrum of the unmarked Bi₂O₃ powder. After laser irradiation, there was almost no change observed in the spectrum of the laser-marked Bi₂O₃ powder; this is probably due to the production of only Bi metal, which is not Raman-active. The PAM/Bi₂O₃ hydrogels showed almost the same Raman spectra before and after laser marking, and they did not present the characteristic amorphous carbon peaks, indicating a low degree of polymer pyrolysis in the high water content and soft network structures. In the supporting information, Figure S3 shows the FT-IR spectra of the Bi₂O₃, laser-marked PAM/Bi₂O₃-1% hydrogel, unmarked PAM/Bi₂O₃-1% hydrogel, and PAM hydrogel materials. Figure S3 also shows that compared to the unmarked PAM/Bi₂O₃-1% hydrogel, the laser-marked sample showed similar absorption bands of the groups including -C-O and N-H from the PAM chains. This indicates that the laser marking of the high water content and soft PAM/Bi₂O₃ hydrogel produced a relatively small amount of oxygen-containing polar groups due to the pyrolysis of the polymer chains.

Water contact angles of the PAM hydrogels, the unmarked and laser-marked PAM/Bi₂O₃-1% hydrogels, and the unmarked and laser-marked PAM/Bi₂O₃-2% hydrogels, which correspond to 28°, 40.5°, 63°, 52°, and 89.5°, respectively, are shown in Figure 5e. Compared to the PAM hydrogel, it is observed that the PAM/Bi₂O₃ hydrogel shows a more

Table 2. Characteristic TGA data of the pure PAM and PAM/Bi₂O₃ hydrogels before and after laser marking.

Samples	$T_{5\%}$ [°C]	$T_{\max}$ [°C]
PAM hydrogel	112.9	415.4
PAM/Bi ₂ O ₃ -1% before laser marking	145.2	536.0
PAM/Bi ₂ O ₃ -1% after laser marking	124.1	520.5

hydrophobic surface. In addition, the laser-marked surface is more hydrophobic than the unmarked surface. The change in the surface properties is mainly due to the formation of a number of small holes on the laser-marked surface and the production of Bi metal on the surface layer. Our explanation is supported by the results reported by Tang et al.^[40] They developed a facile laser-marking method for fabricating a superhydrophobic surface on an aluminum alloy. Their results showed that the formation of a rough surface with irregular protrusions induced by laser irradiation contributed significantly to the generation of excellent superhydrophobicity.

All results for the PAM and PAM/Bi₂O₃ hydrogels confirmed that the addition of the laser-sensitive Bi₂O₃ particles enabled excellent laser marking properties for high water content, soft and transparent PAM hydrogels. The mechanism for the laser-induced blackening of the PAM/Bi₂O₃ hydrogels is based on the formation of elemental black Bi metal on the surfaces. The pyrolysis of the polymer chains in the network was confirmed, but it is unlikely that the carbonized material is produced due to the high water content in the network structures, which does not contribute to the formation of laser-induced darkening on the hydrogel surface. For practical applications of PAM/Bi₂O₃ hydrogels, their mechanical properties and swelling property need to be investigated.

2.6. The Mechanical and Swelling Properties of PAM and PAM/Bi₂O₃ Hydrogels

Figure 6a and b shows compression property tests and the compression stress–strain curves of the PAM and PAM/Bi₂O₃ hydrogels. The representative stress–strain curves show that the maximum stress of the PAM hydrogel was approximately 0.12 MPa. After embedding 1% and 2% Bi₂O₃ inside the network structures, the maximum stress increased from 0.12 to 0.20 MPa and 0.15 MPa, respectively. From the viewpoint of the molecular chain movement, Bi₂O₃ can be used as reinforcement to improve the rigidity and strength of the PAM hydrogels by blocking the movement of polymer chains, which is the primary enhancement mechanism of inorganic particle-filled polymer composites. However, the PAM/Bi₂O₃ hydrogel with 2% Bi₂O₃ exhibits a lower compression stress than the PAM/Bi₂O₃ hydrogel with 1% Bi₂O₃. This means that a high content of Bi₂O₃ in the PAM hydrogels leads to an inhomogeneous network structure and a decrease in the compression stress. In addition, the swelling properties of PAM and PAM/Bi₂O₃ hydrogels as a function of time are shown in Figure 6c. It can be observed that the swelling ratio of the PAM and PAM/Bi₂O₃ hydrogels first increased rapidly and then gradually reached a value of ≈600%. Compared to the PAM hydrogel, the PAM/Bi₂O₃ hydrogels did not show large changes in their swelling property.

Fig. 6. The mechanical and swelling properties of PAM and PAM/Bi₂O₃ hydrogels. (a) Illustration of the compression property test for the hydrogels. (b) The results of the compression stress–strain curves of the PAM and PAM/Bi₂O₃ hydrogels. The strain is defined as the ratio of the change in the length along the direction of load to the original length of the specimen. (c) The swelling property of the PAM and PAM/Bi₂O₃ hydrogels as a function of time.

3. Conclusion

Laser marking of wet and soft PAM/Bi₂O₃ hydrogel materials can be achieved by simply embedding Bi₂O₃ particles inside PAM hydrogels and a subsequent laser treatment without damaging the three-dimensional structures of the hydrogels. The marking properties of the PAM/Bi₂O₃ hydrogel materials were determined by the loading content of the Bi₂O₃ particles embedded inside the PAM network structures and the laser power employed. The optimum conditions for laser marking of PAM/Bi₂O₃ hydrogels are a Bi₂O₃ content of 1 and 2% and a laser power of 35.3 W. The Bi₂O₃ particles dispersed in the surface layer of the PAM hydrogels can absorb the laser energy and heat up the surrounding water molecules, which result in the decomposition of Bi₂O₃ to black bismuth metal and water evaporation from the hydrogel, respectively. Both factors contribute to the formation of the black marking and the visual appearance of the surface of the PAM/Bi₂O₃ hydrogels after laser irradiation. The laser marking on the surface does not influence the inner structures of the hydrogels. A slight polymer pyrolysis can be observed after the laser treatment; this has a limited effect on the laser marking properties of the hydrogels. The laser treatment of PAM/Bi₂O₃ hydrogels can lead to the generation of relatively hydrophobic surfaces, depending on the Bi₂O₃ loading content. The embedding of Bi₂O₃ particles as reinforcements inside the PAM network structures can significantly improve the thermal stability and enable the enhancement of the rigidity and strength of the PAM hydrogels. The facile method of embedding laser-sensitive particles inside three-dimensional networks is very promising for applications that involve the marking and decoration of soft and wet hydrogel products.

4. Experimental Section

4.1. Chemicals and Materials

Acrylamide (AM, 98%) and polyethylene glycol (PEG, $M_w = 1500$) are commercial products of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Analytical grade bismuth oxide (Bi₂O₃) with a particle size of 80–200 nm was purchased from Alfa Aesar, Thermo Fisher Scientific Inc., Shanghai, China. *N*, *N'*-Methylene-bis-acrylamide (MBA), *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TEMED), and potassium persulfate (K₂S₂O₈, KPS) were purchased from J&K Chemical Ltd. (Shanghai, China) and used as received. Deionized water purified by a Millipore Milli-Q system was used in all experiments.

4.2. Preparation of Bi₂O₃ suspension

A total of 0.6 g of PEG was dissolved in 30 ml of deionized water to obtain a transparent aqueous solution. 5, 10, 20, 30, 60, and 90 mg of Bi₂O₃ were added to 5 ml of the PEG solution mentioned above, and the mixture was stirred until a homogeneous and uniform Bi₂O₃ suspension in aqueous solution was obtained. During this process, the addition of PEG can help to improve the dispersion of Bi₂O₃ in water by the physical adsorption of hydrophilic and water-soluble PEG chains onto Bi₂O₃ particles.

4.3. Preparation of PAM/Bi₂O₃ Hydrogel Samples

A series of PAM/Bi₂O₃ hydrogels were prepared by the in situ free radical polymerization of AM in the presence of Bi₂O₃. Three gram of the monomer AM, 0.06 g of the cross-linker MBA, and 2 ml of the KPS aqueous solution with a concentration of 25 mg ml⁻¹ were added into 5 ml of the Bi₂O₃ suspension in a glass circular cylinder tube under stirring. The mixture was sonicated for 2 min, and oxygen was eliminated by bubbling nitrogen through the mixture for 5 min. After 75 μ L of the TEMED accelerator was added to the mixture, the reaction was carried out at room temperature for at least 6 h. After the reaction, the hydrogel samples were submerged in water and swollen sufficiently to remove unreacted monomers and other small molecules. By controlling the loading content of the Bi₂O₃ added, a series of PAM/Bi₂O₃ hydrogels was prepared. Finally, cylinder-shaped hydrogel samples with dimensions of 20 mm in diameter and 25 mm in height were obtained. The samples obtained were labelled with the code "PAM/Bi₂O₃-Bi₂O₃ content" (i.e., "PAM/Bi₂O₃-1%" refers to PAM/Bi₂O₃ hydrogels containing 1 wt% Bi₂O₃). The details of the formulation for preparing PAM/Bi₂O₃ hydrogels with various Bi₂O₃ contents are listed in the Table S1 of the supporting information.

4.4. Instruments and Characterization

Laser-marking experiments of the wet and soft hydrogels were carried out on a beam-controlled Nd: YAG laser-marking machine (KDD-50, Suzhou KiTe laser technology, China) equipped with the EZCAD 2.7.0 software. The focal length and spot size of the laser beam were fixed at 219 mm and 100 μ m, respectively. The laser scanning speed was set to 450 mm/s, and the pulse repetition frequency was 3.88 kHz. The process of laser marking was performed in air by scanning the sample surface line by line with a Nd: YAG pulsed laser beam. The distance of the adjacent lines during laser-marking was 0.06 mm. The software was used to design and create various marking symbols and characters and tune the laser parameters, including the laser operating power. To study the effect of the laser operating current on the laser marking of hydrogels, the laser operating current was set to 10, 15, and 20 A, which correspond to the laser powers of 23.5, 35.3, and 47.0 W, respectively. The

laser-marked hydrogel surface materials were dried in a vacuum oven at 30 °C until they reached a constant weight prior to XPS, Raman, TGA, and XRD measurements.

XPS was employed to analyze the laser-marked surfaces of the PAM/Bi₂O₃ hydrogels by using an ESCALAB 250Xi spectrometer (Thermo Science and Technology) with a monochromatic Al-K α X-ray source ($h\nu = 1486.6$ eV).

The Raman spectra of the laser-marked surfaces of PAM/Bi₂O₃ hydrogels were obtained on a DXR laser Raman spectrometer (Thermo Science and Technology) with a laser wavelength of 780 nm, a laser power of 7 mW, and a slit width of 50 μ m.

Thermogravimetric analysis was performed on 4 mg laser-marked samples using a NETZSCH-TG 209 F1 (NETZSCH, Germany) thermogravimeter at 20 °C min⁻¹ from 30 to 600 °C under oxygen flow.

The XRD patterns were collected on a powder diffractometer (RINT2000, Rigaku) using Cu-K α X-rays with a wavelength of 1.54 Å as the radiation source. The dried hydrogel samples were scanned in a 2θ range from 5° to 70° at a scanning rate of 0.02° s⁻¹.

The morphologies and structures of the surfaces and cross sections of the hydrogel samples after laser marking were observed on a JEOL JSM-6010LA scanning electron microscope with an acceleration voltage of 15 kV. Prior to the SEM tests, the laser-marked hydrogel samples were freeze-dried to maintain the same structures as those for samples in the swollen and wet state. The morphology of the wet and soft hydrogels after laser marking was also examined on a metalloscope (ECLIPSE-LV150N, Nikon) and a stereomicroscope (Phoenix Technology Company).

Water contact angle measurements of the laser-marked surfaces of hydrogels were performed on a goniometer (JC2900D1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd, Shanghai, China). A MilliQ water drop of 5 μ L was slowly and steadily placed on the laser-marked sample surface with a microsyringe. The contact angle was measured in air at room temperature within 30 s of the addition of water drop, and photographs were taken. The average contact angle from at least five different locations on each hydrogel surface was determined.

The mechanical test was conducted at room temperature using a universal testing machine (WDT-1000, Shenzhen Kai Li Test Instrument Co., China). For the compression tests, cylindrical samples of the as-prepared hydrogels were used, with dimensions of 20 mm in diameter and 25 mm in height. The hydrogel samples were compressed at a loading speed of 2 mm min⁻¹.

Swelling properties of PAM/Bi₂O₃ hydrogels were tested by immersing the as-prepared hydrogels in excess of deionized water at 25 °C for 3 days till the swelling equilibrium was reached. During this period, the weights of the swollen sample were determined as a function of time. The swollen samples were then dried in a vacuum oven at 30 °C until a constant weight was obtained. The swelling ratio (Q) was evaluated using $Q = W_s/W_d$, where W_s and W_d are the weights of the swollen sample and the corresponding dried sample, respectively.

Article first published online: February 08, 2017

Manuscript Revised: January 24, 2017

Manuscript Received: December 7, 2016

- [1] R. Langer, D. A. Tirrell, *Nature* **2004**, 428, 487.
- [2] M. Choi, J. W. Choi, S. Kim, S. Nizamoglu, S. K. Hahn, S. H. Yun, *Nat. Photonics* **2013**, 7, 987.
- [3] M. P. Lutolf, J. A. Hubbell, *Nat. Biotechnol.* **2005**, 23, 47.

- [4] A. S. Hoffman, *Adv. Drug Delivery Rev.* **2002**, 54, 3.
- [5] G. Jalani, R. Naccache, D. H. Rosenzweig, L. Haglund, F. Vetrone, M. Cerruti, *J. Am. Chem. Soc.* **2016**, 138, 1078.
- [6] R. H. Pelton, P. Chibante, *Colloids Surf.* **1986**, 20, 247.
- [7] D. Kuckling, C. D. Vo, S. E. Wohlrab, *Langmuir* **2002**, 18, 4263.
- [8] Z. Cao, B. Du, T. Chen, J. Nie, J. Xu, Z. Fan, *Langmuir* **2008**, 24, 12771.
- [9] B. R. Saunders, B. Vincent, *Adv. Colloid Interface Sci.* **1999**, 80, 1.
- [10] J. Kim, S. Nayak, L. A. Lyon, *J. Am. Chem. Soc.* **2005**, 127, 9588.
- [11] M. Pandeewar, S. P. Senanayak, K. S. Narayan, T. Govindaraju, *J. Am. Chem. Soc.* **2016**, 138, 8259.
- [12] N. A. Peppas, J. Z. Hilt, A. Khademhosseini, R. Langer, *Adv. Mater.* **2006**, 18, 1345.
- [13] S. Lin, H. Yuk, T. Zhang, G. A. Parada, H. Koo, C. Yu, X. Zhao, *Adv. Mater.* **2016**, 28, 4497.
- [14] J. N. Hanson Shepherd, S. T. Parker, R. F. Shepherd, M. U. Gillette, J. A. Lewis, R. G. Nuzzo, *Adv. Funct. Mater.* **2011**, 21, 47.
- [15] K. M. C. Tsang, N. Annabi, F. Ercole, K. Zhou, D. J. Karst, F. Li, J. M. Haynes, R. A. Evans, H. Thissen, A. Khademhosseini, J. S. Forsythe, *Adv. Funct. Mater.* **2015**, 25, 977.
- [16] G. M. Whitesides, *Nature* **2006**, 442, 368.
- [17] W. E. Williams, M. A. Duarte, Marking of mold inserts to produce marked contact lenses, US5641437, **1997**. <http://patft.uspto.gov/netacgi/nph-Parser?Sect2=PTO1&Sect2=HITOFF&p=1&u=/netahtml/PTO/search-bool.html&r=1&f=G&l=50&d=PALL&RefSrch=yes&Query=PN/5641437>
- [18] G. L. Wickes, K. L. Opdyke, W. J. Appleton, J. M. Vandewinckel, Method of making plastic molds for molding contact lenses, US5456864, **1995**. <http://patft.uspto.gov/netacgi/nph-Parser?Sect2=PTO1&Sect2=HITOFF&p=1&u=/netahtml/PTO/search-bool.html&r=1&f=G&l=50&d=PALL&RefSrc h=yes&Query=PN/5456864>
- [19] Z.-F. Zhou, C. Yu, X.-Q. Wang, W.-Q. Tang, C.-F. Wang, S. Chen, *J. Mater. Chem. A* **2013**, 1, 7326.
- [20] A. F. Lasagni, D. Yuan, P. Shao, S. Das, *Adv. Eng. Mater.* **2009**, 11, B20.
- [21] W. Jing, Y. Chunxi, W. Yizao, L. Honglin, H. Fang, D. Kerong, H. Yuan, *Soft Mater.* **2013**, 11, 173.
- [22] J. Zhang, T. Zhou, L. Wen, J. Zhao, A. Zhang, *ACS Appl. Mater. Interfaces* **2016**, 8, 1977.
- [23] Z. Cao, Y. Lu, C. Zhang, D. Wu, Y. Hu, Q. Zhang, G. Liu, A. Shi, C. Liu, *J. Changzhou Univ. Nat. Sci. Ed.* **2016**, 28, 7.
- [24] W. Zhong, Z. Cao, P. Qiu, D. Wu, C. Liu, H. Li, H. Zhu, *ACS Appl. Mater. Interfaces* **2015**, 7, 24142.
- [25] E. H. Amara, F. Haïd, A. Noukaz, *Appl. Surf. Sci.* **2015**, 351, 1.
- [26] J. Penide, F. Quintero, A. Riveiro, A. Fernández, J. D. Val, R. Comesaña, F. Lusquiños, J. Pou, *Appl. Surf. Sci.* **2015**, 336, 118.
- [27] L. E. Khoong, Y. C. Lam, H. Y. Zheng, X. Chen, *J. Appl. Phys.* **2010**, 107.
- [28] Y. M. Noor, S. C. Tam, L. E. N. Lim, S. Jana, *J. Mater. Process. Technol.* **1994**, 42.
- [29] A. Pérez Del Pino, P. Serra, J. L. Morenza, *Appl. Surf. Sci.* **2002**, 197–198, 887.
- [30] M. Oujja, M. Sanz, E. Rebollar, J. F. Marco, C. Domingo, P. Pouli, S. Kogou, C. Fotakis, M. Castillejo, *Spectrochim. Acta Part A* **2013**, 102, 7.
- [31] H. Zheng, G. C. Lim, *Opt. Lasers Eng.* **2004**, 41, 791.
- [32] H. Y. Zheng, D. Rosseinsky, G. C. Lim, *Appl. Surf. Sci.* **2005**, 245, 191.
- [33] S. Sanna, V. Esposito, C. Graves, J. Hjelm, J. W. Andreasen, N. Pryds, *Solid State Ionics* **2014**, 266, 13.
- [34] L. Leontie, M. Caraman, M. Delibas, G. I. Rusu, *Mater. Res. Bull.* **2001**, 36, 1629.
- [35] Raghvendra, P. Singh, *J. Eur. Ceram. Soc.* **2015**, 35, 1485.
- [36] K. M. Davis, K. Miura, N. Sugimoto, K. Hirao, *Opt. Lett.* **1996**, 21, 1729.
- [37] P. Pouli, D. C. Emmony, C. E. Madden, I. Sutherland, *Appl. Surf. Sci.* **2001**, 173, 252.
- [38] J.-H. Eom, H.-J. Jung, J.-H. Han, J.-Y. Lee, S.-G. Yoon, *ECS J. Solid State Sci. Technol.* **2014**, 3, 315.
- [39] K. Itoh, I. Kudryashov, J. Yamagata, T. Nishizawa, M. Fujii, N. Osaka, *J. Phys. Chem. B* **2005**, 109, 271.
- [40] M.-K. Tang, X.-J. Huang, Z. Guo, J.-G. Yu, X.-W. Li, Q.-X. Zhang, *Colloids Surf. A* **2015**, 484, 449.