

Transfer of micro/nanostructured films by gel method

Yu Fu¹, Guoshuai Song¹, Yan Li¹, Yonghua Jiao², Sheng Yang², Tieqiang Wang¹, Haodong Shi¹, Yatao Tian¹

¹College of Sciences, Northeastern University, Shenyang 110819, People's Republic of China

²College of Life and Health Sciences, Northeastern University, Shenyang 110819, People's Republic of China

E-mail: fuyu@mail.neu.edu.cn

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A new method of transferring micro/nanostructured films using gel as a transfer carrier is developed, which could transfer the films from their parent substrates to a variety of surfaces, even onto the inner wall of some containers. The advantages of this method over a traditional transfer are the ease of processing and the potential for the alteration of the transfer conditions. Agarose was used as the gel carrier to transfer two types of electrochemically deposited gold films and chemically deposited silver films. Scanning electron microscopy characterisation showed that the morphology of the film underwent no noticeable changes after transfer. In addition, the gold film was transferred onto ELISA plates, where ELISA was performed. The results showed that the plate modified by the gold film had a higher sensitivity than the unmodified plate. This may be attributed to the micro/nanostructure of the gold film, which increased the surface area of the plate, enhancing the adsorption of the antibody. This study indicated that the use of gel as the transfer carrier was an effective manner in which to transfer two-dimensional micro/nanostructures: this could expand the range of applications for such films with considerable potential in the fields of analysis and biotechnology

1. Introduction: Research into micro/nanostructured film can provide not only models for basic science but also new components for high-performance devices. Thus, micro/nanostructured films have a wide range of pure and applied scientific application prospects which have attracted sustained attention [1]. So far, there have been a series of film preparation technologies used for the preparation of micro/nanofilms, such as self-assembly, LB technology, spin coating, electrochemical deposition, chemical solution deposition, physical vapour deposition, chemical vapour deposition etc. [2–10]. These methods have their own characteristics and advantages, but are also subjected to the influences and restrictions of various conditions. The preparation of the substrate (substratum) therein plays a pivotal role for the success of film preparation. On the one hand, the surface of the prepared substrate is directly involved in the formation of the film or even determines the nanostructure thereof [11]; on the other hand, because of the requirements of the various preparation technologies and their effects on the physical and chemical properties of the substrate, the substrate limits the range of application of the film and its preparation technologies to some extent. For example, film prepared by electrochemical deposition is only applicable to conductive substrates, and spin-coating requires smooth, flat substrate surfaces. Therefore, existing film preparation technology can be effectively extended by developing a technology that can transfer the micro/nanostructured film from the substrate to the surface of other kinds of materials and expand the likely application.

The most commonly used transfer carrier is polydimethylsiloxane (PDMS) – a kind of cross-linked polymer elastomer. Transfers with PDMS as the carrier are mainly used for preparing patterned surfaces [12]. The preparation process is indicated as follows: the patterned transferred object is first carried on the surface of the carrier through contact with the PDMS carrier. Then using the lower surface energy of PDMS, the patterned transferred object is transferred to the surface of the target through contact with the target surface. This contact transfer has strict requirements on the condition control during the process and also inevitably causes certain mechanical effects on the transferred object. Therefore, the morphology and structure of the transferred

object will be influenced and it may be attached to a certain amount of PDMS residue. Tape [13] and gold film [14] can also be used for transferring a surface pattern and micro/nanostructure. Unfortunately, they also face certain post-transfer problems, such as difficulty in removing the transfer tools, harsh removal conditions or residues on the surface. The aforementioned analysis suggests that, because of problems such as complexity of operation, and a tendency to damage the surface and properties of the transferred object. when used as transfer carriers, insoluble materials – such as PDMS and tape – are inapplicable to the transfer of nanostructured film [15]. On the contrary, these problems can be solved, to some extent, by using gel as the transfer carrier.

The network structure of the colloidal particles or polymers in the gel in its semi-solid state is elastic and rigid to some extent. However, in the case of temperature change, it converts from a sol to a gel. For example, agarose is soluble in water at 80°C or above; it converts into gel as the temperature decreases and forms a sol as the temperature rises. Using the convertibility of this gel between liquid and semi-solid states, this study developed a transfer method using agarose gel as the carrier. The process is shown in Fig. 1. Firstly, we prepared the high-temperature water sol of agarose and an agarose sol layer on the surface of the film by drop-coating; we then cut and peeled the film according to the size of the target substrate; subsequently, we attached the peeled film to the target surface; and finally, we removed the agarose layer by hot-water washing to complete the transfer. This transfer was simple and called for relatively mild conditions. Moreover, it imposed no requirements on the conditions or such as delicacy of operation, high temperature, corrosion or use of organic solvents; it also complied well, and was compatible with the shape and material of the target substrate. Therefore, it was applicable to various surfaces, including the inner walls of containers. The development of this method can help micro/nanostructured film overcome the limitations on substrate preparation and expand its applicability. Moreover, it provided new ideas for the creation of novel nanofilm materials (Fig. 2).

2. Results and discussion: Two micro/nanostructured films were selected as the transferring target in this study, including the gold

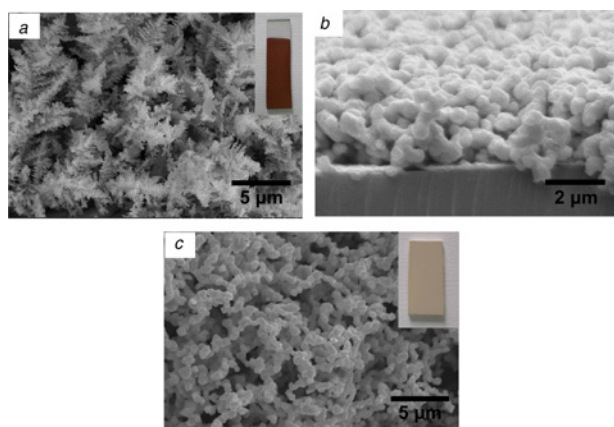


Figure 1 SEM images of the gold film (a) and the silver mirror films (cross-sectional view (b) and surface (c)). Insets show the Au and Ag films

film prepared by the electrochemical method [16] and the silver film prepared using the chemical solution deposition technique. The gold film was prepared on an indium tin oxide (ITO) surface modified by a multilayer film (assembled layer-by-layer using electrochemical deposition). Fig. 1a shows the surface morphology of the gold film: it uniformly covered the surface of the ITO. The gold particle length was of micron scale with nanometre branches and exhibited a coral-like three-dimensional structure.

The silver film was prepared on a glass sheet activated by SnCl_2 using a classical silver mirror reaction. It had two layers. The upper layer was a thick loose layer composed of silver particles, whereas the lower layer was a compact layer with a continuous structure and was close to the substrate, as shown in Fig. 1b. The scanning electron microscope (SEM) micrograph of the surface of the silver film (Fig. 1c) shows that the upper layer was aggregated by silver particles, resulting in a loose structure.

The agarose was used as the carrier to transfer the two micro/nanostructured films in this study. Agarose is a linear polymer extracted from red algae. It can form a water sol at a temperature of 80°C or above and develops into a semi-solid gel as the temperature decreases to between 35 and 40°C . It has typical gel properties and favourable biocompatibility. Fig. 1 shows the transfer process. Firstly, we prepared the agarose sol in hot water and dropped the sol onto the surface of the film before solidification. Because of the mobility of the sol, the gel molecules penetrated the micro/nanostructured film. After solidification of the gel, the gel layer and the micro/nanostructured film form a stable composite structure [17]. The composite film can be stripped from the substrate using tweezers or after cutting to fit the target substrate. Since we intended to conduct ELISA testing, the composite film was pressed and cut using an aluminium cylinder suited to the size of the ELISA plate. The cut-down composite film can be transferred into the

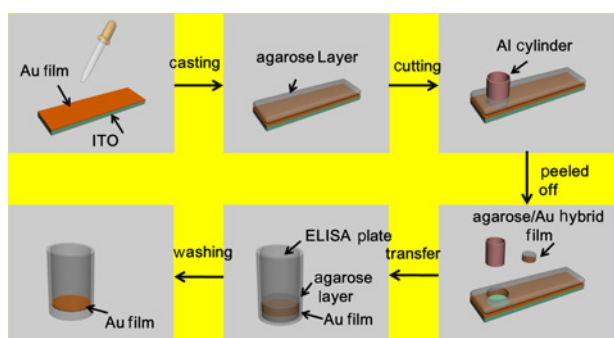


Figure 2 Gel transfer process

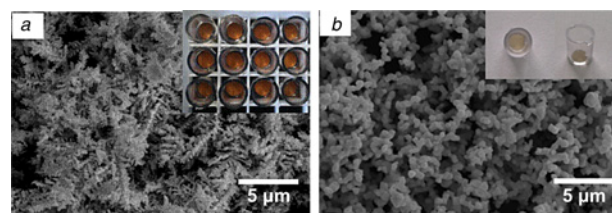


Figure 3 SEM images of the gold film (a) and the silver mirror film (b) after transfer. The insets are the pictures of the transferred films in plates

pores of the ELISA plate. With the assistance of water or ethyl alcohol, the composite was spread onto the bottom surface of the pores. With the slow volatilisation of the water or ethanol, the composite film adhered to the bottom surface of the pores. Finally, by washing the composite film in hot water, the agarose gel layer can be liquefied and removed to complete the transfer. To confirm whether or not the transfer process had adverse effects on the micro/nanostructure, the morphologies of the two transferred films were characterised by SEM, as shown in Fig. 3. The transferred microstructure of the gold film retained its original coral-like three-dimensional structure. The morphology of the silver film also showed no significant changes and retained its integrity. Meanwhile, the images also suggested that the macroscopic properties of the film remained continuous, uniform and free from damage. This showed that gel transfer technology using agarose was feasible and successful for the two micro/nanostructured films processed here. In addition, we also transferred the film to various target substrates, such as silicon, ceramics, metal etc. The results showed that micro/nanostructured films can be successfully transferred onto these materials and retain their structures intact before and after transfer.

Owing to its unique, coral-like micro/nanostructure, the gold film prepared by electrochemical method had potential applications in the fields of biological analysis, disease diagnosis etc. [18]. However, the further fusion of this method with biotechnology was thought to be restricted by the substrate preparation. This study was based on agarose transfer technology; its characteristics included a wide application range, favourable biocompatibility and mild operating conditions and it helped to extend the range of possible future uses of such gold film prepared by the electrochemical method.

To demonstrate the feasibility of this transfer method in a biology application, the ELISA plate, with its transferred gold micro/nanostructured film, was analysed. Fig. 4 shows the detection results. As the concentration of the pre-tested carcinoembryonic antigen (CEA) increased, the ELISA plates, modified or unmodified using gold film, both showed increased ultraviolet absorption in a favourably

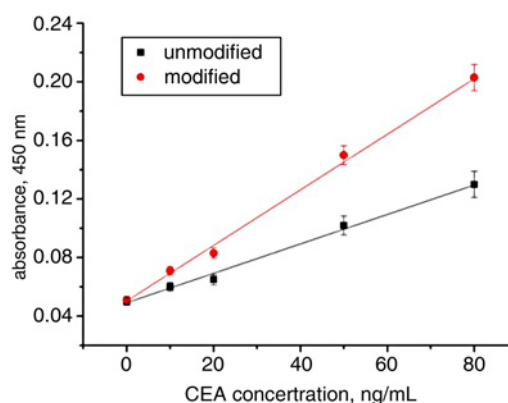


Figure 4 ELISA for CEA in carbonate buffer solution. Black square: gold film-modified plate; red circle normal plate ELISA signal

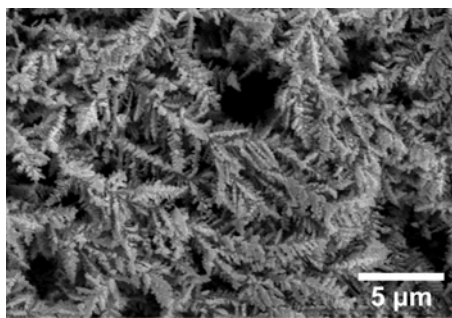


Figure 5 SEM image of the gold film after ELISA

linear relationship. The ELISA plate modified by gold film had a greater rate of ultraviolet absorption increase, which suggested that the ELISA detection results from the ELISA plate with its transferred golden film were superior to its unmodified counterpart. This advantage may be attributed to the fact that the micro/nanostructure of the gold film increased the internal surface area of the ELISA plate and the micro/nanostructure intensified the adsorption ability of the ELISA plate for protein. At the same time, the gold film detected using ELISA was examined by SEM, as shown in Fig. 5. The gold film after ELISA detection retained its original surface morphology and did not exhibit significant changes. This result indicated that the gold film obtained using the proposed agarose gel transfer method was stable and could be used in the field of biological detection.

3. Conclusion: Using agarose gel as a carrier, this study successfully transferred micro/nanostructured films prepared by the electrochemical method and solution deposition method onto the target substrate. Moreover, it detected the enhancement effect of the film on the post-transfer ELISA signal. This study offered a new and effective way in which to apply micro/nanostructured films and provided a new concept for the creation of novel nanostructured films, having great potential in the field of bioinstrumentation.

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