Synthesis of Nickel Ferrite Nanoparticles by Sol-Gel Method

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Nickel ferrite (NiFe₂O₄) is a well-known spinel magnetic material. Its preparation by the classical solid-state reactions requires a high calcination temperature and hence induces the sintering and aggregation of particles. In this work, NiFe₂O₄ nanoparticles were prepared by the sol-gel method using polyacrylic acid (PAA) as a chelating agent. Compared with the conventional method, this process showed good stoichiometric control and allowed the production of spinel NiFe₂O₄ powders at a relatively low temperature. It was shown that pure spinel NiFe₂O₄ nanoparticles with a diameter of 5~30 nm and a specific surface area of 20~55.2 m²/g could be produced by calcining the gel precursors with various molar ratios of PAA to total metal ions (0.5~2.0) in air at 300°C for 2h. As the molar ratio of PAA to total metal ions increased, particle sizes decreased but the crystallinity increased, revealing PAA not only worked as a chelating agent to disperse the cations homogeneously but also contributed its combustion heat to increase the crystallinity of NiFe₂O₄ nanoparticles. Moreover, the magnetic analysis showed the resultant NiFe₂O₄ nanoparticles were nearly superparamagnetic. Their saturation magnetization at 25°C (0.19 emu/mol) was slightly lower than that for bulk materials due to small size.

Fig. 1 Thermalgravimetric and differential thermal analyses of the gel.

The molar ratio of PAA to the total metal ions was 1.0. Almost no weight loss was observed in the temperature range of above 250°C, implying the formation of NiFe₂O₄.
Fig. 2 X-ray diffraction patterns for the particles calcined at 300°C (A) and 400°C (B).

The molar ratio of PAA to total metal ions = 0.5 (a), 1.0 (b), 1.5 (c), 2.0 (d). Except when the molar ratio of PAA to total metal ions was 0.5 at which a few impurity peaks were observed, the XRD pattern for each case showed all the characteristic peaks for a pure crystalline phase of nickel ferrite spinel, marked by their indices.
The molar ratio of PAA to total metal ions = 0.5 (a), 1.0 (b), 1.5 (c), 2.0 (d). Except when the molar ratio of PAA to total metal ions was 0.5, the crystallinity and diameters (5–20nm) of particles were similar and particle agglomeration was not serious.
The molar ratio of PAA to total metal ions for the gel precursor was 2.0 and the calcination temperature was 300°C. No significant hysteresis was observed, revealing the resultant NiFe2O4 nanoparticles were nearly superparamagnetic.
Nietzsche, Deleuze, and Nāgārjuna: Mapping the Dialectics of Will/Desire

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This paper aims to explore the correspondences between the dialectical analysis (the unique way of logical argumentation) of Nietzsche’s will and that of Deleuze’s desire—the discursive axis of two influential thinkers whose critiques of representation dominate the formation of postmodern theory and beyond. In addition, I make a comparative study of their dialectics and that of Nāgārjuna. The major Nietzschean/Deleuzean texts explored in this paper are some of those which foreground the everlasting deterritorialized movement of will (and its related themes—Overman and Eternal Recurrence) and desire: Nietzsche’s Thus Spoke Zarathustra and The Will to Power; and Deleuze’s Difference and Repetition, Nietzsche and Philosophy, Anti-Oedipus and A Thousand Plateaus. As for Nāgārjuna’s work, I choose to focus on his masterpiece and mostly valued one—Mūlamadhyamakakārikā (中論). The focus of this study is to attempt a mapping (characteristic of rhizomatics) of how their special dialectics of will/desire (Nihilism), without ever attempting to create another Absolute Truth, sets forth the non-totalizable multiplicities that characterizes the world of becoming.

On the other hand, many Nietzsche/Deleuze scholars, though recognizing the ontological implication of willing/desiring, just emphasize the positive forces of will and desire by which they call “politics” in the world of becoming. They fail to further explore the correspondences between Nietzsche’s and Deleuze’s special dialectical argumentation that is aimed at negating all reductive “philosophical trees” by employing ambiguous discourses that have multiple/contingent meanings, for reality is always becoming and multiple (e.g. Nietzsche’s nihilism). In other words, though recognizing both everyday existence and the categories by which humans comprehend it are self-contradictory and incoherent, paradoxically, Nietzsche and Deleuze adopt a dialectical analysis to challenge and highlight the absurdities of metaphysics and morality and all other Western modes of thinking. Yet, their dialectics—a philosophy of contradictions in which “opposing ideas are presented in agonistic competition with one another” (Martin 1991)—happens to create a dynamic form of philosophizing that serves to deconstruct both sides of every equation and to illuminate the arbitrary and mutable character of the concepts themselves.

Likewise, though Nāgārjuna (龍樹菩薩, an Indian philosopher and saint who founded the Buddhist school Madhyamika 中道, which holds a middle view of existence as voidness—no such thing as an intrinsic nature of all things) often refutes the validity of logic, most Buddhist scholars still considers his theoretical analysis as “dialectical” in a sense of “unique logical argumentation.” Above all, both the Nietzschean/Deleuzean nihilism and Nāgārjuna’s voidness/nihilism maintain that universal becoming is based on a principle of “relativity” (e.g. Nietzsche’s power shows the relations of forces). In Buddhist terminology, it is called “Dependent Origination,” which is functioning according to our volitional activities/willing (ignorance). In fact, both Nietzsche / Deleuze and Buddhism emphasize “the centrality of humans in a godless cosmos and neither looks to any external being or
power for their respective solutions to the problems of existence” (Loy 1998).
Functionalized 3D-Hydrogel Plugs Covalently Patterned Inside Hydrophilic Poly(dimethylsiloxane) Microchannels for Flow-Through Immunoassays

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Hydrogel has been widely applied in the field of medicine, separation, and biology for many years because of their well ordered fibrous structure, physical flexibility, and high water retaining ability. In addition, the functional groups on the hydrogel can be easily modified to immobilize various biomolecules for bioassays. With the aid of the native hydrophilic environment, protein activity can be retained for a longer period of time in the hydrogel compared to the surface-bound proteins. Such superior properties of the hydrogel have been used for making biosensors and enzyme reactors for affinity assays to capture proteins or cells. Under the restricted channel space, the mass transfer can be enhanced compared to the batch system and cross contamination can be avoided by multi-channel design. Integration of the hydrogel with microfluidic channels has also been attempted for fabricating functional elements such as valves and pH sensors as well as reactors or concentrators for protein analysis. PDMS-based microfluidic device can be fabricated via a simplified bonding process by treating plasma oxidization. Integration of a hydrogel and polydimethylsiloxane (PDMS)-based microfluidic device can greatly reduce the cost of developing channel-based devices. However, there are technical difficulties including the hydrophobic and inert surface properties associated with PDMS as well as back pressure and fragile material associated with the use of hydrogel in microchannels.

In our previous studies, we successfully developed a surface modification technique to create long-term hydrophilic layers on the PDMS surface by coating polyethyleneimine (PEI) and poly(acrylic acid) (PAA) in sequence and cross-linking to form polyelectrolyte multilayers (PEMS). In this study, we would like to take an advantage of such a long-term hydrophilic coating in making 3D hydrogel plugs within PDMS channels for bioassay development. Since polyacrylamide has a high porosity for biomolecules, it was chosen as the material in hydrogel formulation on the developed channel-based protein chip.

In this experiment, the photoinitiator (PI), benzophenone, was preincubated in the PEMS modified PDMS channel before photopolymerization as shown in scheme 1. Once penetrated into the bulk substrate, benzophenone can be retained in the hydrophobic PDMS inner layer. Therefore, photopolymerization can be initiated from the bulk substrate upon UV irradiation. Figure 2 shows the cross section fluorescence image of the hydrogel patterned inside the PDMS microchannel. The fluorescence was emitted from the PDMS in a depth of 20-30 μm after polymerization, supporting the fact that PI could penetrate into the substrate to form covalent bonding. While leaving open channels in the width around the hydrogel plug could allow the sample and the buffer to flow through with no back pressure. In addition, the long-term hydrophilicity and low nonspecific binding property associated with PEMS surface can be conserved for the nonpatterned area, leading to hydrogel plugs in extremely hydrophilic and permeable environment in a restricted channel space for bubble-free fluid transport and affinity interaction. Figure 3 shows the fluorescence image of three hydrogel plugs patterned in situ in a microfluidic channel. Since the shape and size of the 3D patterning is controlled by the microscope objective without a mask, the method is
straightforward, convenient, and applicable for most laboratories.

In order to capture the antigen through the antibody, a strategy to covalently photopattern 3D hydrogel plugs with functionalized protein G inside microfluidic channels on a hydrophilic PDMS substrate coated with polyelectrolyte multilayers (PEMS) is presented. Protein G is known to have a high binding affinity ranging from $10^9$ to $10^{10}$ M$^{-1}$ with many kinds of immunoglobulins, a well-oriented antibodies can be immobilized on the hydrogel plugs via protein G. The successful immobilization of protein G within the hydrogel was examined by chemiluminescence detection using a HRP-conjugated secondary antibody. As shown in figure 3c, strong chemiluminescence was clearly detected within the hydrogel with a very weak background from the rest of the channel area.

The developed protein chip was investigated for quantitative immunoassays in detecting ER$\alpha$. In order to capture ER$\alpha$ protein, the oriented monoclonal anti-ERR was bound to protein G immobilized in the hydrogel and Cy3-labeled E2 was applied as the fluorescence probe for quantitative immunoassays in detecting ERR. Figure 4 shows the fluorescence images of measured sample solution with sequence diluted concentration from 500 to 31.25 ng/mL and the calibration curve deduced from the detected signals can be fit into the linear equation: $y = 1.2351x + 27.914$ with $R^2 = 0.9794$. In addition, the relative standard deviations (RSD) were found to be less than 9.43% for repetitive measurements. To examine the accuracy of quantification using the constructed calibration curve, ERR (50 ng/mL) was spiked into bovine serum and detected by the channel-based protein chips containing protein G-immobilized hydrogel plugs. The concentration of the spiked sample was determined to be around 48.93 ng/mL based on the calibration equation shown in Figure 4, which gives about only 3% deviation from the exact amount (50 ng/mL) spiked, indicating a good accuracy for complicated samples.

The specificity of the signal detected for ER$\alpha$ was also investigated by competitive assays performed by co-incubating 30 M Cy3-E2 with various concentrations of nonlabeled E2 solutions ranging from $10^{-13}$ to 0 M. Results shown in Figure 4c indicate that the fluorescence intensity decreases with increasing the concentration of nonlabeled E2. There was virtually no signal detected when the E2 concentration was greater than $10^{-17}$ M due to a complete displacement of Cy3-E2 by E2. These results confirm that the signals detected are specific for ER$\alpha$, and the background nonspecific binding is minimal. These results confirms that integration of PDMS-based protein chip with long-term hydrophilic coating and functionalized hydrogel is suitable for quantitative analysis with high sensitivity and specificity.
Scheme 1. The fabrication scheme for protein G-immobilized hydrogel microfluidic protein chip. (a) The PDMS channel surface was coated with PEMS by layer by layer modification; (b) Absorption of PI into the PEMS-modified PDMS channel wall; (c) Protein G was covalently bonded to NPA molecules for copolymerization with the acrylamide/bisacrylamide. (d) The UV light emitted from the objective irradiates on the incubated precursor solution for in-situ synthesis of hydrogel beads in the PEMS-modified PDMS channel. (e) Hydrogel plugs were formed within three PDMS channels.

Figure 2. The fluorescence images acquired from the cross section of PDMS channel. (a) The photoinitiator-implanted PDMS microchannel before polymerization. (b) The polymerized hydrogel in the PDMS channel. The dotted line indicates the interface between channel and PDMS inner layer.

Figure 3. The CCD images of (a) the hydrogel plugs in the PDMS microfluidic channels; (b) the enlarged channel image of patterned hydrogel. (c) The chemiluminescence of protein G emitted from the hydrogel.
Figure 4. Immunoassay of ERα in the hydrogel plugs with immobilized anti-ERα. (a) Fluorescence images obtained from ERα solutions with different concentrations. (b) Calibration curve constructed from the measurements of (a). The error bar indicates the standard deviation for each measurement with n=3. (c) Competitive assays by co-incubating various concentrations (as indicated) of non-labeled E2 with 30 nM Cy3-E2 in each ERα-bound channel.
The similarities and diversities of signal pathways leading to consolidation of conditioning and consolidation of extinction of fear memory

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It has been shown that extinction of memory could be blocked by the NMDA receptor antagonists and MAPK kinase (MEK) inhibitors in the amygdala, as assessed by a fear-potentiated startle paradigm, and in the hippocampus, as measured with one-trial inhibitory avoidance task. In contrast, extinction of a conditioned taste aversion appeared not to depend on NMDA receptors and MAPK cascade in the insular cortex. Extinction of auditory fear memory was impaired in cannabinoid receptor 1-deficient mice or in protein phosphatase 1-inhibited mice. In the present study, we aimed to accomplish two goals: (1) to differentiate the signal cascades that underlie long-term behavioral changes between consolidation of conditioning and consolidation of extinction of fear memory; and (2) to construct the causal relationship among protein synthesis, calcineurin expression, CREB phosphorylation, and extinction of a learned response. Here, we show for the first time that an intra-amygdala injection of transcription inhibitor actinomycin D at the dose that blocked acquisition failed to affect extinction of a learned response. Conversely, protein synthesis inhibitor anisomycin blocked both acquisition and extinction. Extinction training-induced expression of calcineurin was blocked by anisomycin but not by actinomycin D. NMDA receptor antagonist, phosphatidylinositol 3-kinase (PI-3 kinase), and MAP kinase inhibitors that blocked the acquisition also blocked the extinction of conditioned fear. Likewise, PI-3 kinase inhibitor blocked fear training-induced cAMP response element-binding protein (CREB) phosphorylation as well as extinction training-induced decrease in CREB phosphorylation, the latter of which was associated with calcineurin expression and could be reversed by a specific calcineurin inhibitor. Thus, molecular processes that underlie long-term behavioral changes after acquisition and extinction share some common mechanisms and also display different characteristics.

In conclusion, we have investigated the similarities and differences between consolidation of conditioning and consolidation of extinction. Both processes depend on the activation of NMDA receptors, PI-3 kinase, and MAPK and require synthesis of new protein within the amygdala. However, they also display different characteristics, namely the differential sensitivity to block by actinomycin D and the state of CREB phosphorylation affected by calcineurin. These data, together with others, suggest a competition theory in which the outcome of blocking reconsolidation– extinction with anisomycin depends on which of these two processes, the strengthening as opposed to weakening of the original memory, is affected to a greater extent.
A model of consolidation of conditioning and consolidation of extinction of memory in the amygdala. Both acquisition and extinction trigger calcium influx through either NMDA receptors or L-type calcium channels in the amygdala. The increase in intracellular Ca^{2+} leads to the activation of protein kinases (e.g., PKA, PI-3 kinase, and MAPK). The activated kinases then translocate into the nucleus in which they phosphorylate CREB to initiate gene transcription and translation. Extinction training not only reactivates original memory this way but also promotes calcineurin synthesis via the existed mRNA. Calcineurin then exerts a negative feedback effect to dephosphorylate kinases and weakens the original memory.