*Chinese Journal of Polymer Science Vol. 31, No. 9, (2013), 1204–1217*

***Chinese Journal of Polymer Science***
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2013

*Review*

# SOME KEY ORDERED MACROPOROUS COMPOSITES

Jian-hua Rong[a], Li-jun Ji[b] and Zhen-zhong Yang[c*]

[a] *Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, China*
[b] *College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China*
[c] *Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

**Abstract** This review summarizes recent progress of the ordered macroporous composites with the opals and inverse opal structure. Synthesis and performance of the composites are emphasized. Composition of the ordered composites is tunable ranging within metal, metal alloy, metal oxide, polymer, carbon and hydrogel. The ordered structure gives brilliant color effects, which is useful for sensors and photonic crystals. The interconnected macroporous structure provides easiness for mass transportation and species culturing.

**Keywords:** Opal; Inverse opal; Ordered macroporous; Composites.

## INTRODUCTION

Natural gemstone (opal) with structural iridescent color is composed of uniform silica colloids (Fig. 1a). The optical performance arisen from Bragg diffraction of visible light by the regular structures is interesting to manipulate photon propagation[1]. During last twenty years, their artificial counterparts (opals or colloidal crystals) have experienced a fast development in control synthesis and potential applications in wave-guides, optic switches, optical filters and sensors[2, 3]. In comparison with natural opals (Fig. 1b), controlling structure and composition of the opal materials becomes flexible either by adjusting particle-particle interaction or under external fields[4–6]. By filtration of another material inside the interstitial voids of an opal, the corresponding macroscopic ordered composites are achieved. Accordingly, an inverse opal is derived after removal of the opal template (Fig. 1c). The inverse opals are also called three-dimensionally ordered macroporous (3DOM) materials, which exhibit the high degree of symmetry imparted by their opal templates. In addition, they also have an open, inter-connected macropore structure and nanosized wall components, which endow them with new properties. Beside the optics, inverse opal materials with interconnected macroscopic pores can find some new applications in fuel cell, photocatalysis and biomedicine[7]. It is noted that composition of the inverse opal materials can be controlled ranging from metals, metal alloys, metal oxides, polymers, carbon to soft responsive hydrogels[8, 9]. In reverse, using inverse opal templates, a series of opal materials with varied composition will be derived.

* Corresponding author: Zhen-zhong Yang (杨振忠), E-mail: yangzz@iccas.ac.cn
Invited paper dedicated to the memory of Prof. Bingzheng Jiang
Received April 6, 2013; Revised May 29, 2013; Accepted June 4, 2013
doi: 10.1007/s10118-013-1324-6

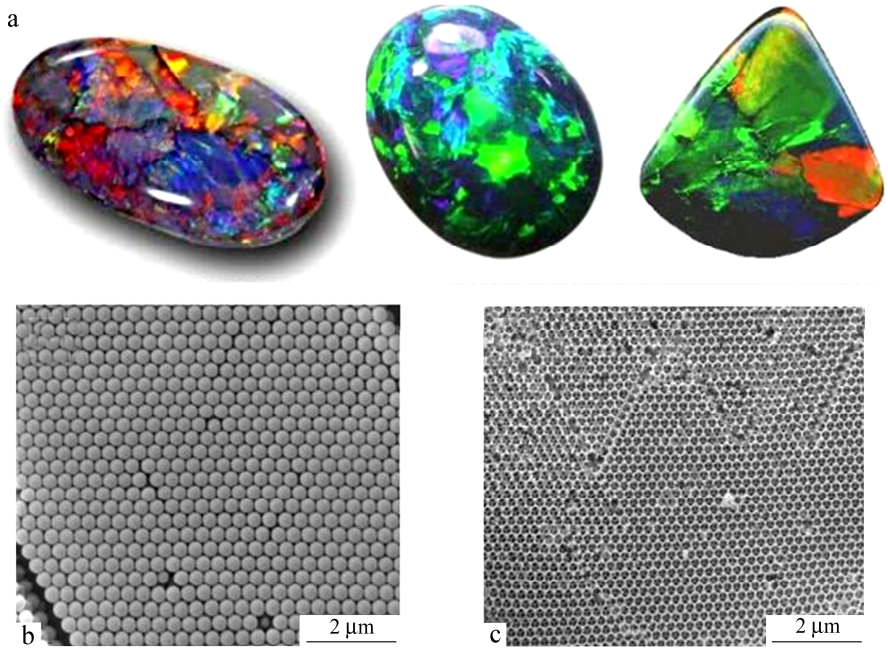



**Fig. 1** (a) Appearance of natural opals; (b) and (c) SEM images of representative opal and inverse opal

The review will summarize recent progress in synthesis and performance of some key opal and inverse opal composite materials.

## SELF-ASSEMBLY

Self-assembly of monodispersed particles, mainly spherical colloids, is a common method to produce colloidal particles. Generally, the spheres pack into hexagonally-close-packed layers in two dimensions (2D) or into mainly face-centered cubic (fcc) arrays in three dimensions (3D). There are usually defects, dislocations and cracks in the obtained structures. Much effort has been expended to prepare large-area and defect-free colloidal crystals *via* adjusting the condition of assembly. Several review papers have well summarized the self-assembly of colloids forming colloidal crystals[5, 6, 10]. We will just emphasize the effects of external fields on the assembly behavior and structures.

Starting from a dispersion of monodisperse particles of silica, polystyrene (PS), poly(methyl methacrylate) (PMMA) or core-shell, opal materials are easily self-assembled (Fig. 2), under gravity sedimentation[11, 12], electric or magnetic field assisted sedimentation[13, 14], spin or dip coating[15–17], doctor blade coating[18, 19], capillary deposition[20–22], crystallization in physically confined cells[23], sonication-assisted drying[24], spray drying[25], inkjet printing[26, 27] and interface assembly[28–32]. The various methods are classified into three main catalogues according to driving force[10], *i.e.* field-induced deposition, flow-induced deposition and volume restriction. Most methods are based on repulsion interactions between colloids in dispersions. An external action (field, flow or solvent evaporation) can drive the particles to approach together after overcoming the repulsion barrier. In a field-induced deposition method, the field of gravity, electric or magnetic drives colloids together to increase the colloid content until exceeding a critical one resulting in a thermodynamically favored crystal formation. In the flow-induced deposition method (such as spin coating, dip coating, doctor blade coating, capillary deposition and assembly under confinement), the assembly is a non-equilibrium process. The colloids are usually driven by the flow filed towards a growth front and stick together stochastically at the front. In the volume restriction method, an opal structure forms after the colloid content increases upon solvent evaporation.

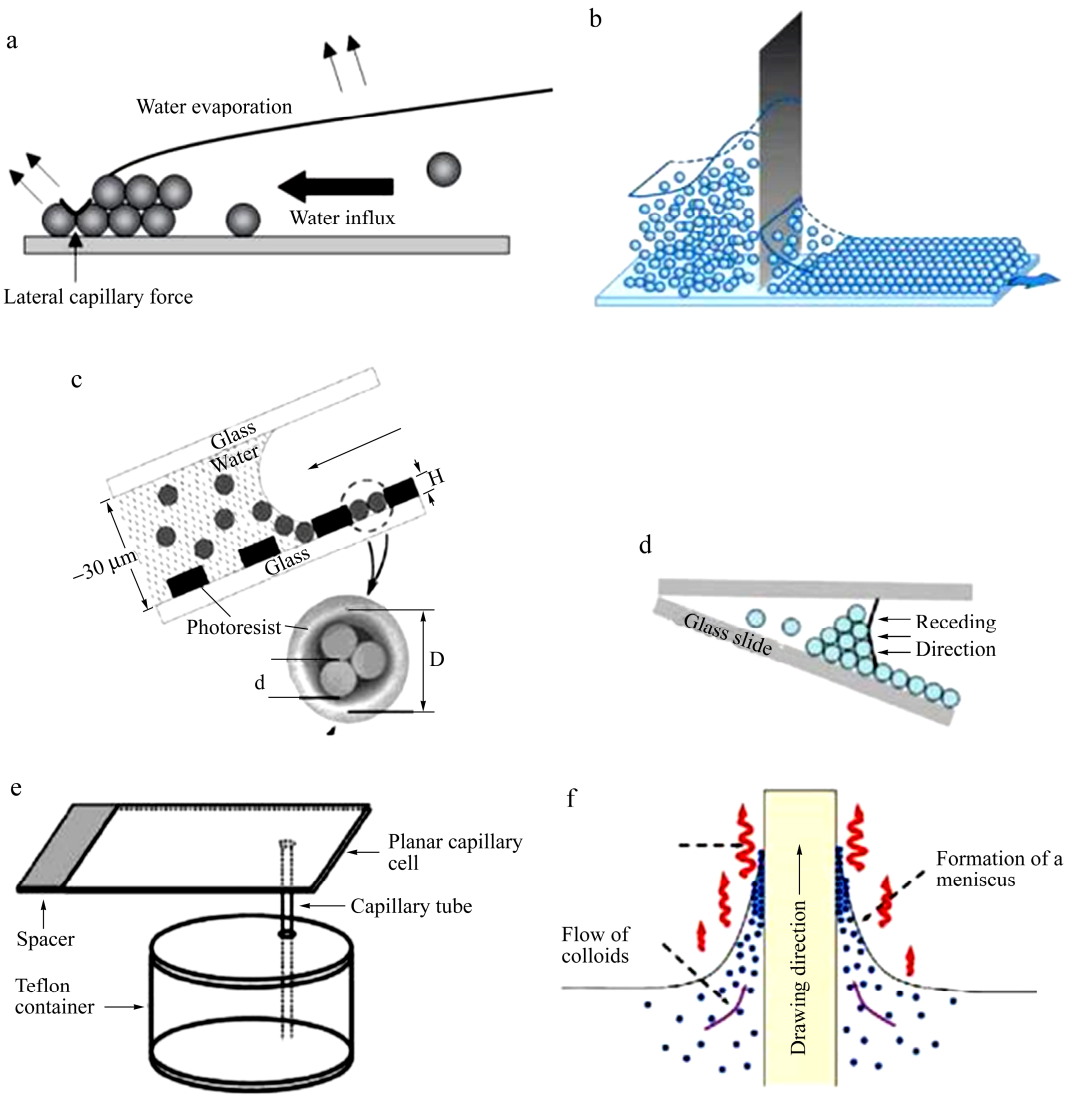



**Fig. 2** Illustrative flow-induced assembly procedures: (a) on a horizontal hydrophilic substrate, (b) a doctor blade coating[19], (c) under a patterned physical confinement template[43], (d) inside a planar capillary cell[20], (e) by gravity sedimentation[21] and (f) vertical deposition[46] (Reproduced with the permission from the literature [19], [20], [21], [43], [46])

***Field-Induced Deposition***

Gravity field sedimentation is usually used to drive formation of opal materials[12, 33]. However, it is a time cost procedure and the ordering quality is not high especially for large colloids. Centrifugation[34], filtration[35], elevating temperature and external electrical[36, 37] or magnetic fields (for paramagnetic ones)[38, 39] are usually used to accelerate the deposition. In order to achieve improved ordered structures, vibrations induced by oscillator[40] or sonicator[24] are applied to improve ordering dynamics of the colloid assembly.

***Flow-Induced Deposition***

Capillary force and convective interaction are two main driving forces in the flow-induced deposition. Typically, after a nucleus first forms at the dispersion outside *via* solvent evaporation, more colloidal particles are driven by the dispersion convective flow towards the nucleus resulting in ordered stacking[41]. Dropping a small amount of dispersion on a horizontal support is the simplest way to obtain a dried thin film by flow-induce deposition. However, the film is heterogeneous due to uncontrollable solvent evaporation. In order to improve the ordering

quality, other methods are proposed including spin coating[15, 42], doctor blade coating[18, 19] and deposition in physical confinement cells[20–23]. In addition, assembly under physical confinement can give more complex structures[43, 44].

Vertical deposition can greatly simplify convective assembly by vertically immersing a substrate into a dispersion, which is pulled upwardly to allow a deposition of the colloids during solvent evaporation[45]. The solvent evaporation rate is correlated with the pull rate. Some key variables of temperature, pressure, humidity, substrate composition and tilting angle, solvent and initial colloid content, can be combined to further control optimal growing conditions for more ordered structures[46–51].

***Volume Restriction Method***

Under the similar mechanism as flow-induced horizontal deposition, the volume restriction method has no horizontal growth front and the dispersion film is kept homogeneous in the horizontal direction during the whole process. This can be achieved by ultrasonication[10, 24]. The opal growth front is downward to the substrate and the sonication can assist re-arrangement of colloids, achieving ordering film at centimeter scale[24].

Spray coating[25] and inkjet printing[26, 27] belong to volume restriction, which are applicable in cases of strong interaction between colloids[25, 26]. Patterned colloidal crystals composed of different colloids could be obtained by inkjet printing[26].

***Interfacial Self-assembly***

Self-assembly of colloids at the air-water or liquid-liquid interface is also effective to fabricate large area colloidal crystals[28, 29, 32]. Upon spreading the colloids, a monolayer of colloidal crystal forms at the interface. The liquid interface acts as a substrate to allow easier free movement and arrangement of colloids than at a solid one. The ordered monolayer is transferred onto a flat substrate *via* dip-coating. The liquid property, colloid surface and a sufficient adhesion of the colloids to the final substrate are crucial for a successful assembly[28, 31]. Binary colloidal crystals with a mixture of colloids with two sizes could be well controlled *via* the air-water interfacial assembly[30].

## TEMPLATE SYNTHESIS

Colloidal crystals templating is a simple and convenient chemical method to obtain porous materials with well-ordered periodicity and interconnected pore structure in two or three dimensions. Generally, the corresponding inverse opals against a colloidal crystal template are derived by infiltrating the interstices of colloidal crystal with desired materials followed by removal of the template (or vice verse) (Fig. 3). This template method is highly versatile and applicable to many different processes and compositions. For example, materialization inside the interstices could be diversified ranging within sol-gel process, electrochemical deposition, precipitation/chemical reduction and polymerization. Composition of the inverse opals, such as metal, inorganic materials and polymers, could be greatly tunable. The recent works on opal template synthesis are summarized in Table 1.

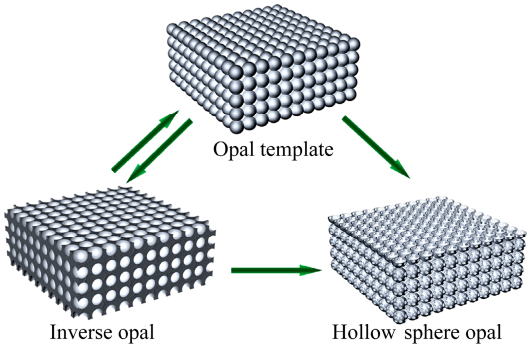



**Fig. 3** Inverse opal and hollow sphere opal by replication of an opal template

**Table 1.** Template synthesis for inverse opals

| Template synthesis method | Material | Advantages | Disadvantages |
|---|---|---|---|
| Sol-gel process | $SiO_2$, $ZrO_2$, $Al_2O_3$, $Fe_2O_3$ and $Sb_4O_6$[9]; $TiO_2$[9, 52, 53]; HA[55]; mesoporous $SiO_2$[56] | Suitable for varied inorganic materials; convenient | May lead to shrink, cracking and defects |
| Electrochemical deposition | Au, Ag, Pt, Co, Ni, W, Pd, CdS and CdSe[9]; $TiO_2$, $SiO_2$[57]; Au and CdSe NPs[58–60]; Au@$SiO_2$[61, 62], Au@Polypyrrole and CdTe@Polypyrrole[63] | Crystalline inverse opals were obtained; reducing shrink after removal of template | Complicated process |
| Precipitation/chemical reaction | NiO and Ni[65]; Carbon[66] | Reducing shrink and defect | Only suitable for a few reactive materials |
| Polymerization | polyacrylic acid[70], poly(2-hydroxyethyl methacrylate) and poly(3-acrylamidophenylboronic acid)[71], poly(N-isopropylacrylamide)[72] | Suitable for many polymer materials | Polymer inverse opals possess low reflective index |

### *Sol-Gel Process*

Sol-gel process of precursors is extensively used to derive inorganic inverse opals with varied composition, such as $SiO_2$, $TiO_2$, $ZrO_2$, $Al_2O_3$, $Fe_2O_3$ and $Sb_4O_6$[9]. Shrinking may lead to cracking and defects during sol-gel process and the sequential removal of the template. By introduction of fluorinated organic acid, the skeleton of titania inverse opal is well controlled against polystyrene opal template[52]. A special opal template in which the colloids are permeable to the precursor, an opal titania of hollow colloids with tunable shell thickness and cavity size is achieved using sulfonated polystyrene opal gel templates (Figs. 4a and 4b)[53]. It is interesting that polymeric gels possess a variety of functional groups, which can induce a favorable growth of desired materials therein. Gel opal is easily deformed under compression, the corresponding oblate titania opal is derived (Fig. 4c)[54]. The sulfonated polystyrene inverse opal gel can induce a favorable growth of a titania inverse opal (Fig. 4d). A hydroxyapatite inverse opal is synthesized by sol-gel process using a carbon inverse opal template[55], which is large of centimeters and strong enough as a cell culture scaffold.

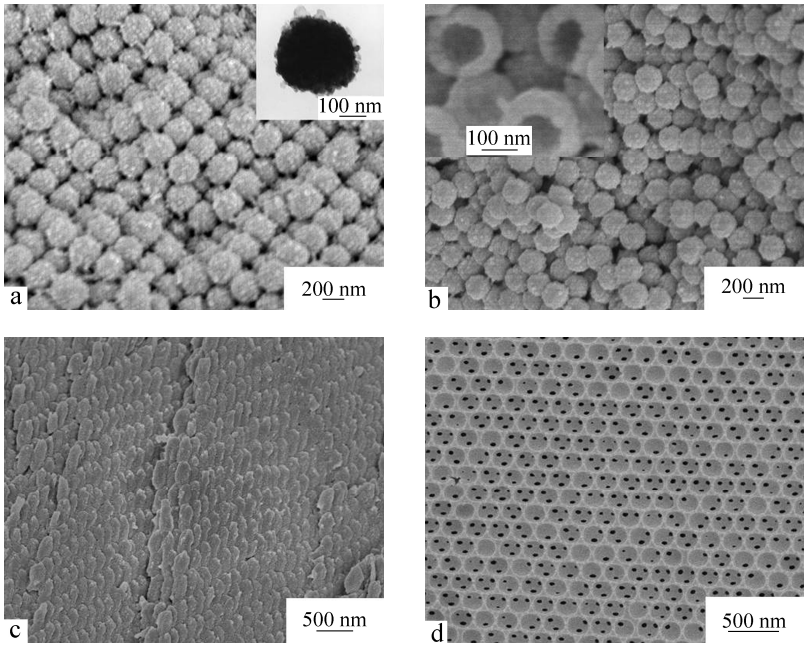



**Fig. 4** SEM images of (a, b) titania opals against a sulfonated polystyrene opal gel with varied shell thickness, (c) an oblate titania opal and (d) a titania inverse opal against a sulfonated polystyrene inverse opal gel

Ordered porous silica materials with hierarchical ordering at three different scales are synthesized using polystyrene latex sphere, triblock copolymer and co-surfactant[56]. The silica skeleton becomes mesoporous and useful in catalyses. Similarly, hierarchically structured inverse opal carbon is synthesized[55], which can integrate interconnected pores at different scales and high specific surface area.

***Electrochemical Deposition***

Although the sol-gel process is convenient, skeleton of the inverse opals is usually amorphous. Calcination at high temperature is required to achieve desired crystal phase, thermal induced internal stress causes considerable shrinking and cracking. Alternatively, electrochemical or electroless deposition is used to synthesize crystalline metal and metal chalcogenide inverse opals including Au, Ag, Pt, Co, Ni, W, Pd and CdS and CdSe[9]. In addition, Pine *et al.* presented a versatile and no high-temperature treatment method for fabricating ordered macroporous materials by assembly of ultrafine colloidal particles of oxides (rather than alkoxide precursors) using monodisperse polystyrene as a template[57]. Besides inorganic nanoparticles, metal nanoparticles can be used to fill the voids of opal templates. Gold nanoparticles of 10-15 nm are used to synthesize gold macroporous materials against polystyrene opal template after calcination[58, 59]. Similarly, inverse opal of CdSe is synthesized[60].

Besides pure metallic or inorganic oxide nanoparticles, gold-silica core-shell nanoparticles with tunable shell thickness are used to fill the voids achieving gold-silica inverse opals with interesting optical performance[61, 62]. Ligand capped gold nanoparticles are used to synthesize gold inverse opal[58]. Nanoparticle/conductive polymer composite inverse opals are synthesized by electrochemical co-deposition[63]. Refractive index of the inverse opals is greatly tunable thus the optical properties. Several other similar strategies, such as chemical vapor deposition, atomic layer deposition and supercritical deposition are also proposed[64].

***Precipitation/Chemical Reaction***

In a typical precipitation/chemical reaction process, after reactants are precipitated in the voids of the opal template, they start to react forming an inverse opal. As an example, NiO and Ni inverse opals are prepared by reducing precipitated metal salt inside an opal template with gas such as $H_2$ or CO[65]. Carbon inverse opal is prepared by infiltrating phenol resin into silica opal template and after drying and carbonization at high temperatures[66]. This chemical reaction technique is advantageous that the as-prepared inverse opal structure can be further strengthened with the reaction under a support of the opal template. Shrinkage and defects are greatly decreased in the inverse opal.

***Polymerization***

Organic polymers have many advantages over inorganic materials, whose network is easily swollen with solvents to tune refractive index. If responsive polymers are used to construct the inverse opals, the inverse opals should be responsive accordingly. Polymeric inverse opals are easily synthesized by infiltrating monomers into an opal template, following polymerization and removal of the template. Characteristic size and shape of the polymer materials are easily controlled by physical parameters[67]. Atom transfer radical polymerization (ATRP) from silica spheres of opal templates is used to synthesize opal-inverse opal interlocked structures, by which a diversity of functional composites can be favorably formed[68].

If responsive polymers are used, the inverse opals may act as sensors[69]. Some hydrogels of pH responsive polyacrylic acid[70], glucose responsive poly(2-hydroxyethyl methacrylate and 3-acrylamidophenylboronic acid)[71], and thermal responsive poly(*N*-isopropylacrylamide)[72] are used as building units for the three dimensional macroscopic ordered structures. The hydrogel inverse opals display brilliant color due to the Bragg diffraction of visible light, which is tunable rapidly with volume. Since hydrogels are infiltrative, other materials are easily to complex with the hydrogel forming composite inverse opals[73]. The polymer inverse materials have shown promising applications in separation and adsorbent media[74], catalytic supports[75, 76], chromatographic materials[77] and sensors[55].

## APPLICATIONS OF THE MATERIALS

The opal and inverse opal materials possess special structures and display many interesting properties. They can be used as photonic crystals or visible sensors from the structural color effect. Mass transportation becomes easier through the interconnected macropores, which will be useful in adsorption and separation, energy storage and transfer, and catalysis or support.

### *Optics and Sensors*

The materials present photonic bandgap (PBG) as photonic crystals attributed to the dielectric constant periodic distribution. Control of refractive index is mainly concerned. Various materials are candidates as the skeleton, including metallic oxide[78], silica[79], polymer[45, 80–85] and metal[86]. For the similar ordered materials but with varied composition of MgO, $MgSO_4$, $CaCO_3$ and $SrCO_3$, optical properties are different[87]. A $CaCO_3$ one shows opalescent colors due to a photonic stop band at visible light range, while the metallic ones have no obvious opal opalescent color.

PBG can be tunable with pore size and the wall thickness besides the composition (refractive index). Color changes with the variables, and many visible sensors based on the PBG shift are developed. A simple detection mechanism is based on the refractive index alteration after the macropores are filled with another fluid. Three robust different dielectric materials (silica, alumina and zirconia) are demonstrated due to the solvent-filling effect on the colors[88]. Their compositional diversity and inexpensive starting materials suggest that the ordered materials would be promising in refractive index sensors for flow applications. Carbon ordered materials are templates synthesized against poly(St-MMA-AA) colloidal crystal[89], the color shifts reversibly upon adsorption of oil that is easily distinguished with naked eyes. In particular, different oils with varied refractive index could be distinguished by the fast color change within 30 s (Fig. 5).

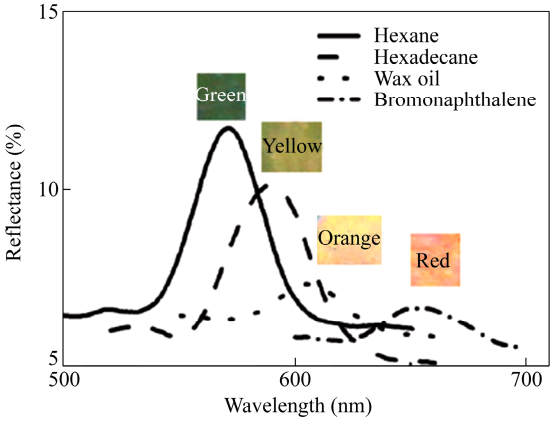



**Fig. 5** Reflection spectra of the carbon inverse opal adsorbing four different oils with varied refractive index

Similarly, the stop band position can be adjusted by some environmental variables such as acidic to alkali environment. A reversible color change of a polyaniline-infiltrated $TiO_2$ film can be obtained when the vapor environment is switched from an acidic to alkali[90]. In a saturated $NH_3$ environment, the stop band changes from 556 to 688 nm, corresponding to a color change from green to red. After placing in HCl vapor, the stop band undergoes a blue-shift and the color turns back to green. This can be explained by the polymer chains transformation between emeraldine base and emeraldine salt, leading to refractive index change. The polyaniline materials possess potential as a gas sensor to fast detect four tested gages of dry gas, ethanol vapor, hydrogen chloride and ammonia.

Polymeric hydrogels are responsive to stimuli such as solvent, pH, electric field, temperature, mechanical pressure, ionic strength and type, and biomolecules, with remarkable volume change. The optical stop band position and color change thereby. The wavelength at the stop band peak of a polyacrylic acid based inverse opal

is tunable within the whole visible spectrum *via* simply altering some parameters such as pH value in aqueous bulk[91]. After a polyacrylamide hydrogel inverse opal is responsive to humidity variation[92], the optical reflection peak shifts noticeably within the visible wavelength range (Fig. 6).

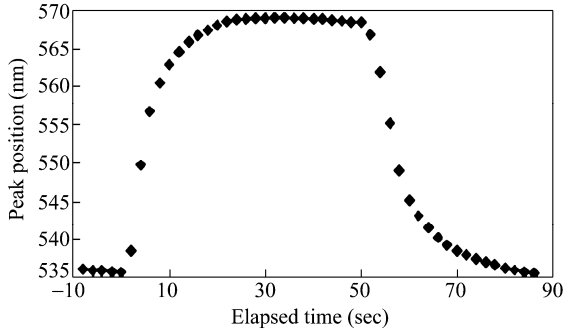



**Fig. 6** Responsiveness of inverse opal polyacrylamide hydrogel to humidity variation (Peak position shifts with time under direct humid air flow from 0 to 50 s.)

In combination of a molecular imprinting of 3-pyridinecarboxamide with a responsive hydrogel photonic crystal, polyacrylamide (PAM) imprinted inverse opal is achieved[93]. A rapid and recoverable response to 3-pyridinecarboxamide is demonstrated by measuring the diffraction peak. The color change of the IPCs can be directly converted into a readable optical signal visible to naked eyes without any labeling treatment.

***Adsorption and Controllable Release***

The materials have large and uniformly distributed pores which are interconnected by twelve small "windows". The window channels enhance accessibility to the active sites, and the short diffusion path of the thin pore walls accelerates material exchange[35, 94–96]. They are promising in adsorption and separation of heavy metal ions, organic molecules and biomacromolecules. The materials of hydroxyapatite or $Ca_{10}(PO_4)_6(OH)_2$ (HAp) can collect cadmium and lead ions from their salt solutions[96].

Introduction of polymeric chains onto pore walls has less influence on blocking the window channels[97]. The functionalized materials after conjugation with 2-mercaptobenzothiazole (MBZ) groups directly or *via* polyethylene glycol (PEG) chains are effective to remove silver (I) and mercury (II) ions. After regeneration by washing with acidic thiourea solution, the materials can recover 90% of the original capacity[98]. Poly(2-hydroxyethyl methacrylate) (PHEMA) is grafted from the pore wall by surface initiated ATRP, to allow a removal of salicylic acid from water (Fig. 7). The materials could be regenerated by a simple extraction with ethanol[99].

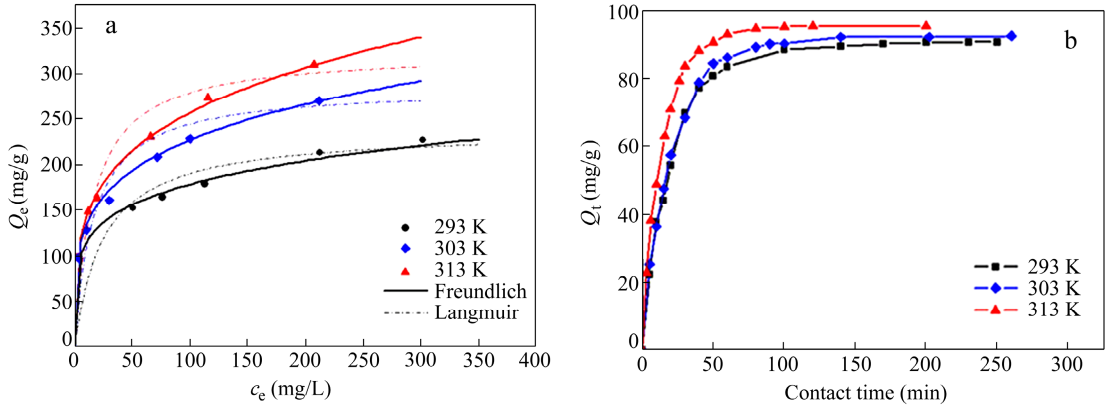



**Fig. 7** Equilibrium adsorption isotherms (a) and kinetic adsorption curve (b) of adsorbents for SA at different temperature on the PHEMA grafted materials

Fe/C nanocomposites are synthesized by sintering a mixture of closely packed polystyrene colloids and ferric nitrate precursor. The as prepared nanocomposites are superoleophilic without modification with low surface energy chemicals. They are highly selective to remove oils from water. After collection of oil with the materials, they can be easily removed from water with a magent (Fig. 8). The materials are easily regenerated after washing oil with ethanol[100].

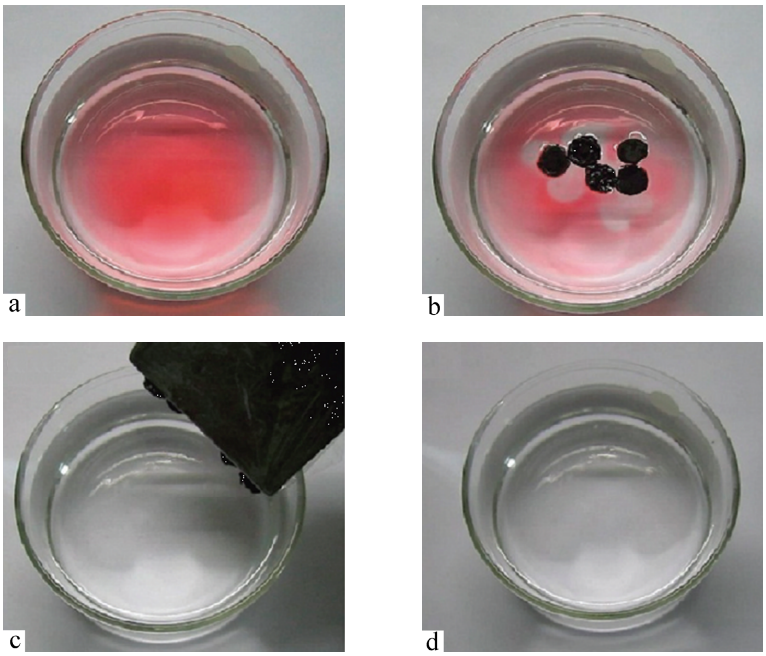



**Fig. 8** Removal of lubricating oil from water by Fe/C with a magnet
(The oil is dyed for clear observation.)

Controllable release is permitted from the ordered materials due to their special pore structure and large pore volume. Bioceramic hydroxyapatite materials are synthesized, antibiotic drug (norfloxacin) *in vitro* release is achieved[101], which can be controlled within 1 h.

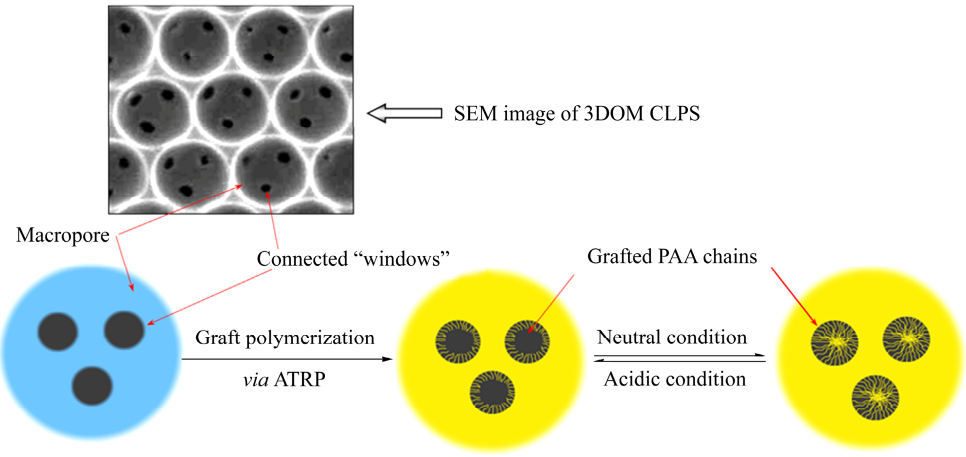



**Fig. 9** Model of the grafted PAA chains on the pore walls for controlling the switch of the connected "windows" by changing pH

Controlling the window switch may control diffusion from the materials. Responsive materials can be grafted onto the window channels to achieve "chemical windows". pH-responsive polymeric chains, for example poly(acrylic acid), are grafted, serving as a permeation valve on the connected "windows" (Fig. 9). The on-off switch of "windows" at different pH values is achieved for storage-release of vancomycin as the model molecule.

***Catalyst Support***

Heterogeneous catalysis is advantageous to recycle. Different from the catalyst support using porous spheres, the ordered macroporous materials especially those with mesoporous pore wall are ideal candidates to support heterogeneous catalysts[102–104]. As an example, the macroporous $La_{0.6}Sr_{0.4}Fe_{0.8}Bi_{0.2}O_{3-\delta}$ (LSFB) material with the nanoporous skeleton, has shown enhanced catalytic activity. High oxygen species concentration and good low-temperature reducibility are responsible for the excellent catalytic activity[105, 106].

A series of highly efficient photo catalysts with the ordered macroporous structure have been reported. $Fe_2O_3$ films developed by a facile layer-by-layer deposition and hydrolysis of $FeCl_3$ have exhibited a rather high photo catalytic activity to degrade dyes in the presence of $H_2O_2$ under visible irradiation. It is explained by enhanced light harvest efficiency and accelerated mass transportation *via* the interconnected macropores. A slow photon enhancement of photo catalytic activity is achieved by adjusting red edge of the photonic stop band of the ordered $Fe_2O_3$ film close to the electronic bandgap of $Fe_2O_3$[107]. The $Bi_2WO_6$ macroporous material with a mesoporous wall has also exhibited enhanced photo catalytic activity to degrade phenol and aqueous ammonia under irradiation of simulated sunlight[108]. $TiO_2$ and $TiO_2/SiO_2$ macroporous materials are capable to photo catalyze the decomposition of methyl orange solutions. Especially, the latter one displays stronger photocatalytic ability since the introduction of Si can increase the transformation temperature of $TiO_2$ from anatase to rutile[109]. Ordered macroporous carbon/refractory metal is synthesized, which is stable at 1000 °C for at least 5 h under high vacuum[110].

$TiO_2$ macroporous materials can support Pt nanoparticles for water-gas shift (WGS) reaction[111]. Gold nanoparticles are supported on $LaFeO_3$ and $CeO_2$, which are useful for soot oxidation[112] and formaldehyde oxidation[113]. Introduction of Au nanoparticles inside the nanoporous walls of $CeO_2$-$Co_3O_4$ macroporous materials can completely decompose formaldehyde into $CO_2$ and $H_2O$ at low temperature as 39 °C[114]. Similarly, Ag nanoparticles can be easily supported within macroporous $SiO_2$[115]. Polymers are advantageous due to their toughness and easier functionalization to bring desired groups. A tri-phase catalyst of polymer-supported PEGs is prepared for phase transfer catalytic synthesis of $\alpha$-butyl phenylacetonitrile[116].

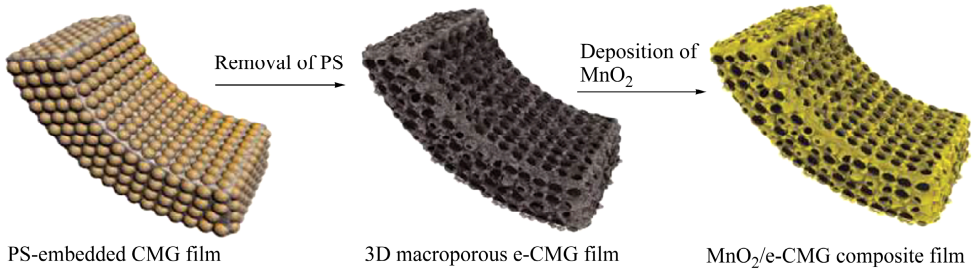



**Fig. 10** Schematic fabrication of the macroporous films through embossing process using PS template for e-CMG film as well as a subsequent deposition process of $MnO_2$ for $MnO_2$/e-CMG film

***Energy Storage***

The macroporous materials are useful in electrochemical energy conversion such as lithium battery[117–124], fuel cell[125–127] and electrodes[128–133]. An enhanced mechanical strength is achieved from the ordered structure. Two-dimensional electrochemical reactions are enhanced in such materials[134], and the energy and power density are greatly improved. High-performance super capacitors are built using a chemically modified graphene (CMG) macroporous structure[135] from a polystyrene colloidal crystal template. A thin layer of $MnO_2$ deposited onto

CMG (Fig.10) facilitates fast ion transport within the electrode while preserving electronic conductivity and endows the electrodes with excellent electrochemical properties.

## REMARKS AND OUTLOOK

Fabrication of both opal and inverse opal composites has experienced a rapid development. Various self-assembly and template approaches have been proposed to improve the ordered extent of the materials and to construct more complex structures. In order to analogue to semiconductor to manipulate electron, the ordered materials should be perfect sufficiently at large scale in order to manipulate photons. It remains challenging to synthesize giant perfect photonic crystals by colloidal assembly. Another key concern is to extend phases of photonic crystals from common face-center-cubic (fcc) crystalline structure to others for example diamond one in order to achieve complete band gap. It will be interesting to achieve individual colloidal photonic crystal by regularly arranging smaller colloids onto a larger one with varied refractive index.

## REFERENCES

1 Joannopoulos, J.D., Meade, R.D. and Winn, J.N., "Photonic crystals: molding the flow of light, 2nd Ed. ", Princeton University Press, New Jersey, 2008, p. 94
2 Mazurenko, D.A., Kerst, R., Dijkhuis, J.I., Akimov, A.V., Golubev, V.G. and Kurdyukov, D.A., Phy. Rev. Lett., 2003, 91: 213903
3 Nair, R.V. and Vijaya, R., Prog. Quant. Electron., 2010, 34: 89
4 Li, F., Josephson, D.P. and Stein, A., Angew. Chem. Int. Ed., 2011, 50: 360
5 Zhang, J., Sun, Z. and Yang, B., Curr. Opin. Colloid. Interf. Sci., 2009, 14: 103
6 Li, Z., Wang, J. and Song, Y., Particuology, 2011, 9: 559
7 Shin, J., Han, S.G. and Lee, W., Anal. Chim. Acta., 2012, 752: 87
8 Stein, A., Li, F. and Denny, N.R., Chem. Mater., 2008, 20: 649
9 Lytle, J.C. and Stein, A., "Recent progress in syntheses and applications of inverse opals and related macroporous materials prepared by colloidal crystal templating. annual reviews of nano research", ed. by Cao G. and Brinker. C.J., Vol. 1. World Scientific Publishing Co., Singapore China, 2006, p. 6
10 Marlow, F., Muldarisnur, Sharifi, P., Brinkmann, R. and Mendive, C., Angew. Chem. Int. Ed., 2009, 48: 6212
11 Iler, R.K., Nature, 1965, 207: 472
12 Davis, K.E., Russel, W.B. and Glantschnig, W.J., J. Chem. Soc., Faraday Trans., 1991, 87: 411
13 Rogach, A.L., Kotov, N.A., Koktysh, D.S., Ostrander, J.W. and Ragoisha, G.A., Chem. Mater., 2000, 12: 2721
14 Chen, L.H., Li, X.Y., Rooke, J.C., Zhang, Y.H., Yang, X.Y., Tang, Y., Xiao, F.S. and Su, B.L., J. Mater. Chem., 2012, 22: 17381
15 Jiang, P. and McFarland, J., J. Am. Chem. Soc., 2004, 126: 13778
16 Mller, M., Zentel, R., Maka, T., Romanov, S.G. and Torres, C.M.S., Adv. Mater., 2000, 12: 1499
17 Yan, Q., Zhou, Z. and Zhao, X.S., Langmuir, 2005, 21: 3158
18 Prevo, B.G. and Velev, O.D., Langmuir, 2004, 20: 2099
19 Yang, H.T. and Jiang, P., Langmuir, 2010, 26: 13173
20 Li, H.L., Dong, W.T., Bongard, H.J. and Marlow, F., J. Phys. Chem. B., 2005, 109: 9939
21 Ye, R., Ye, Y.H., Zhou, Z.T. and Xu, H.H., Langmuir, 2013, 29: 1796
22 Sun, J., Tang, C.J., Zhan, P., Han, Z.L., Cao, Z.S. and Wang, Z.L., Langmuir, 2010, 26: 7859
23 Park, S.H. and Xia, Y.N., Adv. Mater., 1998, 10: 1045
24 Li, Y.Z., Kunitake, T. and Fujikawa, S., Colloids and Surfaces A: Phys., 2006, 275: 209
25 Cui, L.Y., Zhang, Y.Z., Wang, J.X., Ren, Y.B., Song, Y.L. and Jiang, L., Macromol. Rapid Commun., 2009, 30: 598
26 Cui, L., Li, Y., Wang, J., Tian, E., Zhang, X., Zhang, Y., Song, Y. and Jiang, L., J. Mater. Chem., 2009, 19: 5499

27 Park, J. and Moon, J., Langmuir, 2006, 22: 3506
28 Retsch, M., Zhou, Z.C., Rivera, S., Kappl, M., Zhao, X.S., Jonas, U. and Li, Q., Macromol. Chem. Phys., 2009, 210: 230
29 Takeda, S. and Wiltzius, P., Chem. Mater., 2006, 18: 5643
30 Dai, Z., Li, Y., Duan, G., Jia, L. and Cai, W., ACS Nano, 2012, 6: 6706
31 Zhang, J.A., Wang, M.Z., Ge, X.W., Wu, M.Y., Wu, Q.Y. and Yang, J.J., J. Colloid Interface Sci., 2011, 353: 16
32 Pileni, M.P., Acc. Chem. Res., 2012, 45: 1965
33 Stöber, W., Fink, A. and Bohn, E., J. Colloid. Interf. Sci., 1968, 26: 62
34 Johnson, N.P., McComb, D.W., Richel, A., Treble, B.M. and Rue, R.M., Synth. Met., 2001, 116: 469
35 Holland, B.T., Blanford, C.F. and Stein, A., Science, 1998, 281: 538
36 Braun, P.V. and Wiltzius, P., Nature, 1999, 402: 603
37 Lumsdon, S.O., Kaler, E.W. and Velev, O.D., Langmuir, 2004, 20: 2108
38 Ge, J.P., He, L., Goebl, J. and Yin, Y.D., J. Am. Chem. Soc., 2009, 131: 3484
39 Xuan, R., Wu, Q., Yin, Y.D. and Ge, J.P., J. Mater. Chem., 2011, 21: 3672
40 Vickreva, O., Kalinina, O. and Kumacheva, E., Adv. Mater., 2000, 12: 110
41 Denkov, N.D., Velev, O.D., Kralchevsky, P.A.; Ivanov, I.B., Yoshimura, H. and Nagayama, K., Nature, 1993, 361: 26
42 Ozin, G.A. and Yang, S.M., Adv. Funct. Mater. 2001, 11: 95
43 Xia, Y.N., Yin, Y.D., Lu, Y. and McLellan, J., Adv. Funct. Mater., 2003, 13: 907
44 Yin, Y.D., Lu, Y., Gates, B. and Xia, Y.N., J. Am. Chem. Soc., 2001, 123: 8718
45 Jiang, P., Bertone, J.F., Hwang, K.S. and Colvin, V.L., Chem. Mater., 1999, 11: 2132
46 Lange, B., Fleischhaker, F. and Zentel, R., Phys. Status Solidi. A, 2007, 204: 3618
47 Wong, S., Kitaev, V. and Ozin, G.A., J. Am. Chem. Soc., 2003, 125: 15589
48 Zheng, Z.Y., Liu, X.Z., Luo, Y.H., Cheng, B.Y., Zhang, D.Z. and Meng, Q.B., Appl. Phys. Lett., 2007, 90: 051910
49 McLachlan, M.A., Johnson, N.P., Rue, R. and McComb, D.W., J. Mater. Chem., 2004, 14: 144
50 Guo, W.H., Wang, M., Xia, W. and Dai, L.H., Opt. Commun., 2012, 285: 1259
51 Cai, Z., Teng, J., Xia, D. and Zhao, X.S., J. Phys. Chem. C, 2011, 115: 9970
52 Galusha, J.W., Tsung, C.K., Stucky, G.D. and Bartl, M.H., Chem. Mater., 2008, 20: 4925
53 Rong, J.H., Ma, J. and Yang, Z.Z., Macrom. Rapid Commun., 2004, 25: 1786
54 Ji, L.J., Rong, J.H. and Yang, Z.Z., Chem. Commun., 2003, (9):1080
55 Ji, L.J., Jell, G., Dong, Y., Jones, J.R. and Stevens, M., Chem. Commun., 2011, 47:9048
56 Sen, T., Tiddy, G.J.T., Casci, J.L. and Anderson, M.W., Angew. Chem. Int. Ed., 2003, 42: 4649
57 Subramanian, G., Manoharan, V.N., Thorne, J.D. and Pine, D.J., Adv. Mater., 1999, 11: 1261
58 Velev, O.D., Tessier, P.M., Lenhoff, A.M. and Kaler, E.W., Nature, 1999, 401: 548
59 Tessier, P., Velev, O.D., Kalambur, A.T., Lenhoff, A.M., Rabolt, J.F. and Kaler, E.W., Adv. Mater., 2001, 13: 396
60 Vlasov, Y.A., Yao, N. and Norris, D.J., Adv. Mater., 1999, 11: 165
61 Wang, D.Y., Salgueirino-Maceira, V., Liz-Marzan, L.W. and Caruso, F., Adv. Mater., 2002, 14: 908
62 Zhang, W.Y., Lei, X.Y., Wang, Z.L., Zheng, D.G., Tam, W.Y., Chan, C.T. and Sheng, P., Phys. Rev. Lett., 2000, 84: 2853
63 Yu, A.M., Meiser, F., Cassagneau, T. and Caruso, F., Nano Lett., 2004, 4: 177
64 Moon, J.H. and Yang, S., Chem. Rev., 2010, 110: 547
65 Yan, H.W., Blanford, C.F., Holland, B.T., Parent, M., Smyrl, W.H. and Stein, A., Adv. Mater., 1999, 11: 1003
66 Zakhidov, A.A., Baughman, R.H., Iqbal, Z., Cui, C.X., Khayrullin, I. Dantas, S.O., Marti, J. and Ralchenko, V. G., Science, 1998, 282: 897
67 Sumioka, K., Kayashima, H. and Tsutsui, T., Adv. Mater., 2002, 14: 1284
68 Liu, B., Jin, Z.G., Qu, X.Z. and Yang, Z.Z., Macromol. Rapid Commun., 2007, 28: 322
69 Ge, J.P. and Yin, Y.D., Angew. Chem. Int. Ed., 2011, 50: 1492
70 Li, J., Ji, L.J., Rong, J.H. and Yang, Z.Z., Chinese Sci. Bull., 2003, 48: 1803
71 Lee, Y.J., Pruzinsky, S.A. and Braun, P.V., Langmuir, 2004, 20: 3096
72 Rong, J.H., Ji, L.J., Niu, Z.W., Li, D., Ma, J. and Yang, Z.Z., Chem. J. Chin. U., 2004, 25: 1771

73 Ji, L.J., Rong, J.H., and Yang, Z.Z., Chem. Commun., 2003: 1080
74 Akolekar, D.B., Hind, A.R. and Bhargava, S.K., J. Colloid Interface Sci., 1998, 199: 92
75 Tanev, P.T., Chibwe, M. and Pinnavaia, T.J., Nature, 1994, 368: 321
76 Deleuze, H., Schultze, X. and Sherrington, D.C., Polymer, 1998, 39: 6109
77 Tennikov, M.B., Gazdina, N.V., Tennikova, T.B. and Svec, F., J. Chromatogr., 1998, 798: 55
78 Holland, B.T., Blanford, C.F. and Do, T., Chem. Mater., 1999, 11: 795
79 Velev, O.D., Jede, T.A., Lobo, R.F. and Lenhoff, A.M., Nature, 1997, 389: 447
80 Yoshino, K., Takeda, H. and Kasano, M., Macromol. Symp., 2004, 212: 179
81 Gates, B., Yin, Y.D. and Xia, Y.N., Chem. Mater., 1999, 11: 2827
82 Bu, H.T., Rong, J.H. and Yang, Z.Z., Macromol. Rapid Comm., 2002, 23: 460
83 Zhang, X., Yan, W., Li, H. and Shen, X., Polymer, 2005, 46: 11958
84 Wang, H., Li, X. and Hong, L., J. Porous Mater., 2006, 13: 115
85 You, B., Shi, L. and Wen, N., Macromolecules, 2008, 41: 6624
86 Li, Y., Ma, B., Zhao, J., Xin, W. and Wang, X., J. Alloy. Compd., 2011, 509: 290
87 Fang, J., Xuan, Y. and Li, Q., Chinese Sci. Bull., 2011, 56: 2156
88 Blanford, C.F., Yan, H., Schroden, R.C., Al-Daous, M. and Stein, A., Adv. Mater., 2001, 13: 26
89 Li, H., Chang, L. and Wang, J., J. Mater. Chem., 2008, 18: 5098
90 Liu, C., Gao, G. and Zhang, Y., Macromol. Rapid Commun., 2012, 33: 380
91 Yang, L.Y. and Liau, W.B., Synth. Met., 2010, 160: 609
92 Barry, R.A. and Wiltzius, P., Langmuir, 2006, 22: 1369
93 Yuan, Y., Li, Z. and Liu, Y., Chem. Eur. J., 2012, 18: 303
94 Stein, A., Micropor. Mesopor. Mat., 2001, 44-45: 227
95 Melde, B.J. and Stein, A., Chem. Mater., 2002, 14: 3326
96 Srinivasan, M., Ferraris, C. and White, T., Environ. Sci. Technol., 2006, 40: 7054
97 Yuan, L.X., Wang, X.M., Zhang, X., Liu, P.G. and Yan, W.D., Chin. Chem. Lett., 2010, 21: 1493
98 Wang, X., Zhang, X., Guo, H., Yuan, L. and Liu, P., Polym. Eng. Sci., 2012, 52: 972
99 Wang, X., Wang, Y., Feng, L., Liu, P. and Zhang, X., Chem. Eng. J., 2012, 203: 251
100 Chu, Y. and Pan, Q., ACS Appl. Mater. Inter., 2012, 4: 2420
101 Wang, X., Wang, Q., Liu, P. and Zhang, X., Soft Matter, 2012, 8: 8847
102 Yuan, J., Dai, H., Zhang, L., Deng, J., Liu, Y., Zhang, H., Jiang, H. and He, H., Catal. Today, 2011, 175: 209
103 Zhang, G., Zhao, Z., Xu, J., Zheng, J., Liu, J., Jiang, G., Duan, A. and He, H., Appl. Catal. B: Environ., 2011, 107: 302
104 Zhao, Z., Dai, H., Deng, J., Du, Y., Liu, Y. and Zhang, L., Micropor. Mesopor. Mat., 2012, 163: 131
105 Ji, K., Dai, H., Deng, J., Song, L., Gao, B., Wang, Y. and Li, X., Appl. Catal. B: Environ., 2013, 129: 539
106 Ji, K.M., Dai, H.X., Deng, J.G., Li, X.W., Wang, Y., Gao, B.Z., Bai, G.M. and Au, C.T., Appl. Catal. A: Gen., 2012, 447–448: 41
107 Xie, H., Li, Y., Jin, S., Han, J. and Zhao, X., J. Phys. Chem. C, 2010, 114: 9706
108 Sun, S., Wang, W. and Zhang, L., J. Mater. Chem., 2012, 22: 19244
109 Li, S., Zhao, D., Zheng, J., Xue, J., Sun, H. and Shen, C., J. Porous Mater., 2012, DOI:10.1007/s10934-012-9618-6
110 Nagpal, P., Josephson, D.P., Denny, N.R., DeWilde, J., Norris, D.J. and Stein, A., J. Mater. Chem., 2011, 21: 10836
111 Liang, H., Zhang, Y. and Liu, Y., J. Nat. Gas Chem., 2008, 17: 403
112 Wei, Y., Liu, J., Zhao, Z., Chen, Y., Xu, C., Duan, A., Jiang, G. and He, H., Angew. Chem. Int. Ed., 2011, 123: 2374
113 Liu, B., Li, C., Zhang, Y., Liu, Y., Hu, W., Wang, Q., Han, L. and Zhang, J., Appl. Catal. B: Environ., 2012, 111–112: 467
114 Liu, B., Liu, Y., Li, C., Hu, W., Jing, P., Wang, Q. and Zhang, J., Appl. Catal. B: Environ., 2012, 127: 47
115 Wu, Q.Z., Yin, Q., Liao, J.F., Deng, J.H. and Li, Y.G., Chin. J. Chem., 2005, 23: 689
116 Wang, Q.Q., Wang, X.M., Feng, L., Xu, X.L. and Xu, Z., Polym. Sci. Ser. B, 2012, 54: 392
117 Yim, C.H., Baranova, E.A., Abu-Lebdeh, Y. and Davidson, I., J. Power Sources, 2012, 205: 414
118 Sadakane, M., Sasaki, K., Nakamura, H., Yamamoto, T., Ninomiya, W. and Ueda, W., Langmuir, 2012, 28: 17766

119 Kotobuki, M., Suzuki, Y., Kanamura, K., Sato, Y., Yamamoto, K. and Yoshida, T., J. Power Sources, 2011, 196: 9815
120 Vu, A. and A. Stein, Chem. Mater., 2011, 23: 3237
121 Woo, S.W., Okada, N., Kotobuki, M., Sasajima, K., Munakata, H., Kajihara, K. and Kanamura, K., Electrochim. Acta, 2010, 55: 8030
122 Cui, W.J., Liu, H.J., Wang, C.X. and Xia, Y.Y., Electrochem. Commun., 2008, 10: 1587
123 Kim, H., Han, B., Choo, J. and Cho, J., Angew. Chem. Int. Ed. 2008, 47: 10151
124 Woo, S.W., Okada, N., Kotobuki, M., Sasajima, K., Munakata, H., Kajihara, K. and Kanamura, K., Electrochim. Acta, 2007, 53: 79
125 Yong, Y.C., Dong, X.C., Chan-Park, M.B., Song, H. and Chen, P., ACS Nano, 2012, 6: 2394
126 Bosco, J.P., Sasaki, K., Sadakane, M., Ueda, W. and Chen, J.G., Chem. Mater., 2009, 22: 966
127 Munakata, H., Yamamoto, D. and Kanamura, K., J. Power Sources, 2008, 178: 596
128 Lin, C.H., Chou, W.J. and Lee, J.T., Macromol. Rapid Commun., 2012, 33: 107
129 Fierke, M.A., Olson, E.J., Bühlmann, P. and Stein, A., ACS Appl. Mater. Inter., 2012, 4: 4731
130 Kotobuki, M., Okada, N. and Kanamura, K., Chem. Commun., 2011, 47: 6144
131 Xuan, J., Jiang, L.P. and Zhu, J.J., Chin. J. Anal. Chem., 2010, 38: 513
132 Hara, M., Nakano, H., Dokko, K., Okuda, S., Kaeriyama, A. and Kanamura, K., J. Power Sources, 2009, 189: 485
133 Woo, S.W., Dokko, K., Nakano, H. and Kanamura, K., J. Power Sources, 2009, 190: 596
134 Kanamura, K., Munakata, H. and Dokko, K., "Nanotechnology for material development on future energy storage, in electrochemical nanotechnologies", ed. by Osaka, T., Datta, M. and Shacham-Diamand, Y., Springer New York, 2010, p. 35
135 Choi, B.G., Yang, M., Hong, W.H., Choi, J.W. and Huh, Y.S., ACS Nano, 2012, 6: 4020