Microstructures and Optical Features of Polymer-Immobilized Non Close-Packed Colloidal Crystalline Array

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ABSTRACT: We have investigated to immobilize non close-packed silica colloidal crystalline arrays in aqueous dispersion with hydrophilic polyethylene glycol acrylate polymer and to examine microstructures of the immobilized colloidal crystalline array by using the angle-resolved reflection spectroscopy and scanning probe spectroscopy (SPM). Above nine of ethylene glycol chain length and below 10 wt % of monomer concentration in the dispersion, the structure of the three-dimensional array in the aqueous dispersion is kept with immobilizing process. Angle-resolved reflection spectra indicate refractive index increase, and interplaner spacing decreases with the increase of the particle volume fraction. The SPM phase images proved the crystal structure of the immobilized colloidal crystalline array of face-centered cubic (fcc) structure. The interplaner spacings of the crystalline structure derived from angle-resolved reflection spectra agree with those derived from SPM topographic images. We have demonstrated the microstructure of the polymer-immobilized colloidal crystalline array directly and open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2308–2314, 2006

Key words: colloidal crystalline array; silica spheres; Bragg diffraction; polymer immobilize; scanning probe spectroscopy

INTRODUCTION

Colloidal crystalline arrays are three-dimensional periodic lattices of self-assembled monodispersed colloidal spheres, most commonly amorphous silica or polymer latex, dispersed in aqueous or nonaqueous media with lattice constants in the mesoscale size range (50–500 nm). Just as atomic crystals diffract X-rays that meet the Bragg condition, colloidal crystalline arrays diffract ultraviolet, visible, and near-infrared light, depending on the lattice spacing; the diffraction phenomena resemble those of opals, which are close-packed crystalline arrays of monodisperse silica spheres. These periodic structures have also been actively explored as functional components in fabricating new types of diffractive devices such as filters and switches,[1] smart optical sensors,[2] and photonic bandgap structures.[3–6] As a matter of fact, recent studies on the unique optical properties of these materials have now evolved into a new, exciting field of research that is often referred to as photonic bandgap crystals.

Two forms of manipulating monodisperse colloidal spheres for the generation of photonic crystals have emerged. One approach involves the assembly of the spheres into close-packed crystalline arrays through sedimentation or solvent evaporation, and typically relies on nonspecific particle–particle "hard sphere" packing to induce order. Particle assembly via this method is attractive in terms of both simplicity and versatility. The second approach utilizes the long-range electrostatic repulsive interactions of charged colloidal spheres suspended in a liquid medium into non close-packed crystalline arrays. The colloidal crystalline array will self-assemble from monodisperse colloidal spheres containing surface functional groups that ionize in solution. If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions, which are surrounded by a diffuse counterion cloud (electrostatic double layer). If the solution medium is pure and contains few other ionic species, the repulsive interaction between spherical macroions can be significant over macroscopic distances greater than 1 μm. The methodology based on electrostatic interactions seems to be the most powerful and successful one for generating multilayer assemblies of mesoscale particles: 3D crystalline assemblies as large as ~1 cm³ have been generated. In this method, however, unfortunately, the low elastic modulus exhibited by a liquid dispersion results in weak shear, gravitational, electric field, or thermal forces having the propensity to disturb the crystalline order and is a severe

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drawback to the practical application of colloidal crystalline arrays in photonic devices.

Recently, approaches to develop robust network matrices have been pioneered to stabilize both organic and inorganic arrays through an *in situ* polymerization of a monomer around the non close-packed colloidal crystalline arrays. Asher and coworkers could form a solid colloidal crystalline arrays matrix by introducing highly purified acrylamide and have been successful in utilizing polymer-immobilized colloidal crystalline arrays in optical filtering and sensing applications.[1,2,7,8] In addition, mechanically robust composite films composed of silica particles in acrylate polymers have been presented by Ford and coworkers, which exhibited a mechanochromic response.[9–11] Although poly acrylamide and its derivatives have been established as standard polymer-immobilized colloidal crystalline arrays matrices, we have focused on the use of polyethylene glycol acrylate (PEGA) hydrogels. Networks based on PEGA tend to exhibit a wider range of amphiphilicity and may offer greater versatility in tuning composite properties.[12–14] Hydrogels are prepared by the photoinitiated free radical polymerization of PEGA in the presence of non close-packed colloidal crystalline array.

In this work, we explore PEGA matrices to extend the successful routes by which stable polymer-immobilized colloidal crystalline arrays can be fabricated. The optical properties and the microstructures of the polymer-immobilized colloidal crystalline arrays are estimated by angle-resolved reflection spectroscopy and scanning probe microscopy. We try to clarify the microstructure directly and open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal.

EXPERIMENTAL

Immobilization of colloidal crystalline arrays

Colloidal silica spheres SI-80P (diameter 74 nm) were purchased from Catalyst and Chemicals Industries Co., Japan. The spheres were shaken in aqueous suspension with an excess of mixed bed ion-exchange resin (AG501-X8(D), Bio-Rad Laboratories, Hercules, CA) to reduce ionic impurities and formed the non close-packed colloidal crystalline arrays.

The non close-packed colloidal crystalline arrays were encapsulated in a hydrogel matrix prepared by an *in situ* photo-polymerization procedure. The matrix materials included a monomer of PEGA, a crosslinker of polyethylene glycol diacrylate (PEGDA), and photoinitiator of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Ciba Specialty Chemicals DAROCUR 1173). The colloidal crystalline array and PEGA/PEGDA mixture was injected between two glass plates separated by a 1 mm silicone rubber spacer and polymerized through exposure to a UV source for 5 min.

Measurements

Optical properties of the polymer-immobilized colloidal crystalline array were evaluated by measuring their reflection spectra at normal incidence, using a multichannel spectrometer (Soma Optics, Fastevert S-2650). Spectral resolution of the multichannel spectrometer is 3.6 nm. Structural analysis of the conditions was performed by angle-resolved reflection spectroscopy. Angle-resolved reflection spectra were measured by changing the angle of incidence θ between the beam and the normal of the sample surface from 9° to 30° and by collecting the light scattered in the Bragg configuration. The Bragg equation was given by (1)

$$m\lambda_{\text{peak}} = 2d_{111}(n_{\text{eff}}^2 - \sin^2\theta)^{1/2} \tag{1}$$

where m is the order of diffraction; λ_{peak} is the wavelength of the diffraction peak; d_{111} is the interplaner spacing between (111) planes; θ is the angle between the incident light and the normal to the diffraction planes (at normal incidence, $\theta = 0$); and n_{eff} is the mean effective refractive index of this crystalline array.

The wavelength λ_{peak} of each reflection peak was plotted against θ. The interplaner spacing d_{111} and n_{eff} were determined by fitting the Bragg condition to the plotted data.

Scanning probe microscopy was observed as topographic images with tapping mode and phase images with viscoelastic mode using Digital Instruments SPM D3100 (Nanoscope IIIa).

RESULTS AND DISCUSSION

Figure 1 shows the appearance and reflection spectra of the non close-packed colloidal crystalline arrays made of silica spheres with various volume fractions. All of them for the given range indicated visible range diffractions caused from Bragg diffraction of the ordered arrays. With increasing volume fraction of silica particles, the peak of diffraction was shifted to low wavelength range (green to blue) caused by the decrease of interplaner spacing. The charged colloidal spheres in aqueous dispersion have peculiar features, which are not seen in close-packed colloidal crystalline array like opal. Their interplaner spacings are easily varied by changing the volume fraction of the spheres. The colloidal crystalline array is formed by mainly electrostatic repulsion between the electric double layers of the spheres. With increase of the volume fraction of the spheres, the electrostatic double layer is compressed and distance between the spheres decreases. Since the electrostatic interaction is isotropic and long-ranged, three-dimensional colloidal crystal grains with the size of 0.001–1 mm³ are easily formed spontaneously. These liquid-phase colloidal crystalline arrays are stable, but will transiently disorder under shock. The colloidal
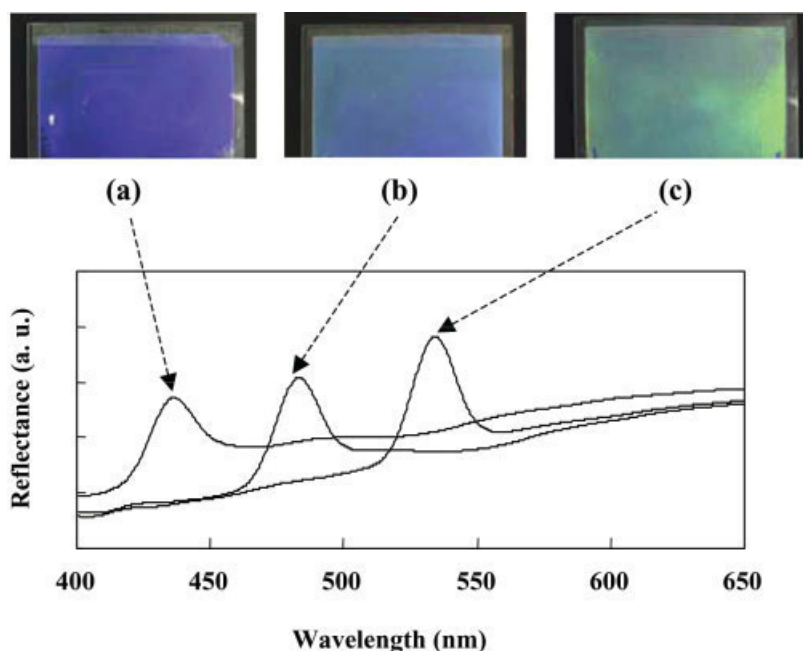
Figure 1　The appearance and reflection spectra of non close-packed colloidal crystalline arrays made of silica particles in aqueous dispersion with various volume fractions; (a) 10 vol %, (b) 7.5 vol%, (c) 5 vol%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crystalline arrays will also disorder upon introduction of ionic impurities that screen the interparticle repulsive interaction.

Table I shows the stability of the non close-packed colloidal crystalline array with the addition of various hydrophilic monomers into the aqueous dispersion. In cases of every monomer, the colloidal crystalline array deformed with above 20 wt % monomers. Above nine of ethylene glycol chain length and below 10 wt % of monomer concentration in the dispersion, the colloidal crystalline array kept the three-dimensional array structure in the aqueous dispersion. This suggests that the creation of a polymer network around the ordered particles with high hydrophobic monomer does not significantly disrupt to the long-range order. On the basis of these results, we used the above nine of ethylene glycol chain PEGA/PEGDA monomers for immobilizing the colloidal crystalline array in this research.

Figure 2 shows the appearance and reflection spectra of the PEGA/PEGDA immobilized colloidal crystalline arrays made of silica spheres with various volume fractions. All of them indicated visible range diffractions and the peak of diffraction were shifted to low wavelength range with increasing of volume fraction, just as liquid-phase colloidal crystalline array (Fig. 1). As these peak positions were almost the same as those of nonimmobilized array, the structure of the three-dimensional array was kept with immobilizing process. This suggests that the creation of a PEGA/PEGDA polymer network around the ordered spheres does not significantly disrupt the long-range order and photopolymerization results in a minor alteration of the stop band positioning. This array forms a solid hydrogel which locks in the periodic order; the array will remain stable in the presence of these polymerizable species provided that the monomers do not contain ionic

TABLE I
Stability of the Non Close-Packed Colloidal Crystalline Array in the Dispersion with Addition of Various Hydrophilic Monomers into the Aqueous Dispersion

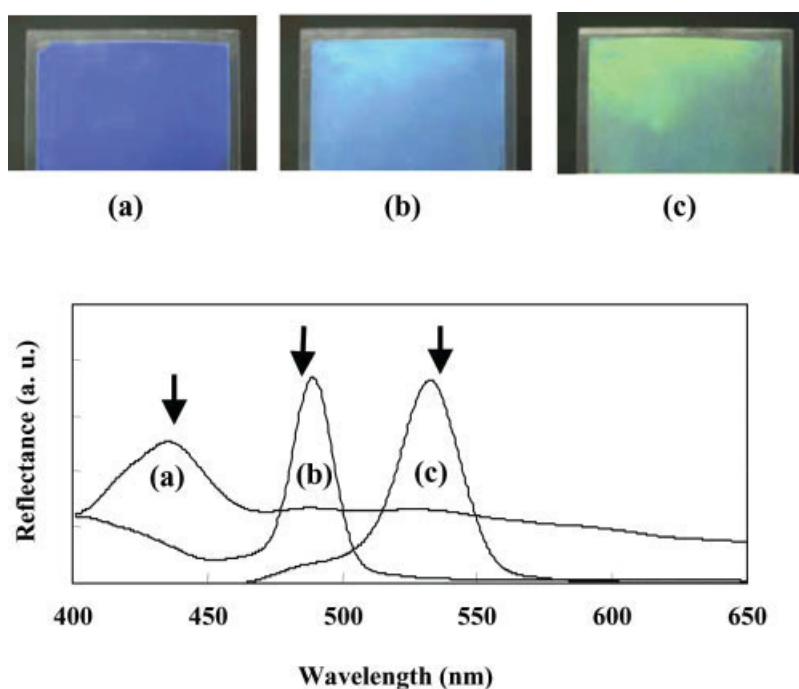| Monomers	MW	m.p.	Conc. (wt %)			
			5	10	20	40
$CH_2=CH-CO-(OCH_2CH_2)_4-OCH_3$	262	−8	O	X	X	X
$CH_2=CH-CO-(OCH_2CH_2)_9-OCH_3$	482	6	O	O	X	X
$CH_2=CH-CO-(OCH_2CH_2)_{13}-OCH_3$	704	25	O	O	O	X
$CH_2=CH-CO-(OCH_2CH_2)_4-OCH_3$	286	−21	O	X	X	X
$CH_2=CH-CO-(OCH_2CH_2)_9-OCH_3$	506	−7	O	O	X	X
$CH_2=CH-CO-(OCH_2CH_2)_{13}-OCH_3$	726	12	O	O	X	X
$CH_2=CH-CO-(OCH_2CH_2)-OH$	116	−90	X	X	X	X

Figure 2 The appearance and reflection spectra of PEGA/PEGDA polymer-immobilized non close-packed colloidal crystalline arrays made of silica particles in aqueous dispersion with various volume fractions; (a) 10 vol %, (b) 7.5 vol %, (c) 5 vol %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

impurities. The polymerization results in only modest changes in the array ordering as evidenced by the modest alterations of the diffraction peak. The hydrogel film is very stable; addition of solutes does not perturb the array ordering since the lattice order no longer depends upon electrostatic interactions between spheres. Polymer network locks colloidal crystalline array in periodic order and stabilize against mechanical shock like weak shear, gravitational field, or thermal forces. However, the composite films contain at least 50 vol % water, resulting in their fragility and propensity for changes in optical performance with water content.

Figure 3 shows the angle-resolved reflection spectra of PEGA/PEGDA polymer-immobilized colloidal crystalline arrays made of 5 vol % silica spheres. The diffraction peak shifted to low wavelength range with increase of the angle. This behavior is explained by the Bragg eq. (1), which applies to diffraction of light caused from a crystalline lattice of colloidal spheres. The (111) planes of the colloidal crystalline array oriented parallel to the surface of the supporting substrate. In the measurements, the incident light and detector were both oriented perpendicular to the (111) plane of this lattice. When the incident light was rotated toward the (111) surface of the crystal within the zx- and zy-planes, the position of the diffraction peak shifted to the shorted wavelengths. As both spectra indicate short wavelengths shift, these colloidal crystalline array may be face-centered cubic structure. The spectrum evolves
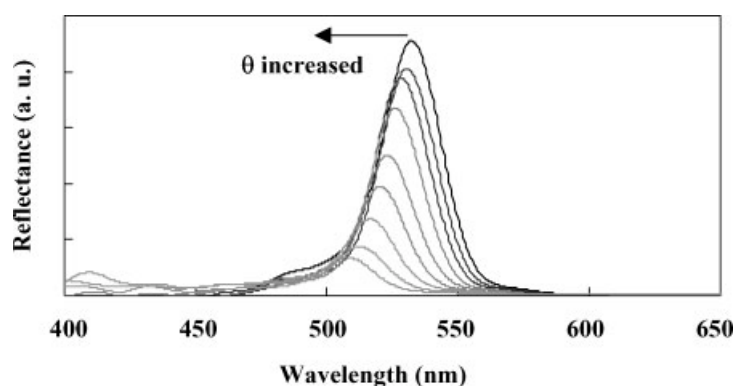

Figure 3 The angle-resolved reflection spectra of PEGA/PEGDA polymer-immobilized non close-packed colloidal crystals made of 5 vol % silica particles.
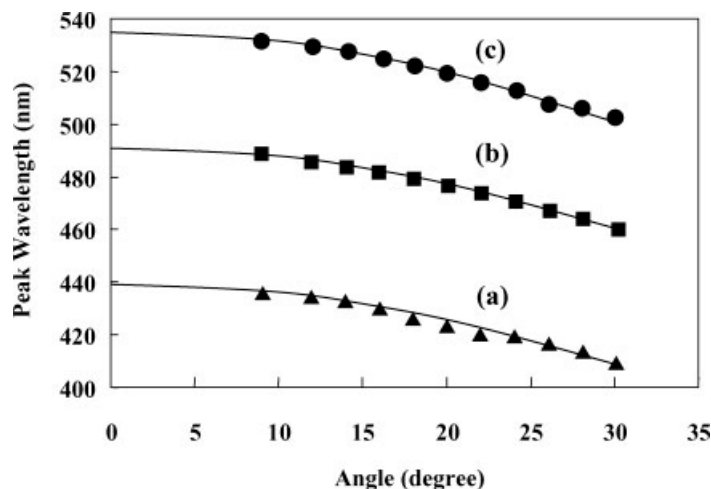
Figure 4 The relationship between an incident angle and the peak of reflection spectra of PEGA/PEGDA polymer-immobilized non close-packed colloidal crystalline arrays made of silica particles in aqueous dispersion with various volume fractions; (a) 10 vol %, (b) 7.5 vol %, (c) 5 vol %.

gradually with increasing θ angle. The peak wavelength of the reflection spectra corresponds to the resonance on a set of (111) plane as a function of the angle. The same results were obtained with 7.5 vol % and 10 vol % dispersions.

The relationship between incident angle and peak of reflection spectra with various volume fractions are shown in Figure 4. The very smooth fitting also supports the view that these structures diffract based on the Bragg law. Fitting of eq. (1), n_{eff} and d_{111} of these arrays are derived in Table II. With increase of the volume fraction, n_{eff} increased and d_{111} decreased. Increase of n_{eff} is caused from increase of refractive index of the dispersion, as refractive index of silica is higher than those of polyethylene glycol acrylate polymer and water. And decrease of the d_{111} is caused from compression of the electrostatic double layer, which raise electrostatic repulsion.

Figure 5 shows the phase image of the colloidal crystalline arrays made of 10 vol % silica spheres. As silica spheres are harder than PEGA/PEGDA polymer matrix, we could observe not only surface layer spheres, but also under lattice layer spheres. So the same probability exists for either stacking sequence, eventually leading to the hexagonal close packed (hcp) phase if the sequence is A B A B. . . to the fcc arrangement if it is A B C A B C. . . . Particles in the second lattice plane are positioned different from those in the first plane, and those in the third plane are different from those in the first and second plane, likely A B C A B C. . . (Fig. 5). This means the crystalline array structure of the PEGA/PEGDA polymer-immobilized colloidal crystals is face-centered cubic (fcc) and supports the results of angle dependence reflection behavior (Fig. 4).

Figure 6 shows scanning probe microscope (SPM) topographic images of the colloidal crystalline arrays

made of various volume fractions of silica spheres. As PEGA/PEGDA polymer matrix included water, what is called "polymer gel" and the matrix partially dried in the condition of SPM observation, silica sphere was contrast to the matrix and was observed clearly. The phenomena of decreasing interparticle distance with increasing volume fraction were detected. The interparticle distances of 10 vol %, 7.5 vol %, and 5 vol %, which were estimated from SPM images were about 180 nm, 200 nm, and 220–240 nm, respectively. These results from SPM correspond to those derived from angle-resolve reflective spectrum. We could demonstrate the microstructure of the polymer-immobilized non close-packed colloidal crystalline array directly. These composite films of polymer-immobilized non close-packed colloidal crystalline array are mechanically robust and exhibit a mechanochromic response. Because of the free spaces inside non close-packed colloidal crystalline arrays, the photonic band gap energy and the dispersion relation of the refractive index of the charged colloidal crystal can be tuned by mechanical stress. Those open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal.

TABLE II
Effective Refractive Index n_{eff} and Interplaner Spacing d_{111} of PEGA/PEGDA Polymer-Immobilized Non Close-Packed Colloidal Crystalline Array Derived from Angle-Resolve Diffraction Spectra and Interparticle Distance d Derived by Using of the Assumption of Face-Centered Cubic Crystalline Structure

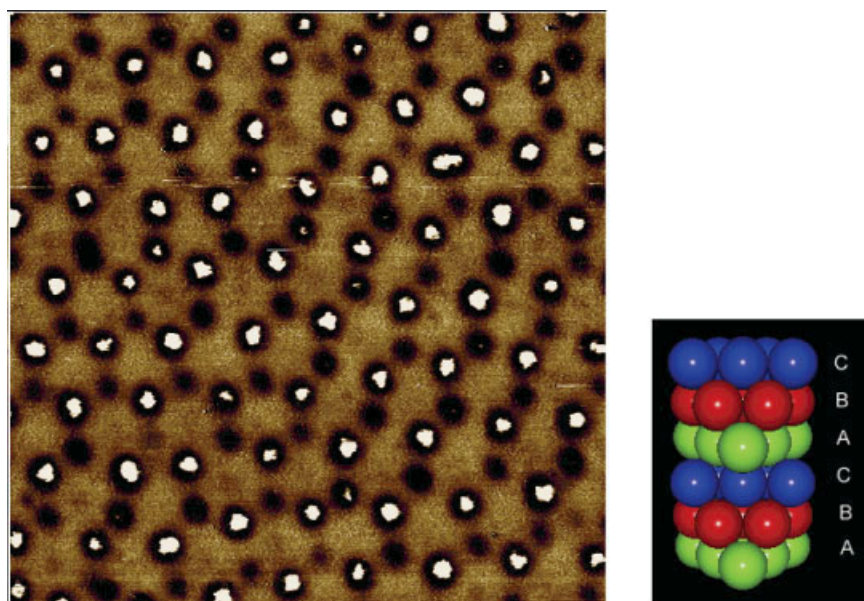|	n_{eff}	d_{111}	d
10 vol %	1.47	160.4	185.2
7.5 vol %	1.42	172.6	199.3
5 vol %	1.40	191.0	220.5

Figure 5 The phase image of scanning probe microscope about PEGA/PEGDA polymer-immobilized non close-packed colloidal crystalline array made of 10 vol % silica particles. The scale bar in the inset corresponds to 200 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

We have formed non close-packed silica colloidal crystalline arrays in aqueous dispersion and investigated to immobilize the colloidal crystalline arrays with hydrophilic polyethylene glycol acrylate (PEGA) polymer. Above nine of ethylene glycol chain length and below 10 wt % of monomer concentration in the dispersion, the condition of the three-dimensional array in the aqueous dispersion is kept with immobilizing process. To examine microstructures of the immobilized colloidal crystalline array, the angle-resolved reflection spectrum and scanning probe spectroscopy

(SPM) were used. Angle-resolved reflection spectra indicated that refractive index increased and interplaner spacing decreased with increase of the particle volume fraction. The SPM phase images proved the crystal structure of the immobilized colloidal crystalline array of face-centered cubic (fcc) structure. The interplaner spacings of the crystalline structure derived from angle-resolved reflection spectra agreed with those derived from SPM topographic images. We have demonstrated the microstructure of the polymer-immobilized colloidal crystalline array directly and open the possibility of tuning the microstructure of colloidal crystalline array for photonic crystal.
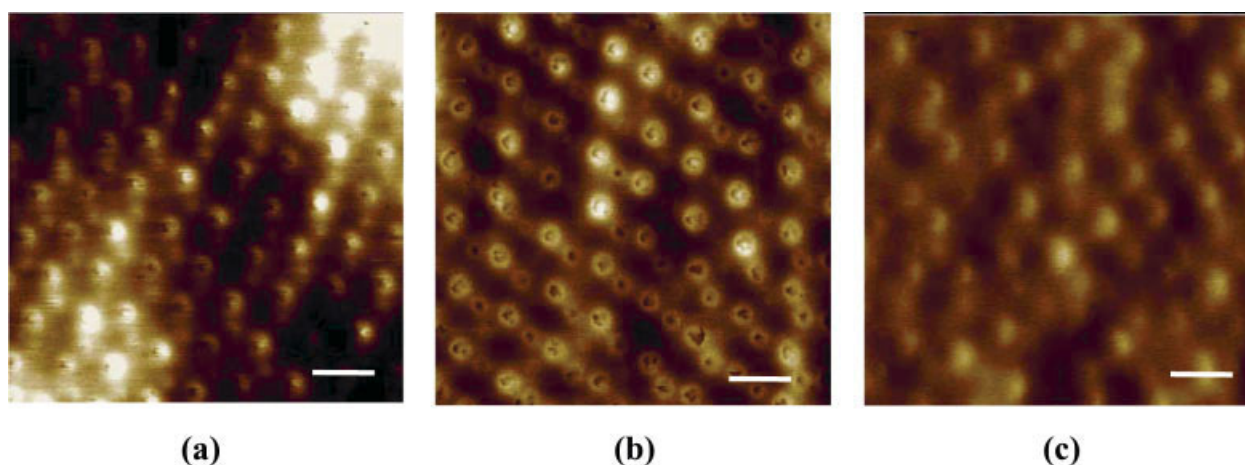

Figure 6 The topographic images of scanning probe microscope about PEGA/PEGDA polymer-immobilized non close-packed colloidal crystalline arrays made of silica particles in aqueous dispersion with various volume fractions; (a) 10 vol %, (b) 7.5 vol %, (c) 5 vol %. The scale bar in the inset corresponds to 200 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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