

Fabrication of nanodiamond-dispersed composite holographic gratings and their light and slow-neutron diffraction properties

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We demonstrate the use of nanodiamond in constructing holographic nanoparticle-polymer composite transmission gratings with large saturated refractive-index modulation amplitudes at both optical and slow-neutron wavelengths, resulting in efficient control of light and slow-neutron beams. Nanodiamond possesses a high refractive index at optical wavelengths and large coherent and small incoherent scattering cross sections with low absorption at slow-neutron wavelengths. We describe the synthesis of nanodiamond, the preparation of photopolymerizable nanodiamond-polymer composite films, the construction of transmission gratings in nanodiamond-polymer composite films, and light optical diffraction experiments. Results of slow-neutron diffraction from such gratings are also presented.

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I. INTRODUCTION

Nanodiamond (ND), an intriguing allotrope of carbon, is a carbon nanoparticle with truncated octahedral architecture [1–3]. ND has been of considerable interest because they are considered to possess superior mechanical, thermal, electrical and optical properties of diamonds such as high hardness, high Young's modulus, low coefficient of friction, high thermal conductivity, low thermal expansion, low heat capacity, high insulation, large bandgap, and high refractive index. These advantages could potentially lead to various applications including alternative composite materials, additive, abrasive, lubricant, plating, heat dissipation materials, biomedical and medicine materials for drug delivery systems and biosensing and imaging, electronics, magnetic recording, coating, luminescent materials, nonlinear optical materials, and single-photon emitters and spin detectors for quantum optics and photonics [4–7]. Here we report on the realization of ND-dispersed nanocomposite holographic gratings for efficient control of light and slow-neutron beams, formed in the so-called photopolymerizable nanoparticle-polymer

composite (NPC) [8], where nanoparticles (ND particles in this case) are uniformly dispersed in monomer capable of radical-mediated chain-growth or step-growth photopolymerization.

Since our first report on volume holographic recording in an NPC dispersed with TiO₂ nanoparticles [9], NPC gratings using various types of inorganic and organic nanoparticles such as SiO₂ [10,11], ZrO₂ [12–15], ZnS [16], luminescent nanoparticles and nanorods [17,18], nanotubes [19], zeolites [20], semiconductor quantum dots [21,22], and hyperbranched polymer [23,24] were reported. The dispersion of nanoparticles in recorded holographic gratings results in large saturated refractive-index modulation amplitudes (Δn_{sat}) and simultaneously makes their mechanical and thermal stability higher in comparison to those recorded in a conventional all-organic photopolymer [25,26]. It was also shown that optical nonlinearities were induced in NPCs dispersed with nanoparticles possessing large optical nonlinearities including nonlinear Bragg diffraction [27], optical multistability [28], light-induced transparency [29], and nonlinear multiwave mixing [30] due to cascaded high-order optical nonlinearities associated with the local-field enhancement [31]. NPCs using various nanoparticles can be used for photonic applications such as holographic data storage [32,33], volume holographic optical elements for wearable headsets

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[34,35], security holograms [18], and distributed feedback plastic lasers [36].

Moreover, in the quest for the realization of efficient slow-neutron beam control and ultrahigh precision measurements using neutron interferometers [37], we have also demonstrated various manipulations of slow-neutron beams at a few nm wavelengths with NPC transmission gratings dispersed with SiO₂ or ZrO₂ nanoparticles. These include two and multibeam splitting and beam deflection with up to 90% efficiency [38–40], i.e., deflective mirror-like functionality. In order to realize such high diffraction efficiency, it is necessary to effectively increase the interaction length of an NPC transmission grating of one-hundred microns thickness by tilting it at a large angle (up to 70°) about an axis parallel to the grating vector. Such a large increase in the effective grating thickness is, however, detrimental to some device applications since it introduces a substantive increase in incoherent scattering and absorption loss of a slow-neutron beam propagating in supporting glass substrates and a host polymer material [41]. It is also better to avoid a large grating tilt in order not to cause a substantial decrease in the diffraction efficiency due to the increased angular selectivity of the tilted grating for a slow-neutron beam with the finite beam divergence of the order of 1 mrad. In order to circumvent such disadvantages, one needs to increase Δn_{sat} for slow neutrons, $\Delta n_{\text{sat},N}$, instead of increasing the effective grating thickness. This calls for an alternative type of nanoparticle possessing stronger interactions with slow neutrons than SiO₂ and ZrO₂ nanoparticles.

In this paper we describe alternative NPC gratings dispersed with ND for light and slow-neutron diffraction. High hardness and low thermal expansion as well as high refractive index of ND in ultraviolet and visible spectral regions provide the realization of highly efficient NPC phase gratings with large Δn_{sat} and high environmental stability. ND is also considered useful in neutron optics for possessing very large coherent and very small incoherent scattering cross sections with low absorption for neutrons [42]. For example, quasispecular reflection of cold neutrons from ND powders was demonstrated [43,44]. ND also provides a possibility for efficient slow-neutron beam manipulation by NPC phase gratings of only a few tens of microns thick as we demonstrated recently [45]. Here we describe the synthesis of ND, the preparation of the NPC, recording of ND-dispersed transmission NPC gratings, and the light optical diffraction experiments. We conclude with results on slow-neutron diffraction from ND-dispersed NPC gratings.

II. HOLOGRAPHIC GRATING FORMATION IN NPC MEDIA

The basic idea of using nanoparticles as secondary species stems from the fact that an increase in the

refractive-index change per one diffusing monomer molecule requires a high refractive index of the monomer in organic multicomponent photopolymer systems [46]. The incorporation of inactive nanoparticles in host photopolymer gives a much higher refractive-index modulation amplitude (Δn) in holographic recording as compared with conventional binder-based photopolymers when a difference in refractive index between nanoparticles and the formed polymer is sufficiently large. The inclusion of nanoparticles also contributes to the suppression of polymerization shrinkage and the improvement of thermal stability [11,25]. The basic mechanism of holographic grating formation can be described as follows: suppose that nanoparticles (ND particles in our case) are uniformly dispersed in a host monomer capable of radical photopolymerization as shown in Fig. 1(a). Spatially nonuniform light illumination produces free radicals by dissociation of initiators and the subsequent reaction of free radicals with monomer molecules leads to the polymerization reaction between monomer radicals and individual monomer molecules in the bright regions. This polymerization process lowers the chemical potential of the monomer in the bright regions, leading to the migration (diffusion) of monomer molecules from the dark to the bright regions. On the other hand, photoinsensitive nanoparticles experience counterdiffusion from the bright to the dark regions since they are not consumed by light exposure and their chemical potential increases in the bright regions due to the consumption of the monomer. Such a polymerization-driven mutual diffusion process essentially continues until the photopolymerization completes. In this way the mutual diffusion of monomer molecules and nanoparticles results in the periodic assembly of nanoparticles during holographic exposure [see Fig. 1(b)] and a refractive-index grating (a phase hologram) is created

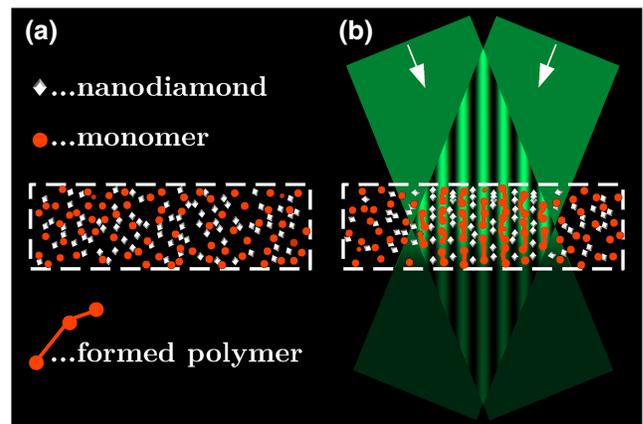


FIG. 1. Schematic of distributions of constituents (monomer, the formed polymer and nanoparticles) (a) before and (b) during holographic exposure to describe the process of holographic assembly of nanoparticles in the formed polymer.

owing to a compositional and density difference between the bright and the dark regions. Indeed, it is confirmed experimentally that the distribution of dispersed inorganic nanoparticles follow the light-intensity interference pattern in the formed polymer: a phase shift of π between the periodic density distributions of formed polymer and inorganic nanoparticles is induced as a result of the mutual diffusion [47–49].

Generally, NPC volume gratings with large Δn_{sat} at short grating spacings are required for light and slow-neutron optics applications for high diffraction efficiency [8]. In particular, thin volume holographic gratings with very large Δn_{sat} ($> 2 \times 10^{-2}$) are required for wearable headsets for augmented and mixed-reality applications in visible spectral regions in order to obtain high diffraction efficiency and wide fields of view [50,51]. In slow-neutron optics a diffractive mirror with $\eta \sim 100\%$ requires large $\Delta n_{\text{sat},N}$ at slow-neutron wavelengths, moderate film thickness, and short grating spacing [39]. Regardless of the wavelengths considered, Δn_{sat} of a holographic phase grating with the first-order (Bragg-matched) periodic spatial modulation formed in NPC media is approximately given by (see Appendix A for a detailed derivation)

$$\Delta n_{\text{sat}} = a_1 \Delta f |n_{\text{NP}} - n_p|, \quad (1)$$

where n_{NP} (n_p) is the refractive index of a nanoparticle (the formed host polymer) at either a light or a slow-neutron wavelength, and Δf is the amplitude of a sinusoidally modulated spatial density of dispersed nanoparticles at their spatially dependent volume fraction f_{NP} (see Appendix A). Here Δf is either smaller than or equal to the spatially averaged volume fraction \bar{f}_{NP} . The parameter a_1 is twice the magnitude of the first-order Fourier component of the refractive-index modulation of a phase grating, i.e., it is unity for a pure sinusoidal waveform and is $4 \sin(r\pi)/\pi$ for a rectangular waveform, with the duty ratio r of the concentration distribution in volume between nanoparticle-rich and -poor regions.

Equation (1) implies the following chief ingredients for the enhancement of Δn_{sat} : (i) a near-sinusoidal form of f_{NP} to minimize the high-order diffraction signals, (ii) large Δf by efficient mutual diffusion of nanoparticles and monomer under holographic exposure, and (iii) large $|n_{\text{NP}} - n_p|$. Item (i) is usually difficult to achieve since the photopolymerization-driven mutual diffusion process is nonlinear, so that the spatial waveform of f_{NP} would contain high-order components [52]. Item (ii) can be realized by large \bar{f}_{NP} and the facilitation of mutual diffusion under appropriate viscosity of the NPC system. Item (iii) is possible in the visible light spectral region since n_p is generally of the order of 1.5 but n_{NP} can be much larger than n_p . ND is a good choice of nanoparticle species for the enhancement of Δn_{sat} at visible light wavelengths

since it possesses a large value of n_{NP} (approximately equal to 2.42 for bulk diamond). In neutron optics the neutron refractive index (n_N) at a neutron wavelength (λ_N) in matter is approximately given by the following formula [53]:

$$n_N = 1 - \frac{\lambda_N^2}{2\pi} b_c \rho, \quad (2)$$

where b_c and ρ are the mean bound coherent scattering length and the atomic number density of matter, respectively. The primary requirement for the enhancement of $\Delta n_{\text{sat},N}$ at λ_N can be translated into a large absolute difference in the scattering length density (SLD) $b_c \rho$ between a nanoparticle and the formed polymer. In other words, nanoparticles having a large value for SLD are desired. Indeed, bulk diamond has a very large value of SLD to be about $11.8 \times 10^{-6} \text{ \AA}^{-2}$ [54], as compared with $2.08 \times 10^{-6} \text{ \AA}^{-2}$ for bulk Si, $3.64 \times 10^{-6} \text{ \AA}^{-2}$ for bulk SiO_2 , and $7.3 \times 10^{-6} \text{ \AA}^{-2}$ for bulk graphite [55], all of them used as materials for neutron beam diffraction at slow-neutron wavelengths and neutron optics in general. Even if the value for ND may be reduced to some extent as compared to that of bulk diamond due to several contaminations of graphite and other organic and inorganic materials on the surface of a ND core [2], the use of ND is highly favorable for constructing NPC gratings at slow-neutron wavelengths since such an NPC grating would possess Δn_{sat} up to 3 times as large as that dispersed with SiO_2 nanoparticles. Thus, high η at slow-neutron wavelengths at relaxed angular selectivity and small tilt angles is achievable. The latter features are very desirable to make slow-neutron beam experiments at limited intensities and with a finite beam divergence of several mrad. The use of ND for NPC gratings also provides other advantages such as very low incoherent scattering loss and low absorption for neutrons. Other approaches for fabricating (optically) thin diffraction gratings that are also used in neutron optics have been put forward in, for instance, Refs. [56,57].

Note that there is no reason why Eq. (1) should not also hold for neutrons. In light diffraction and slow-neutron diffraction experiments η depends on the product of Δn_{sat} being proportional to $a_1 \Delta f$ [see Eq. (1)] and the grating thickness (d). Because it is possible to estimate $a_1 \Delta f$ and d from light-diffraction measurements only, one can assess the performance of a recorded NPC grating at slow-neutron wavelengths from measured values for $a_1 \Delta f d$ and a known value for $|(b_c \rho)_{\text{NP}} - (b_c \rho)_p|$, or alternatively one can estimate $|(b_c \rho)_{\text{NP}} - (b_c \rho)_p|$ from optically estimated values for $a_1 \Delta f d$ and the measurement of η in slow-neutron diffraction experiments. Such discussions are given in Sec. III D.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Synthesis and analysis of nanodiamonds

1. Synthesis of surface-modified nanodiamonds

We synthesize a cluster of ND by the detonation of trinitrotoluene and hexogen charges between 40/60 and 60/40 in wt%. The purification process used to recover the detonated ND particles from the detonation soot involves the acid treatment in water solvent for the removal of metal oxides originated from a container, followed by the decantation treatment to remove residual graphite having sp^2 orbitals. Organic modification on the surface of each ND core is made with silane coupling agent in an organic solvent after the ultrasonication of ND aggregates with ceramic (ZrO_2) microbeads used as crushing agents. ND suspension sol is finally prepared in a solution of methyl isobutyl ketone (MIBK). Figure 2(a) illustrates a ND sol in a vial. The opacity indicates non-negligible broadband absorption in the visible as a result of remaining sp^2 graphite layers on the surface of a ND core. Figure 2(b) shows a transmission electron microscopy (TEM) image of surface-modified ND deposited on carbon-coated grids after evaporating a tetrahydrofuran suspension of the ND sol. It can be observed that each ND has the size of the core possessing the sp^3 structure to be approximately 4 nm on average and that they aggregate due to their lateral diffusion during the evaporation process. Note that remaining sp^2 layers are not detected in the TEM image.

2. Analysis of surface-modified nanodiamonds

In order to quantitatively examine remaining graphite components in surface-modified ND, we perform Raman spectroscopy by using a commercial Raman microscope (LabRAM HR Evolution LabSpec 6, HORIBA Scientific). Figure 3 shows the UV-Raman spectrum of synthesized ND after the purification process at an excitation laser wavelength of 325 nm and at excitation laser power of

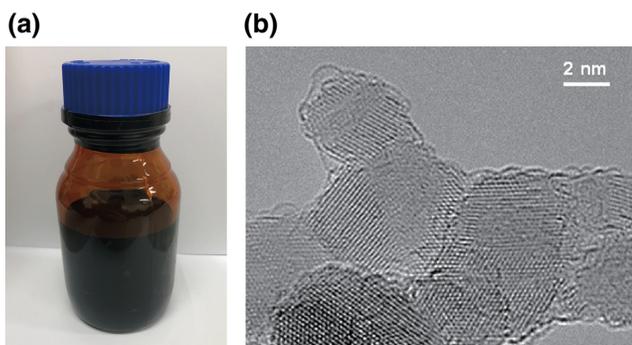


FIG. 2. (a) Photograph of a ND sol in a vial. (b) TEM image of surface-modified ND.

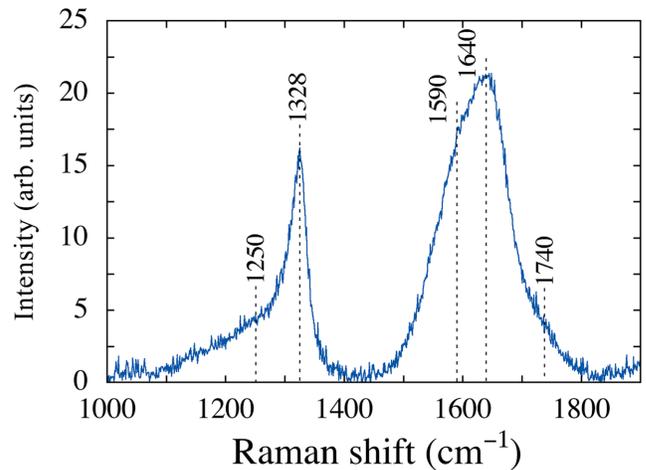


FIG. 3. Raman spectrum of surface-modified ND after the purification process.

0.8 mW. Clear Raman peaks can be attributed to a down-shifted peak at 1328 cm^{-1} from ND with respect to that from bulk diamond (1332 cm^{-1}) and to an O-H bending peak at 1640 cm^{-1} from one of the H_2O vibrational modes, respectively [2,58]. Other possible peaks from contributions from smaller ND particles or smaller coherent scattering domains separated by defects in larger ND particles at 1250 cm^{-1} , the G-band peak of graphitic sp^2 carbon at 1590 cm^{-1} and a $C=O$ stretching peak at 1740 cm^{-1} that is coming from surface functional groups [58] are not noticeable. However, it is known that the formation of non-diamond carbons occurs after the growth of the diamond sp^3 structure as a result of a decrease in pressure below the diamond-graphite equilibrium during detonation [58]. Therefore, such a noncarbon layer must remain on the ND surface even after the purification process, as is also confirmed from the opacity of the ND sol shown in Fig. 2(a). The content of graphitic sp^2 carbon is considered to be more or less a few wt% in our surface-modified ND as the relative Raman peak at 1590 cm^{-1} partially hidden in the broad peak centered at 1640 cm^{-1} is very similar to the result in Ref. [58].

We also carry out the thermogravimetric analysis (TGA) by using a commercial TGA and differential thermal analysis (DTA) system (EXSTAR TG/DTA6200, Seiko Instruments) to quantify the ratio of the components in the surface-modified ND. It is done at a heating rate of $20^\circ\text{C}/\text{min}$ from 25°C to 815°C under air flow. The mass ratio is calculated using the weight loss % at the onset temperatures of the decomposition of grafted organics, diamond and nondiamond carbon contents, and inorganic species. The result is shown in Fig. 4. It is found that grafted organics at 25.9 wt% attached by the silane coupling agent is decomposed first (see the second shoulder near 600°C) followed by the decomposition of the diamond and nondiamond carbon contents (ND and graphite)

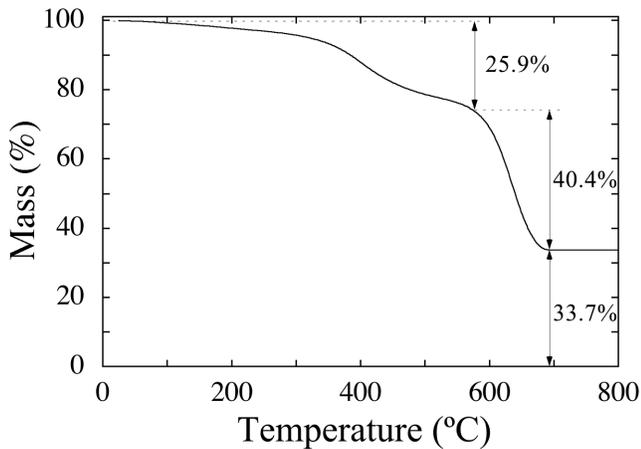


FIG. 4. TGA curve of surface-modified ND under an air flow.

at 40.4 wt% (see the abrupt change near 680°C), leaving behind the remaining metals and oxides such as ZrO_2 at 33.7 wt% introduced during the crushing and surface-modification processes.

We further measure the hydrodynamic size dispersion of the surface-modified ND. Figure 5 shows the size dispersion of surface-modified ND in tetrahydrofuran solution obtained by means of a dynamic light scattering instrument (Zetasizer, Malvern Panalytical). It is found that the size distribution exhibits a typical broad peak stemming from aggregates as reported for colloidal solutions of SiO_2 nanoparticle and ND [59,60]. The hydrodynamic median-average size (d_{50}) is approximately 9.6 nm that must include the outer layers of the surface-modified ND. This result indicates that the main volume of the surface-modified ND is occupied by soot (mainly the contents of graphite and ZrO_2) and organic components. From the results shown in Figs. 2(b)–5 we may deduce the geometric structure of a multilayered concentric sphere of our

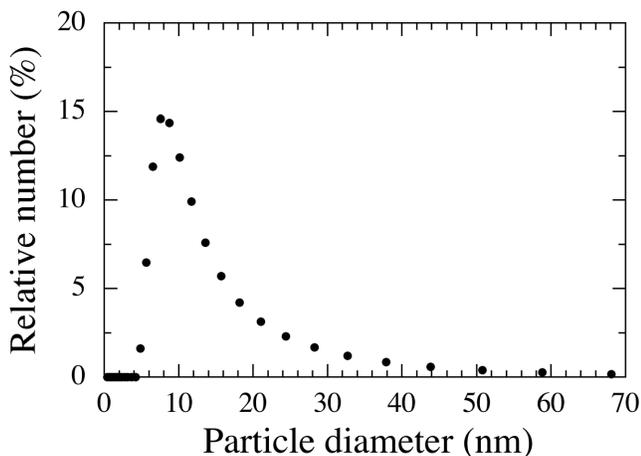


FIG. 5. Size distribution of surface-modified ND in tetrahydrofuran solution.

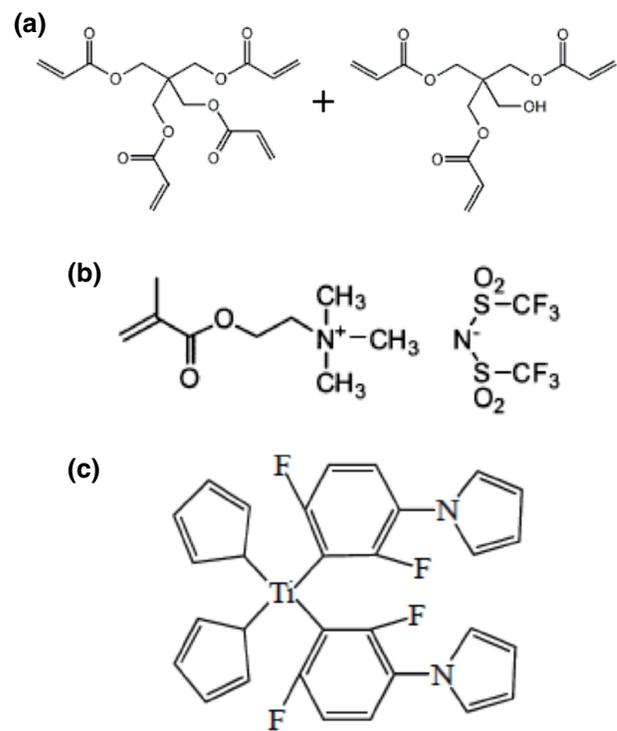


FIG. 6. Chemical structures of (a) PETIA, (b) MOE-200T, and (c) Irgacure784.

surface-modified ND by use of the core radius of the sp^3 ND (2 nm) and the radius of the surface-modified ND (4.8 nm) provided that a given wt% value of the graphite component in the surface-modified ND is used. Let us assume that the weight fraction of the ND core and graphite components are 35.4 and 5 wt%, respectively, resulting in the weight fraction of the diamond and nondiamond contents of 40.4 wt%, which would be an appropriate assumption for well-purified ND [61]. It is then straightforward to approximately estimate the relative volume fractions of the ND core and the shell portion (soot and organic layers). Using known numerical values for densities of bulk diamond (3.51 g/cm^3), graphite (2. g/cm^3), ZrO_2 (5.68 g/cm^3), and acrylate (1.18 g/cm^3), we find 7.2, 6.8, 18.3, and 67.7 vol% for ND, graphite, ZrO_2 and grafted organics, respectively. We can then estimate the layer thickness of each component measured from the surface of the ND core to be 0.5, 0.8, and 1.5 nm for graphite, ZrO_2 , and grafted organics, respectively.

B. Preparation of samples

We disperse the ND sol to a blend of two acrylate monomers, tri- and tetrapentaerythritol acrylate (PETIA, Daicel-ALLNEX Ltd.) of refractive indices of $n_D = 1.487$ and 1.515 in liquid and solid phases, respectively, and a single functional ionic liquid monomer (MOE-200T, Piotrek) of refractive indices of $n_D = 1.43$ and 1.45 in liquid and

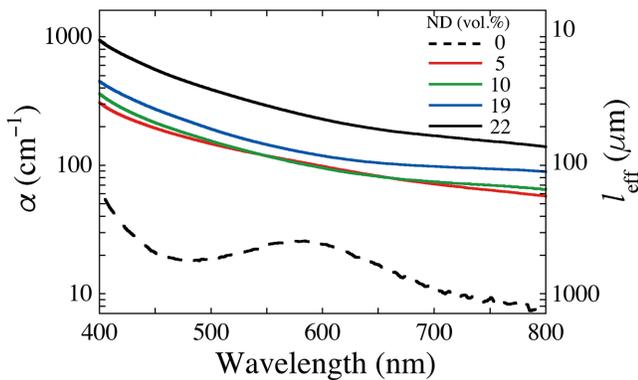


FIG. 7. Spectral absorption coefficients and the corresponding effective thickness for uniformly cured NPC-film samples at various doping concentrations of ND.

solid phases, respectively, at various ratios in wt%. The concentration of ND after evaporation of MIBK is as high as 22 vol%. As shown later, we find that the unity wt% ratio of PETIA to MOE-200T gave the highest value for Δn_{sat} . Titanocene (Irgacure784, Ciba) with the refractive index of $n_D = 1.76$ is used as a radical photoinitiator to provide the photosensitivity in the green. The concentration of the photoinitiator is 4.3 wt% with respect to the monomer blend. These chemical structures are shown in Fig. 6. MIBK is removed from the mixed syrup containing the ND sol. The syrup is kept in a vial at 60°C for 6 h and then cast on a spacer-loaded glass substrate. Finally, it is covered with another glass plate to be used as NPC-film samples.

Figure 7 shows spectral absorption coefficients α and the effective thickness [$l_{\text{eff}}(\equiv 1/\alpha)$] of uniformly cured NPC-film samples without and with ND at different doping concentrations. It can be seen that the optical absorption due to the inclusion of ND extends over the whole visible spectral range as seen in Fig. 2(a). However, it can also be seen that values for l_{eff} at a wavelength of 532 nm are of the order of 100 μm at ND concentrations lower than 20 vol%, substantially thick enough for our use as holographic gratings.

C. Holographic recording and light-diffraction experiments

1. Experimental setup for holographic recording and a method for data analysis

In a holographic recording experiment we use a two-beam interference setup to record unslanted and plane-wave transmission gratings in ND-dispersed NPC films at grating spacing (Λ) of 0.5 μm and 1 μm by two mutually coherent beams of equal intensities from a diode-pumped frequency-doubled Nd:YVO₄ laser operating at a wavelength of 532 nm. A low-intensity He-Ne laser beam

operating at a wavelength of 633 nm is employed as a readout beam to monitor the buildup dynamics of a recorded plane-wave transmission NPC grating since the photoinitiator employed is insensitive in the red. All the beams are *s* polarized. We characterize NPC gratings by measuring the buildup dynamics of the diffraction efficiency (η) at a probe wavelength of 633 nm. Here, η is defined as $I_1/(I_0 + I_1)$, where I_1 is the first-order diffracted probe intensity and I_0 is the transmitted probe intensity. Then, d is estimated by measuring the saturated η (η_{sat}) as a function of Bragg-angle detuning ($\Delta\theta_B$) from a phase-matched Bragg angle probed at 633 nm after the completion of the recording process and then by fitting the data to Kogelnik's coupled-wave formula that describes light diffraction in the Bragg (two-wave coupling) regime [62–64] as given by

$$\eta_{\text{sat}}(\Delta\theta_B) = \frac{\sin^2 \left\{ \frac{\pi \Delta n_{\text{sat}} d}{\lambda \cos \theta_B} \left[1 + \left(\frac{\lambda \cos \theta_B \sin \Delta\theta_B}{\Lambda \Delta n_{\text{sat}}} \right)^2 \right]^{1/2} \right\}}{1 + \left(\frac{\lambda \cos \theta_B \sin \Delta\theta_B}{\Lambda \Delta n_{\text{sat}}} \right)^2}, \quad (3)$$

where λ is a readout wavelength in vacuum, Λ is grating spacing and θ_B is a phase-matched Bragg angle inside a sample.

2. Light-diffraction properties

The buildup dynamics of Δn at 532 nm are evaluated by using Kogelnik's formula with the already measured buildup dynamics of η and d at 633 nm by multiplying the time series of Δn evaluated at 633 nm with a factor being the ratio of Δn_{sat} measured at 532 nm to that measured at 633 nm. The rationale of using Kogelnik's formula for evaluating d and Δn_{sat} is discussed later in this subsection.

Figure 8(a) illustrates a photograph of a ND composite grating (approximately 10 mm in diameter) recorded in an NPC-film sample dispersed with 19 vol% ND. Figure 8(b) shows the same grating viewed from the top. Good uniformity and high transparency of the grating are seen. The shallow brownish color is a result of absorption by the residual graphite component attached to the peripheral of ND particles. Figure 8(c) shows a TEM image of the cross section of the recorded grating. The dark (bright) banded areas correspond to high-concentration portions of ND (the formed polymer), confirming holographic assembly [47] of ND in the formed polymer.

Figure 9(a) shows the dependence on ND concentration of Δn_{sat} evaluated at a wavelength of 532 nm for a NPC grating of 1- μm spacing at different ratios of [MOE-200T] with respect to the sum of [PETIA] and [MOE-200T] all measured in wt%. The recording intensity at 75 mW/cm² is chosen so as to maximize Δn_{sat} . It can be seen that Δn_{sat} peaks at the ND concentration of 15 vol% and at [MOE]/([PETIA]+[MOE])=0.50,

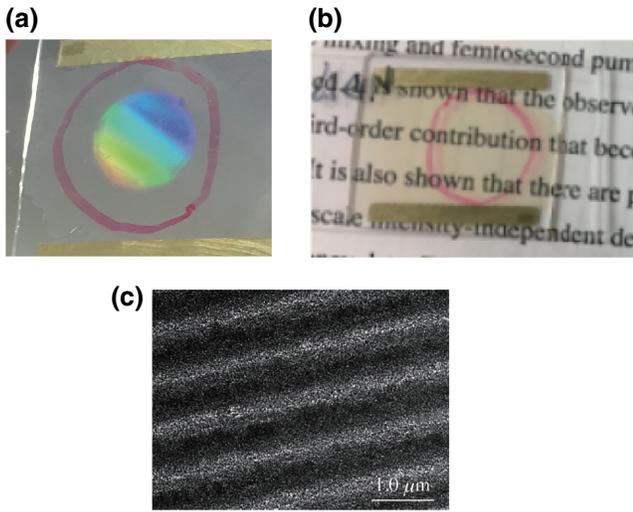


FIG. 8. (a) Photograph of a recorded NPC transmission plane-wave grating (circularly marked in red) at grating spacing of $1 \mu\text{m}$ under white-light illumination from a fluorescent lamp. (b) Photograph of the same grating viewed from the top. (c) TEM image of the cross section of the NPC grating.

i.e., $[\text{MOE}] = [\text{PETIA}]$ in wt%. The observed decrease in Δn_{sat} at ND concentrations higher than 15 vol% is caused by increased light scattering that results in a decrease in intensity-interference fringe contrast. The optimum condition of $[\text{MOE}] = [\text{PETIA}]$ maximizing Δn_{sat} is found by the following consideration: an increase in $[\text{MOE-200T}]$ lowers the viscosity of the blend monomer, facilitating the mutual diffusion of unreacted monomer and ND so that $a_1 \Delta f$ in Eq. (1) increases, as seen in Fig. 9(b). Too much addition of MOE-200T, however, inhibits the development of cross-linking network structures during holographic exposure, resulting in a decrease in $a_1 \Delta f$ and thus in Δn_{sat} . It can be seen in Fig. 9(b) that $a_1 \Delta f$ peaks at the ND concentration of 15 vol% ($\bar{f}_{\text{NP}} = 0.15$) and at $[\text{MOE-200T}] / ([\text{PETIA}] + [\text{MOE-200T}]) = 0.50$. But the peak value of 0.01 is much smaller than the ND concentration of 15 vol% (i.e., 0.15). We speculate that because the spatial density distribution of ND after holographic exposure is more or less rectangular with $r \approx 0.55$ [see Fig. 8(c)], such a small value (approximately equal to 0.07) for $a_1 \Delta f / \bar{f}_{\text{NP}}$ is caused by insufficient mutual diffusion of ND and monomer molecules during holographic exposure. A further increase in Δf by facilitating the mutual diffusion is necessary to increase Δn_{sat} . An increase in $|n_{\text{NP}} - n_p|$ due to a decrease in n_p at higher concentration of MOE-200T also contributes to an increase in Δn_{sat} but only marginally. In order to estimate $a_1 \Delta f$ from extracted values for Δn_{sat} [see Eq. (1)], we measure values for n_p of uniformly cured polymer films without ND dispersion at various ratios of $[\text{MOE-200T}]$ to $[\text{PETIA}]$ by means

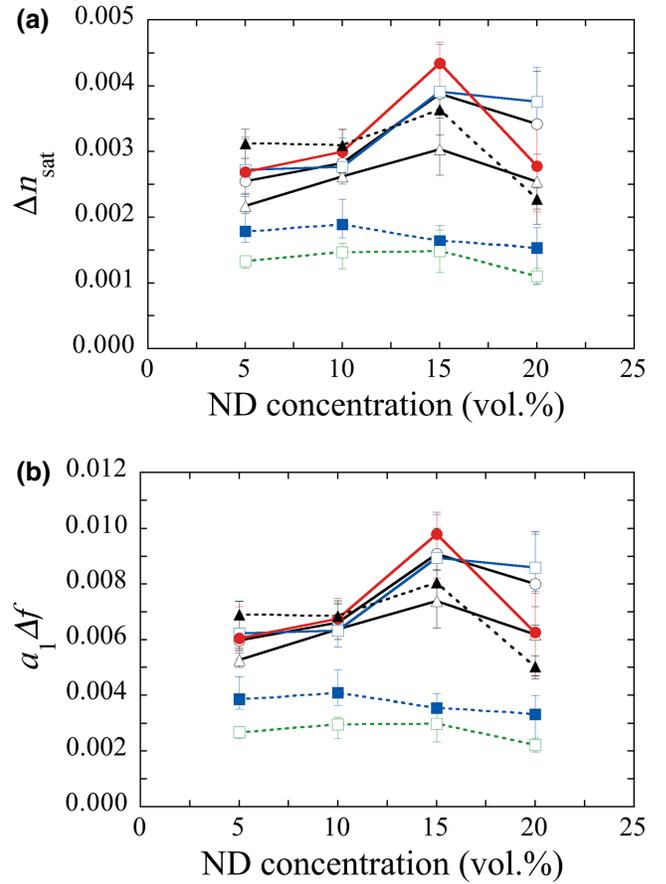


FIG. 9. Dependences of (a) Δn_{sat} and (b) $a_1 \Delta f$ on concentration of dispersed ND in an NPC grating of $1 \mu\text{m}$ spacing at different ratios of $[\text{MOE-200T}]$ with respect to the sum of $[\text{PETIA}]$ and $[\text{MOE-200T}]$. All symbols shown in the figures correspond to 0 (Δ), 0.25 (\circ), 0.40 (\square), 0.50 (\bullet), 0.60 (\blacktriangle), 0.75 (\blacksquare), 1 (\square), respectively.

of an Abbe refractometer (DR-M2, ATAGO). The refractive index of a surface-modified ND, n_{NP} , is evaluated from a refractive-index measurement of a ND-dispersed polymer film after uniform curing by the so-called m-line spectrometer by a prism coupler [65], from which n_{NP} is determined by 1.9420 via a volume fractional estimation using Eq. (A1) with help of the known n_p . A simple volume fractional estimation of n_{NP} by using our estimated volume fractions of the constituents shown in the previous subsection is also carried out. It is found that n_{NP} is 1.7713 with refractive indices of 2.4173 [66], 2.7733 [67], 2.1745 [68], and 1.492 [69] for diamond, graphite, ZrO_2 , and acrylate, respectively. The calculated value is lower than the measured one. We speculate that the main discrepancy results from the use of the simple volume fractional calculation: the geometric structure (i.e., a multilayered concentric sphere) must be taken into account in the calculation [70], which would be left for our future investigation.

Figure 10(a) shows the buildup dynamics of η at 532 nm, that is extracted from that at 633 nm, for an unslanted and plane-wave transmission NPC grating of $1\ \mu\text{m}$ spacing at the optimum ND concentration (15 vol %) and the optimum recording intensity ($75\ \text{mW}/\text{cm}^2$). Furthermore, we use the optimum ratio $[\text{MOE}]/([\text{PETIA}]+[\text{MOE}])$ of 0.5. We refer to this sample as NPC grating no. 1. We note

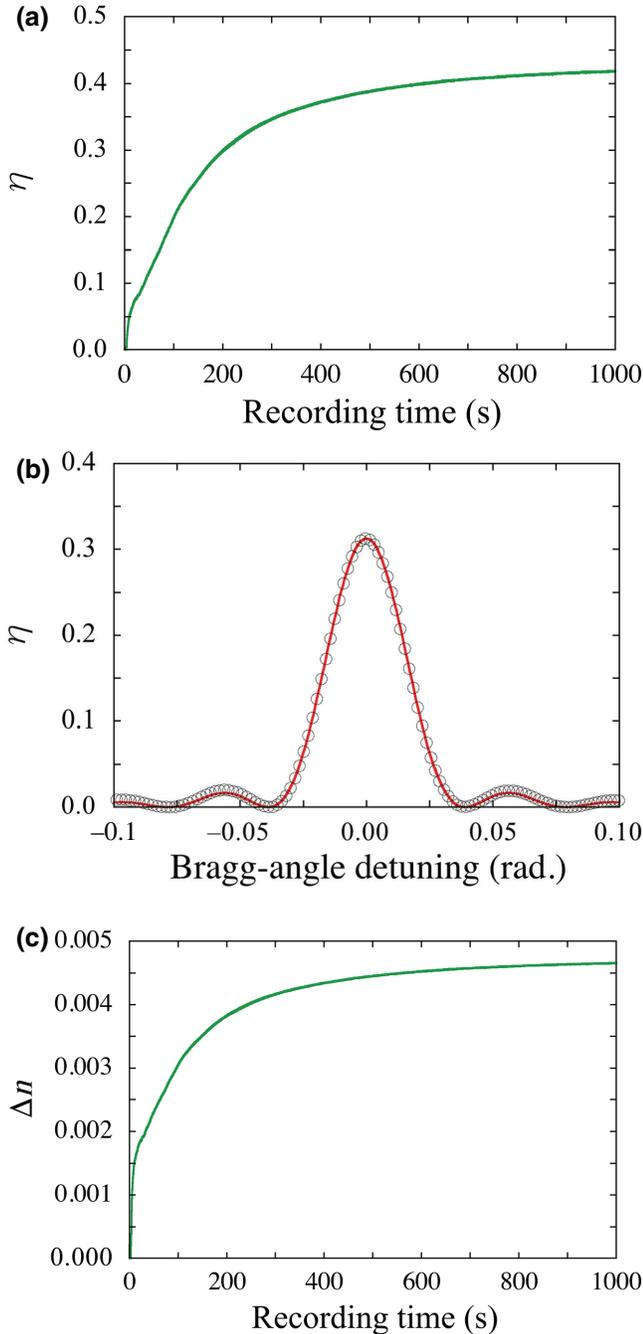


FIG. 10. (a) Extracted buildup dynamics of η at 532 nm from a ND composite grating of $1\ \mu\text{m}$ spacing. (b) Bragg-angle detuning curve at 633 nm. The solid line is the least-squares fit to the measured data. (c) Extracted buildup dynamics of Δn at 532 nm.

that the measured curve of η shown in Fig. 10(a) is presented at 532 nm in order to evaluate the performance of light diffraction at the same wavelength as a recording one (532 nm) in order for our present results to be applicable to a more generic case of non-plane-wave recording where readout has to be done at the same Bragg-matched wavelength. Figure 10(b) shows the Bragg-angle detuning curve probed at 633 nm after the saturation of η . The solid curve in red denotes the least-squares curve fit of the data to Kogelnik's formula from which we find d to be $25.29 \pm 0.02\ \mu\text{m}$. It can be seen that the curve fit follows well with the measured data, indicating that the recorded NPC grating is uniform along the film's thickness direction [63]. Figure 10(c) shows the corresponding buildup dynamics of Δn at 532 nm. It can be seen that NPC grating no. 1 has Δn_{sat} of approximately 4.7×10^{-3} . This value is similar to that reached by SiO_2 nanoparticle-dispersed NPC gratings at the same grating spacing used in previous slow-neutron diffraction measurements [38,40]. We also find values for $a_1 \Delta f$ and $a_1 \Delta f d$ to be approximately 0.011 and $0.268\ \mu\text{m}$, respectively, with $n_p = 1.4980$.

An unslanted and plane-wave transmission volume grating with a spacing of $0.5\ \mu\text{m}$ is also recorded in a ND-dispersed NPC film at the optimum ND concentration (15 vol %) and at the optimum recording intensity ($75\ \text{mW}/\text{cm}^2$). Furthermore, we use the optimum ratio $[\text{MOE}]/([\text{PETIA}]+[\text{MOE}])$ of 0.5. We refer to that sample as grating no. 2. Figure 11(a) shows the buildup dynamics of η at 532 nm, which is extracted from that at 633 nm. Figure 11(b) shows the Bragg-angle detuning curve probed at 633 nm after the saturation of η from which we find d to be $35.31 \pm 0.04\ \mu\text{m}$. Figure 11(c) shows the corresponding buildup dynamics of Δn at 532 nm. It can be seen that grating no. 2 has reached Δn_{sat} of approximately 2.2×10^{-3} , which is smaller than that of grating no. 1. Such a decrease in Δn_{sat} at shorter grating spacing is a typical trend of multicomponent photopolymer including NPC materials [8] as a result of facilitated photoinitiator's counter diffusion to, the cluster formation of photoinactive species in and the spatial extension of the polymer network into the dark regions. We also find $a_1 \Delta f$ and $a_1 \Delta f d$ to be approximately 0.005 and $0.175\ \mu\text{m}$, respectively. They are smaller than those of NPC grating no. 1. However, such a drawback in $a_1 \Delta f$ and $a_1 \Delta f d$ may be compensated for, to some extent, in slow-neutron diffraction for the following reasons: it is well known that the Klein-Cook parameter (Q) and the grating strength parameter (ν) classify wave diffraction in several diffraction regimes [71–74]. They are given by $Q = 2\pi\lambda d/n\Lambda^2$ and $\nu = \pi d \Delta n_{\text{sat}}/\lambda \cos \theta_B$, respectively, where λ is a readout wavelength in vacuum, n is the average refractive index of a phase grating of interest, and θ_B is the Bragg angle given by $\cos^{-1} \sqrt{1 - (\lambda/2n\Lambda)^2}$. When the conditions of $Q\nu/\cos \theta_B > 1$ and $Q/\nu \cos \theta_B > 20$ are met,

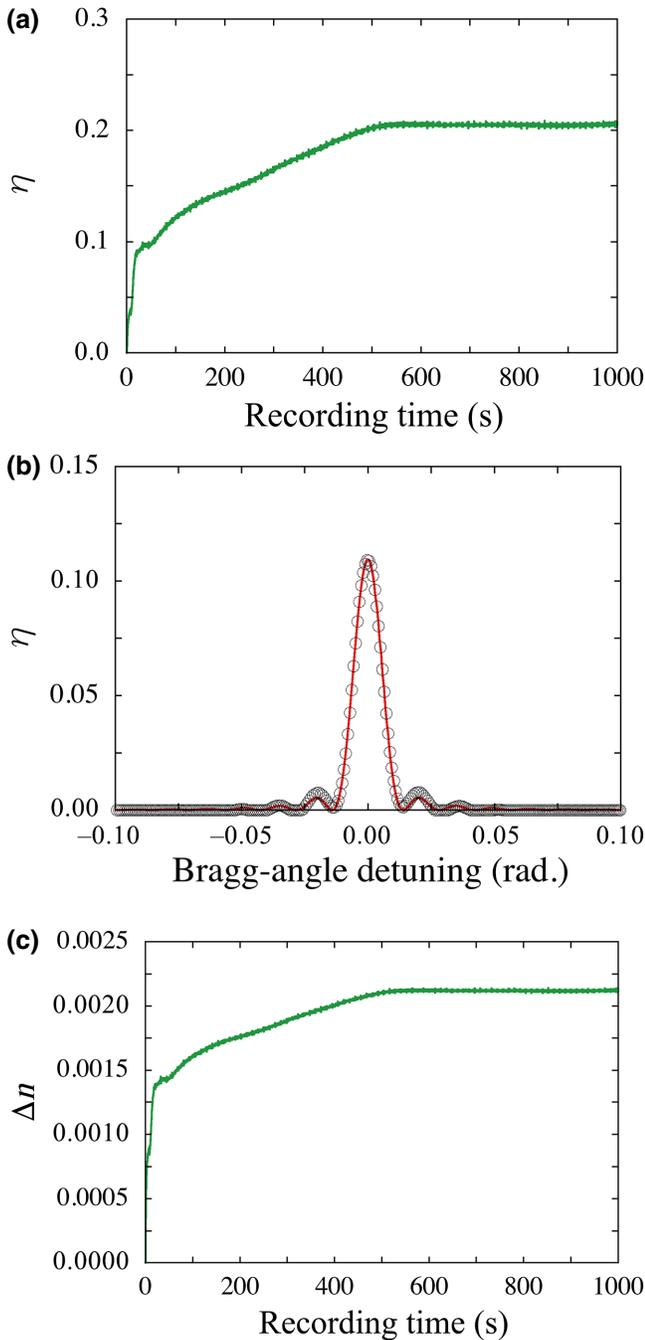


FIG. 11. (a) Extracted buildup dynamics of η at 532 nm from a ND composite grating of $0.5 \mu\text{m}$ spacing. (b) Bragg-angle detuning curve at 633 nm. The solid line is the least-squares fit to the measured data. (c) Extracted buildup dynamics of Δn at 532 nm.

diffraction occurs in the Bragg diffraction (two-coupled waves) regime, i.e., two waves propagate in a thick grating, resulting in detectable signal power only in the narrow angular range around the Bragg angle. In contrast, when the conditions of $Qv/\cos\theta_B < 1$ and $Q/v\cos\theta_B < 20$ are met, diffraction is in the Raman-Nath diffraction (multiple coupled waves) regime, which features many overlapping

diffraction orders almost independent of the angle of incidence in a thin grating. Otherwise, diffraction is in the intermediate diffraction regime, for which considerable overlap of diffraction orders occurs in spite of clearly observable dependence of the diffraction efficiency on Bragg detuning (or angle of incidence), described by the rigorous coupled-wave analysis (RCWA) [75]. In our case, gratings no. 1 and no. 2 have $(Qv/\cos\theta_B, Q/v\cos\theta_B)$ of (39, 77) and (157, 658), respectively, at $\lambda = 532 \text{ nm}$ and $n = 1.5646$. This means that light diffraction by both NPC gratings is in the Bragg-diffraction regime, confirming the validity of our analysis in evaluating d and Δn_{sat} . We also find that grating no. 2 has factors of approximately 4 and 10 in $Qv/\cos\theta_B$ and $Q/v\cos\theta_B$, respectively, as compared with those of grating no. 1. The result of our slow-neutron diffraction experiment is described in the next subsection.

D. Slow-neutron diffraction

1. Experimental setup and a method for data analysis

Neutron-diffraction experiments are carried out at the beamline PF2/VCN of the Institut Laue-Langevin (ILL) in Grenoble, France. The measurement principle is illustrated in Fig. 12. The gratings are—similarly to the light diffraction measurements—mounted in transmission geometry. With the gratings tilted to the angle ζ around an axis parallel to the grating vector in order to effectively adjust d , the incident angle θ is varied to measure Bragg-angle detuning curves in the vicinity of θ_B (as given by the Bragg equation $\lambda_N = 2\Lambda \sin\theta_B$) at a slow-neutron wavelength λ_N . Very cold neutrons with a broad wavelength distribution in the range of about 2.5 to 10 nm are available at PF2/VCN [76]. A Ti/Ni neutron mirror is necessary to redirect the incident neutron beam to make use of the full collimation length and to obtain a narrower wavelength distribution like the one shown in Ref. [41]. The divergence of the beam is about 2 mrad. A 2D detector with $2 \times 2 \text{ mm}^2$ pixel size is used to detect the diffraction spots. The typical measurement time per incident angular position θ is about 1 h. Since Λ is large compared to λ_N , $\theta_B \approx \lambda_N/(2\Lambda)$ is of the order of 3 mrad. Given the spatial resolution of the detector system (pixel size = $2 \times 2 \text{ mm}^2$), about one and a half meters distance had to be maintained between the grating and the 2D detector to be able to observe well-separated diffraction spots. We define the diffraction efficiency of the i th diffraction order as $\eta_i = I_i/I_{\text{tot}}$ ($i = 0, \pm 1, \pm 2, \dots$), where I_i and I_{tot} are the measured intensities of the i th and the sum of all measured diffraction orders, respectively. At each incident angle the sum over all pixels in each separated diffraction spot at the 2D detector (see Fig. 12)—each associated with one diffraction order—is calculated and the resulting intensities (corrected for background) plugged into the definition for η_i . While the second-order diffraction from grating no. 1 is clearly detectable, it is marginal for grating

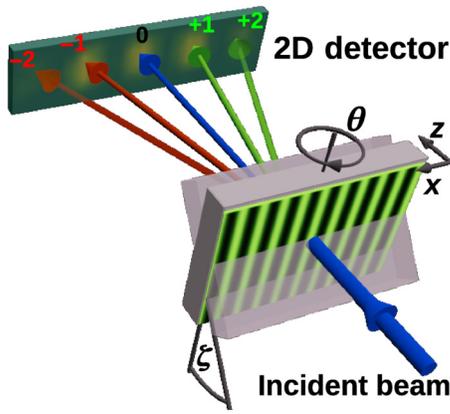


FIG. 12. Schematic of the measurement setup for slow-neutron diffraction by a NPC transmission grating. Upon stepwise rotation through angles θ about the y axis, the neutron beam incident from the lower right direction is split into several diffracted beams that are measured by a 2D detector. Neutrons arriving at corresponding diffraction-order positions are detected to calculate η_i of the i th diffraction order as a function of θ . The NPC transmission grating could be tilted by an angle $\zeta < 90^\circ$ to increase the thickness d by a factor $1/\cos \zeta$.

no. 2 and neglected in the analysis as well as in the data plots (see below).

For neutrons, the Klein-Cook and grating strength parameters can be written as $Q_N = 2\pi d\lambda_N/(\Lambda^2 \cos \zeta)$ and $\nu_N \approx \pi d\Delta n_{\text{sat},N}/(\lambda_N \cos \zeta)$, where we use that $\cos \theta_B \approx 1$. According to the criteria for assigning diffraction regimes at the end of Sec. III C, neutron diffraction by gratings no. 1 and no. 2 should be expected to occur in the RCWA diffraction regime and in the Bragg-diffraction regime, respectively, as $(Q_N \nu_N, Q_N/\nu_N)$ are (1.35, 3.53) and (6.50, 23.29) for gratings no. 1 and no. 2, respectively. Consequently, the data for gratings no. 1 and no. 2 should be analyzed by the RCWA and Kogelnik's coupled-wave theory, respectively.

2. Results of slow-neutron diffraction

In Fig. 13, Bragg-detuning curves for gratings no. 1 and no. 2 are plotted. For the data set of Fig. 13(a), least-squares fits with the RCWA are made (solid curves), whereas for the data set of Fig. 13(b), Kogelnik's coupled-wave theory is used for the fitting procedure (solid curves). Since both gratings are relatively thick (in terms of $Q_N \nu_N$ and Q_N/ν_N) so that they are expected to exhibit a considerable wavelength selectivity in η , we perform wavelength averaging by numerical integration of the product of the respective fit model function and a triangular or exponentially-modified-Gaussian-shaped wavelength distribution [41]. From both fits for gratings no. 1 and no. 2 we extract d , n_s [for $s = 1, 2$ in Eq. (A4)], $\bar{\lambda}_N$ and, $\Delta n_{\text{sat},N}$ [see Eq. (A7)].

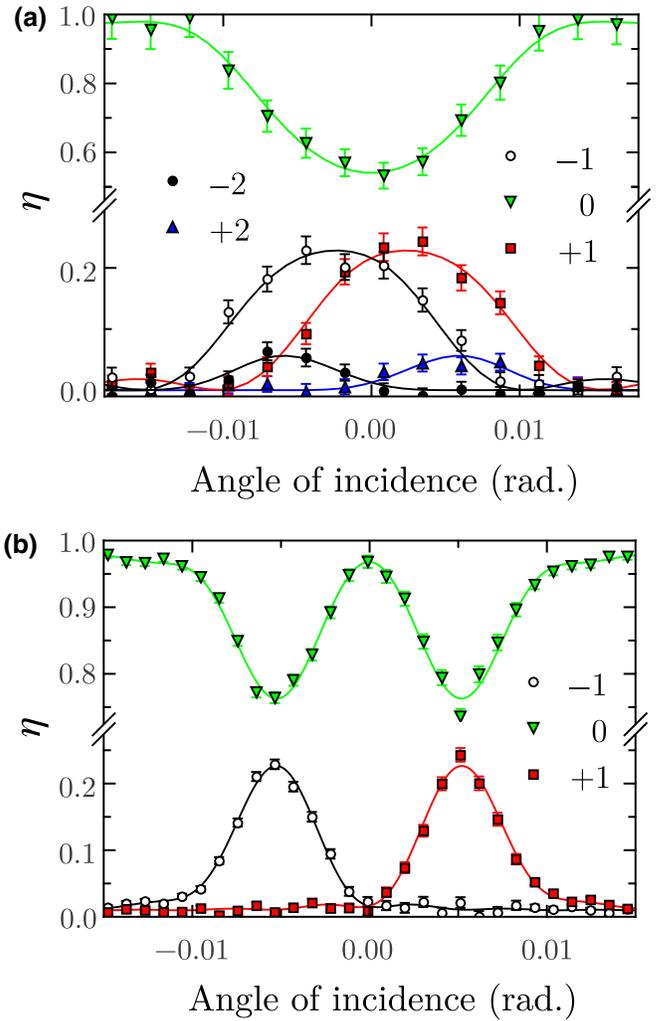


FIG. 13. (a) Bragg-angle detuning curve for grating no. 1 at $\bar{\lambda}_N$ of 4.75 nm, tilted at $\zeta \approx 70^\circ$. Solid curves correspond to least-squares fits of RCWA calculations to the data, additionally taking into account the wavelength distribution by averaging. (b) Bragg-angle detuning curve for grating no. 2 at $\bar{\lambda}_N$ of 5 nm, tilted at $\zeta \approx 70^\circ$. Note that a slight difference in $\bar{\lambda}_N$ from that in Fig. 13 (a) is due to the experiments having taken place during different beam times, with slightly different setups. Solid curves correspond to least-squares fits of Kogelnik's theory to the data, additionally taking into account the wavelength distribution by averaging. Data are made available by the ILL (see Refs. [77,78]).

A summary of parameter estimations for gratings no. 1 and no. 2 is given in Table I. The values for $a_1 \Delta f$ are obtained from the light-diffraction experiments described in the previous subsection.

As one can see, d as obtained from neutron diffraction agrees well with light-diffraction results. Considering the magnitudes of $\Delta n_{\text{sat},N}$ and n_2 for grating no. 1 points to the refractive-index profile of grating no. 1 not being completely sinusoidal, as $|n_2|$ is non-negligible compared to $|n_1|$. The minus sign of n_2 indicates that there is a phase

TABLE I. Summary of parameters for gratings no. 1 and no. 2. Uncertainties given here are based on rounding up the estimations produced by the fitting procedures and taking into account the usual precision in slow-neutron diffraction from NPC gratings (see, for instance, our Refs. [38–42]). Note that the tilt angle ζ is nonzero only in the slow-neutron experiments as shown in Fig. 12.

Grating	No. 1	No. 2
	($\Lambda = 1 \mu\text{m}$)	($\Lambda = 0.5 \mu\text{m}$)
Light diffraction		
d [μm]	25.29 ± 0.02	35.31 ± 0.04
Δn_{sat}	$\approx 4.7 \times 10^{-3}$	$\approx 2.2 \times 10^{-3}$
$a_1 \Delta f$	≈ 0.011	≈ 0.005
Slow-neutron diffraction		
d [μm]	25.0 ± 1.4	33.2 ± 1.4
$\bar{\lambda}_N$ [nm]	4.8 ± 0.3	5.0 ± 0.1
$\Delta n_{\text{sat},N} = 2 n_1 $ [$\times 10^{-5}$]	1.3 ± 0.1	0.9 ± 0.1
n_2 [$\times 10^{-6}$]	-1.9 ± 0.3	N/A (see text)
$(b_c \rho)_{\text{NP}}$ [$\times 10^{-6} \text{\AA}^{-2}$]	≈ 3.4	≈ 4.4

shift of π between the first and the second Fourier components of the refractive-index profile of this grating. This is consistent with our TEM observation of the nonsinusoidal ND density distribution after holographic exposure shown in Fig. 8. In contrast, the neutron diffraction measurements for grating no. 2 only showed negligible second-order contributions. Thus, the quantity n_2 is not available for this sample. The extracted value $\Delta n_{\text{sat},N}$ for slow neutrons is related to the SLD of ND, $(b_c \rho)_{\text{NP}}$, from Eqs. (1) and (2) such that

$$\begin{aligned}
 \Delta n_{\text{sat},N} &= a_1 \Delta f |n_{\text{NP},N} - n_{p,N}| \\
 &= a_1 \Delta f \left| 1 - \frac{\bar{\lambda}_N^{-2} (b_c \rho)_{\text{NP}}}{2\pi} - 1 + \frac{\bar{\lambda}_N^{-2} (b_c \rho)_p}{2\pi} \right| \\
 &= \frac{a_1 \Delta f \bar{\lambda}_N^{-2}}{2\pi} |(b_c \rho)_{\text{NP}} - (b_c \rho)_p| \\
 &\approx \frac{a_1 \Delta f \bar{\lambda}_N^{-2}}{2\pi} |(b_c \rho)_{\text{NP}}|, \tag{4}
 \end{aligned}$$

where the last step is acceptable for ND since values for SLD of polymer, $|(b_c \rho)_p|$, are typically around $1 \times 10^{-6} \text{\AA}^{-2}$, which is expected to be considerably smaller than $|(b_c \rho)_{\text{NP}}|$. Rearranging Eq. (4) to obtain

$$|(b_c \rho)_{\text{NP}}| = \frac{2\pi \Delta n_{\text{sat},N}}{a_1 \Delta f \bar{\lambda}_N^{-2}}, \tag{5}$$

we are now in a position to assess the SLD of ND in structured nanocomposite materials from light- and neutron-diffraction data. The estimations for SLDs for gratings no. 1 and no. 2 resulting from Eq. (5) are given in Table I. As expected, the two values for SLDs are not

very different from each other and are surely of the correct order of magnitude. The estimation for grating no. 1 is smaller than that for grating no. 2.

For comparison, we also perform an estimation for $|(b_c \rho)_{\text{NP}}|$ in an alternative way, i.e., by calculating the volume fractional averaged value of the surface-modified ND as done for its effective refractive index described in Sec. III B. We find $|(b_c \rho)_{\text{NP}}| \approx 3.0 \times 10^{-6} \text{\AA}^{-2}$ by using known bulk values for SLDs of diamond, graphite, ZrO_2 , and grafted organics (acrylate) with their volume fractions in our surface-modified ND. As one can see, we obtain the same order of magnitude and the numerical value of the estimation is quite close to the values in Table I, suggesting consistency of the two approaches. Obviously, as similar to the case of the effective refractive-index calculation, the volume fractional averaging procedure is not theoretically well supported for the structure of a multilayered concentric sphere. Despite this, the calculated value for $|(b_c \rho)_{\text{NP}}|$ is in good agreement with values obtained from our slow-neutron diffraction measurement, reflecting the effect of nondiamond components such as graphite and other inorganic and organic materials on the effective SLD of our surface-modified ND.

Since the slow-neutron diffraction efficiency of an NPC grating depends on $\Delta n_{\text{sat},N}$ that is proportional to $a_1 \Delta f$ [see Eq. (4)], another interesting possibility arising from the analysis in the present paper is the *a priori* assessment of slow-neutron diffraction properties of an NPC grating in advance from light-diffraction data (assessing $a_1 \Delta f$) only. Such quantitative information provides a solid estimation for predicting grating performance in slow-neutron diffraction experiments. In practice, the latter can be a valuable tool to save scarce neutron beam time that would otherwise be used inefficiently for samples of previously unknown low neutron-optical performance.

IV. CONCLUSION

We successfully demonstrate volume holographic recording in NPCs dispersed with ND at a recording wavelength of 532 nm. ND is synthesized by a detonation method, followed by the removal of residual graphite and the surface treatment. We find that the surface-modified ND can be uniformly dispersed in an acrylate monomer blend as high as 22 vol%. They act as nanoparticles and participate in the photopolymerization-driven mutual diffusion and phase-separation dynamics of ND and monomer during holographic exposure. As a result, such holographic assembly of ND in the formed polymer induces the spatial density modulation of ND, leading to the formation of ND-dispersed holographic phase gratings, which is evidenced by the observation of the cross section of a recorded grating. Unslanted and plane-wave transmission volume gratings with Δn_{sat} as high as 4.7×10^{-3} (2.2×10^{-3}) at a wavelength of 532 nm and at grating spacing

of 1 μm (0.5 μm) are recorded in NPC films dispersed with ND of 15 vol%. Because refractive-index differences between the surface-modified ND and the formed polymer are large at both visible and slow-neutron wavelengths, our proof-of-principle demonstration of recording high-contrast gratings paves the way for efficient manipulation of light and slow-neutron beams.

Our slow-neutron diffraction experiments show that ND-dispersed NPC gratings are excellent candidates for use in neutron optics. Their diffraction properties for slow neutrons have reached values almost comparable to those of the best SiO_2 -dispersed NPC gratings reported so far [38,39]. In particular, we demonstrate that ND-dispersed NPC gratings easily provide diffraction efficiencies higher than 20% at relaxed angular selectivity, preferable for loosely collimated slow-neutron beams with rather wide wavelength distributions. The rather high values of the diffraction efficiency of our NPC gratings at light and neutron wavelengths indicate that the NPC gratings do not exhibit any significant structural inhomogeneities. ND-dispersed NPC gratings presented here clearly possess a potential to outperform SiO_2 -dispersed NPC gratings. We also show that a good prediction of the expected slow-neutron diffraction performance of NPC gratings is possible from light-diffraction data only: by taking into account a refractive-index profile, $a_1 \Delta f$ (from light diffraction) and a literature value for SLD of dispersed nanoparticles, a solid prediction for $\Delta n_{\text{sat},N}$ and, thus, the slow-neutron diffraction efficiency can be made. Conversely, and probably more importantly, given some knowledge about a grating's refractive-index profile from light and neutron diffraction, it is possible to yield information about the SLD of a dispersed nanomaterial such as ND, in our case. Indeed, we develop a method to establish an estimation of SLD of the surface-modified ND, which may help to extract some information concerning the surface state.

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APPENDIX: REFRACTIVE-INDEX MODULATION AMPLITUDE FORMED IN NPC MEDIA

Consider an unslanted and plane-wave phase grating recorded in an NPC medium containing the formed host polymer of the refractive index n_p and dispersed spherical nanoparticles of the refractive index n_{NP} with their position-dependent and periodically modulated volume fractions of $f_p(x)$ and $f_{\text{NP}}(x)$ at a position x , respectively. We may approximate a periodically modulated refractive

index $n(x)$ with the grating vector \mathbf{K} along the x direction under the Maxwell-Garnett approximation [79] with $0 \leq f_{\text{NP}}(x) \ll 1$ and $n_p \approx n_{\text{NP}}$ as

$$\begin{aligned} n(x) &= n_{\text{NP}} f_{\text{NP}}(x) + n_p f_p(x) \\ &= n_p + f_{\text{NP}}(x)(n_{\text{NP}} - n_p), \end{aligned} \quad (\text{A1})$$

where the second equality comes from the relation that $f_p(x) + f_{\text{NP}}(x) = 1$ at any x . Since $n(x)$ is periodic in x , $f_{\text{NP}}(x)$ can be written as

$$f_{\text{NP}}(x) = \Delta f g(x), \quad (\text{A2})$$

where Δf is the modulation amplitude of $f_{\text{NP}}(x)$ and $g(x)$ is a dc-biased periodic function with an oscillation amplitude of ± 1 and the spatial period $\Lambda (= 2\pi/|\mathbf{K}|)$. Note that $\Delta f \leq \bar{f}_{\text{NP}}$, with \bar{f}_{NP} being the spatially averaged value of $f_{\text{NP}}(x)$ and $0 < \bar{f}_{\text{NP}} \ll 1$.

Furthermore, we note that $g(x)$ is a non-negative function and is much smaller than $1/\Delta f$, since $0 \leq f_{\text{NP}}(x) \ll 1$. It is expressed, in terms of a Fourier series, by

$$g(x) = \sum_{q=-\infty}^{\infty} g_q \exp(iqKx), \quad (\text{A3})$$

where $K = |\mathbf{K}|$ and $g_q = g_{-q}^*$ due to $g(x)$ being a real function. In particular, g_0 is given by $\bar{f}_{\text{NP}}/\Delta f$.

Likewise, $n(x)$ can be expressed in terms of a Fourier series by

$$n(x) = \sum_{s=-\infty}^{\infty} n_s \exp(isKx), \quad (\text{A4})$$

where $n_s = n_{-s}^*$ for a pure phase grating. Using Eqs. (A1)–(A4), we find

$$\begin{aligned} n_0 &= n_p + g_0 \Delta f (n_{\text{NP}} - n_p) \\ &= n_p + \bar{f}_{\text{NP}} (n_{\text{NP}} - n_p) \\ &= n_p \bar{f}_p + n_{\text{NP}} \bar{f}_{\text{NP}}, \end{aligned} \quad (\text{A5})$$

where $\bar{f}_p = 1 - \bar{f}_{\text{NP}}$ is used. Also, we find from Eqs. (A1)–(A3) that

$$n_s = g_s \Delta f (n_{\text{NP}} - n_p), \quad (s \neq 0). \quad (\text{A6})$$

Therefore, the refractive-index modulation amplitude Δn_{sat} of the first-order (Bragg-matched) component for

$n(x)$ is given by

$$\begin{aligned}\Delta n_{\text{sat}} &\equiv 2|n_1| \\ &= 2|g_1|\Delta f |n_{\text{NP}} - n_p|. \end{aligned} \quad (\text{A7})$$

When we set $2|g_1| = a_1$, we can express Δn_{sat} as

$$\Delta n_{\text{sat}} = a_1 \Delta f |n_{\text{NP}} - n_p|, \quad (\text{A8})$$

which is Eq. (1). It is straightforward to find from Eq. (A3) that a_1 is unity for a pure sinusoidal waveform of $n(x)$ and is $4 \sin(r\pi)/\pi$ for a rectangular waveform of $n(x)$.

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