Research Article

Study of the Carbonization and Graphitization of Coal Tar Pitch Modified with SiC Nanoparticles

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Silicon carbide nanoparticles (nSiC) have been used to modify coal tar pitch (CTP) as a carbon binder. The influence of ceramic nanoparticles on the structure and microstructure was studied. The structure of CTP-based carbon residue with various nSiC contents was analyzed by using SEM with EDAX, Raman spectroscopy, and X-ray diffraction. The effect of ceramic nanofiller on the crystallite sizes (L_c, L_a) and the c-axis spacing (d_{002}) in carbonized samples after heating from 1000 to 2800°C was analyzed. Ceramic nanofillers inhibit structural changes in carbonized samples heated to 1000°C. After heating CTP with nSiC above 2000°C, the carbon samples contained two carbon components differing in structural ordering. Ceramic nanoparticles increase carbon crystallite growth, while their impact on the c-axis spacing is low.

1. Introduction

Coal tar pitches (CTPs) are the most important binders used in the synthetic graphite industry due to their ability to form pure carbon residues in high yield, together with good adhesive properties after carbonization and graphitization [1]. Graphitized materials display the high electrical conductivity needed to produce electrodes for metal processing and anodes and cathodes for aluminium oxide electrolysis. Physical and mechanical properties of graphitic carbons make them unique materials for working under extreme conditions, that is, elevated temperature, corrosive ambient conditions, and thermal stresses [2]. These properties are directly related to the microstructure and the structure of carbon materials, which, in turn, are formed during high-temperature treatment. During the early stage of annealing to about 1000°C, chaotically oriented structural units (graphene layers) are formed and further high-temperature treatment is required to convert them into graphitic structure. Such structural changes lead to a decreasing band gap between the valence and conduction bands and to improvement of the electrical conductivity of the carbon [3].

At present, emphasis is focused on the development of carbon-based technologies involving improved methods of processing from raw materials to end products, taking into account new environmental regulations and energy efficiency aspects. In particular, energy consumption is considered when producing some graphite products, requiring temperatures close to 3000°C. Thus, improved energy efficiency for the manufacture of graphite products by optimization of the graphitization process seems to be a challenge for this industry.

The study presents one of the possible ways to manufacture carbon electrode products at lower processing temperatures.

Silicon carbide is known as a filler that can improve the oxidation resistance of carbon materials [4–7]. This component has already found application in C/C composites [8–10]. SiC in various nanometric forms can also enhance the mechanical properties of synthetic carbons [11–15].

Nano-Si-derived additives including nSiC can act as graphitization catalysts [16–18]. Conversion of silicon component into carbide phase in the presence of CTP-based carbon may occur already at 1300°C [19, 20]. The presence of SiC phase in

carbon matrix may lead to a change in the mechanism of the graphitization process. This ability seems to be a promising way of enhancing the structural and microstructural changes of graphitized materials and optimizing high-temperature processing to manufacture them at lower graphitization temperatures.

The objective of the study was to determine the influence of nSiC particles on CTP conversion into carbon and graphitic phases.

2. Materials and Methods

CTP with softening point 103°C was modified with nSiC, 45–55 nm particle size from NanoAmor.

First, nSiC filler was deagglomerated in ethanol suspensions by a sonication process. DLS analysis of the as-received powder showed that it consisted of grain fractions in the range from about 750 to 1200 nm, and, after the sonication process, the powder consisted of grain fractions ranging from 80 to 1050 nm. The DLS spectrum of the sonicated powder additionally contains a band corresponding to the presence of small amounts of larger aggregated grains having an average size of about 1450 nm.

After that process, the suspensions containing the determined amounts of the ceramic filler and CTP powder were mechanically mixed for 5 minutes at room temperature. To evaporate ethanol from the mixture, the suspensions were dried at 70°C for 24 hours. Finally, the compositions were heated to 165°C to transform CTP into liquid state and mechanically stirred for 15 minutes. The detailed procedure of nSiC deagglomeration and homogenization with CTP is described elsewhere [21]. According to this procedure, CTP samples containing different amounts of nSiC from 2% to 10% were prepared. The samples were then heat-treated at 1000, 2000, and 2800°C. Annealing to 1000°C was carried out in a furnace under argon flow at 90 l/h with a heating rate of 2°C/min. Heat treatment at higher temperatures was carried out in an Acheson furnace. The microstructural and structural changes occurring in CTP-based carbon binder precursors containing various amounts of nSiC during heat treatment to 2800°C were studied. Samples were analyzed by Scanning Electron Microscopy with Energy Dispersive Spectroscopy Analyzer (SEM + EDS) using a Nova NanoSEM 200 microscope connected to an EDAX EDS point analyzer. X-ray diffraction (XRD) was carried out using an X'Pert Pro from Philips, and Raman spectroscopy was carried out using a Horiba LabRAM HR spectrometer connected to a camera with a laser whose excitation wavelength was 532 nm. The results of XRD and Raman spectroscopy were analyzed using Fityk software version 0.9.8. Deconvolution of the complex peaks was carried out using the Pseudo-Voigt function.

3. Results and Discussion

The microstructure of the CTP-based carbons modified with nSiC was studied by SEM + EDS. EDS analysis of carbon samples with nSiC contents of 2% (Figure 1) and above shows silicon element as an indicator of the presence of SiC. SEM and EDS studies indicated that SiC nanoparticles
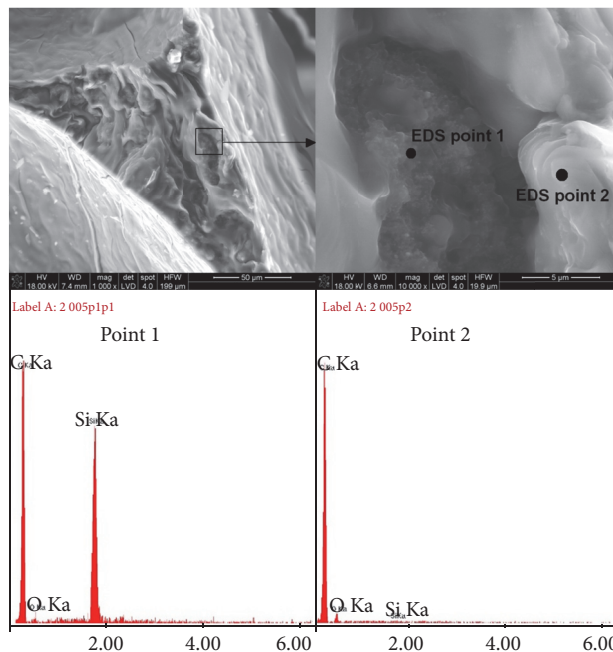

FIGURE 1: CTP-based carbon materials with 2% nSiC contents after heat treatment at 1000°C.

were found in the carbon matrix in the form of clusters of micrometre size. Such clusters were separated from each other by areas with slightly lower nSiC content (Figure 1). The presence of such ceramic clusters was characteristic for all the modified carbon samples, independently of the content of the ceramic filler, and they were formed as a result of secondary agglomeration of the nanoparticles after homogenization in liquid CTP and the initial stage of carbonization. The presence of the carbide phase with different grain sizes in liquid CTP can cause differential conversion of CTP into carbon, resulting in the formation of carbon crystallites that differ in size and structural ordering at elevated temperatures. It is also necessary to take into account the catalytic effect of the carbide in contact, initially with liquid pitch and then with gradually condensed aromatic structures converted into fine crystalline turbostratic carbon and also to a better ordered phase corresponding to the graphitic phase. Processes related to the formation of carbon phases and their subsequent recrystallization occur with varying intensity. It has been confirmed in numerous publications that the catalytic effect of the SiC involves the formation of a graphite structure by dissolving disordered carbon phase and the precipitation of better ordered carbon at the SiC/C interface [22]. Dissociation of the nanoparticles takes place at a different rate; smaller nanoparticles are more quickly degraded in polycrystalline carbon matrix. Such a mechanism reveals the Raman spectra and XRD analysis of CTP-based carbon samples.

The Raman spectra, ratio of I_D/I_G intensities, R, and crystallinity of samples containing different amounts of SiC heated from 1000 to 2800°C are shown in Figures 2–5. The spectra of CTP-derived carbon residue obtained at 1000°C show two broad peaks at 1350 cm^{-1} and 1590 cm^{-1}
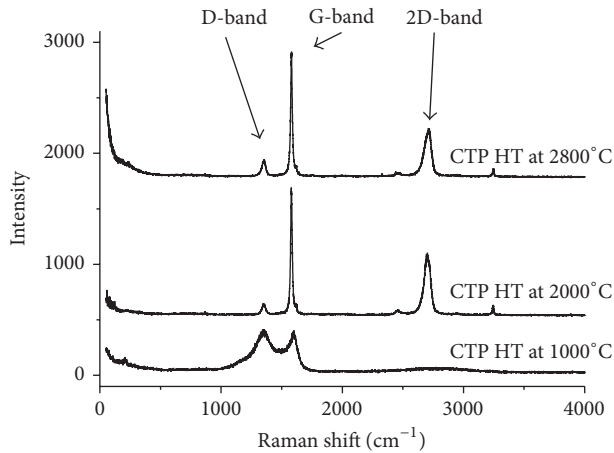
FIGURE 2: Raman spectra of pure CTP after heating to 1000°C, 2000°C, and 2800°C.

FIGURE 3: Raman spectra I_D/I_G ratio and crystallite sizes (L_a) of CTP-based carbon samples with different nSiC contents after heating to 1000°C.

FIGURE 4: Raman spectra I_D/I_G ratio and crystallite sizes (L_a) of CTP-based carbon samples with different nSiC contents after heat treatment at 2000°C.

(Figure 2). The peak at about 1350 cm^{-1}, known as the D-band, corresponds to disordered carbon phase in carbon residue. The intensities of the D- and G-bands for the samples containing various amounts of nSiC annealed at various temperatures differ slightly; the respective R changes (I_D/I_G) for carbonized samples are also shown in the figure, together with the changes in the apparent crystallite thickness, L_a. This parameter was determined from the equation proposed by Cançado et al. [23]. The intensity ratios of carbon residue obtained at 1000°C are relatively high, indicating the presence of a large fraction of disordered carbon phase in the structure of the material (Figure 3). Carbon residues modified with nSiC after heating to 1000°C constitute a polycrystallite microstructure consisting of small size crystallites, L_a, and a higher I_D/I_G ratio as compared to pure carbon samples. These relationships show the inhibiting effect of the presence of nSiC in carbon residue on the parameter L_a and structural ordering of carbon residue.

After heating carbon samples with the ceramic nanofiller to 2000°C, the crystallite sizes change and I_D/I_G values differ significantly from those observed for the samples obtained at 1000°C (Figure 4). I_D/I_G ratio for samples containing 10% ceramic nanofiller decreased from 0.666 for the CTP-based pure carbon to 0.351, while the crystallite size (L_a) increased from 28.6 nm for the pure carbon residue to 54.4 nm for the CTP with 10% nSiC. An nSiC content of 2% causes a significant decrease in I_D/I_G ratio, indicating the presence of a higher fraction of the ordered graphitic phase in carbon samples. The Raman spectra of the samples obtained at 2000°C show second-order Raman peaks, known as the 2D-bands, at about 2700 cm^{-1} (Figure 2). These peaks can be used to characterize the structure of carbon materials and their susceptibility to the graphitization [24].

For samples annealed at 2800°C, variations in the R parameter and crystallite sizes in function of nSiC are more complex (Figure 5). Nanoparticle grain fractions in the initial powder after deagglomeration and homogenization varied from 80 to 1050 nm. It is probable that smaller ceramic nanoparticles dissolve above 2000°C more easily in carbon
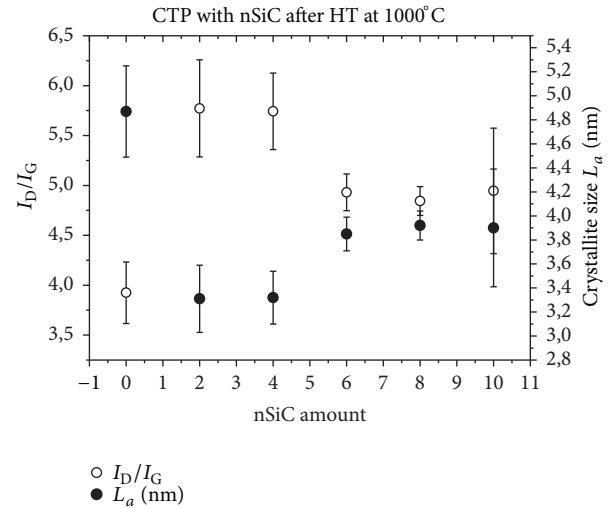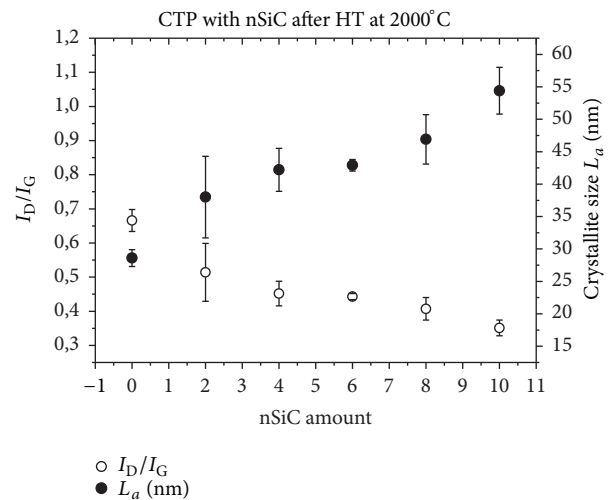
matrix, resulting in the formation of small carbon crystallites until carbide dissolution occurs.

In this case, the correlation between the amount of carbide and R and L_a parameters seems to be randomized. The study indicates that, above 2000°C, SiC reacts with the carbon matrix in a different way. Apart from the probable catalytic graphitization in the presence of carbide phase by dissolution of less ordered carbon phase followed by its precipitation into a better ordered carbon component, reactions of the decomposition of silicon carbide and silicon evaporation can take place. It is also expected that the observed structural changes in carbon phase depend upon the state of dispersion of carbide filler. Additional evidences for the proposed mechanism of interaction of nSiC nanoparticles with carbon
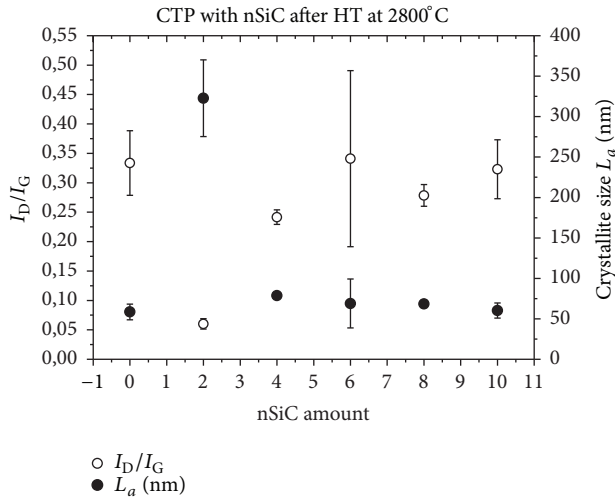
FIGURE 5: Raman spectra I_D/I_G ratio and crystallite sizes (L_a) of CTP-based carbon samples with different nSiC contents after heat treatment at 2800°C.

matrix are provided by the XRD study. The diffractograms clearly show a reduction in the SiC content in samples heated above 2000°C, and, in the case of samples heated at 2800°C, the peak deriving from SiC disappears (Figure 6).

Phase analysis of carbon samples containing 10% nSiC after heating to 2800°C (Figure 6) revealed that the samples either are composed of carbon phase with silicon carbide or contain only pure carbon fraction. Quantitative analysis of the samples modified with nSiC component revealed its decrease already after annealing at 2000°C. The amount of the silicon carbide in carbon samples shown in Figure 7 was determined in relation to the initial amount of the CTP in samples before its annealing. Samples obtained at 2800°C do not contain any content of nSiC. Carbon samples obtained at 1000°C display turbostratic structure consisting of two carbon phases (1 and 2) differing in structural parameters d_{002} (Figure 8). Heating the samples to higher temperatures leads to an increase in the crystallinity of both phases and improvement of their structural ordering (a decrease in d_{002}).

The analysis was carried out for all samples based on deconvolution of the (002) peak into two carbon components, which enables acceptable function fitting. The second carbon phase (carbon phase 2), due to the higher 2θ values, represents the carbon component with a better structural ordering.

The image of these changes is complex, in particular when analyzing the impact of the amount of nanoparticles on the structure and microstructure of the carbon matrix.

The changes of the c-axis spacing (d_{002}) and L_c (apparent crystallite height) with amount of ceramic filler and temperature for both analyzed phases are shown in Tables 1 and 2. In accordance with our expectations, the higher the temperature, the smaller the value of d_{002} for both carbon phases. Higher changes in d_{002} parameter occur in the case of phase 2.

Inconsistency has emerged between the results obtained from the two tests (Raman spectra, XRD) in the case of the samples heated to 2000°C. The XRD analysis indicates an
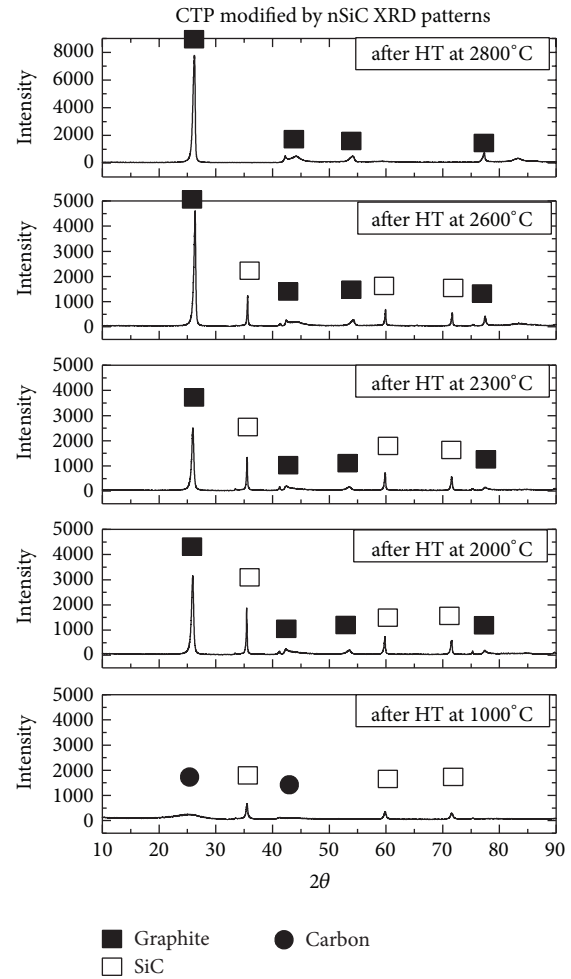

FIGURE 6: XRD patterns of CTP-based carbon residue with 10% nSiC after annealing to different temperatures of 1000 to 2800°C.

increase of the crystallites measured in the [002] direction up to 8 wt% SiC, and, for the maximum SiC content, L_c is close to the value obtained for pure carbon residue. On the contrary, the Raman studies show monotonic growth of crystallites in the [011] direction (L_a) with increasing SiC content.

This difference can be explained, on the one hand, by the different sizes of the analyzed areas of the samples determined by the two techniques. Raman study enables the analysis of sample size area of nanometric sizes, while the XRD measurements concern average sample areas of the order of several micrometres. Thus, a microstructural image of the measured feature by means of XRD seems to be closer to the real material, particularly when samples have a heterogeneous structure.

On the other hand, the Raman spectra make it possible to determine the apparent crystallite thicknesses (L_a), while the XRD diffractograms allow the crystallite heights (L_c) to be measured. It cannot be ruled out that the recrystallization of carbon residue in the presence of nSiC is an anisotropic process and changes in the size of crystallites in the "a" direction are stronger than those in the "c" direction.

TABLE 1: Interplanar distance (d_{002}) of carbon phases 1 and 2.

nSiC amount	Carbon phase 1			Carbon phase 2		
	1000°C	2000°C	2800°C	1000°C	2000°C	2800°C
			d_{002} [nm]			
0	0,397	0,346	0,340	0,348	0,343	0,338
2	0,407	0,348	0,342	0,350	0,344	0,339
6	0,393	0,347	0,343	0,348	0,343	0,339
10	0,393	0,347	0,343	0,349	0,343	0,339

TABLE 2: Crystallite size (L_c) of carbon phases 1 and 2.

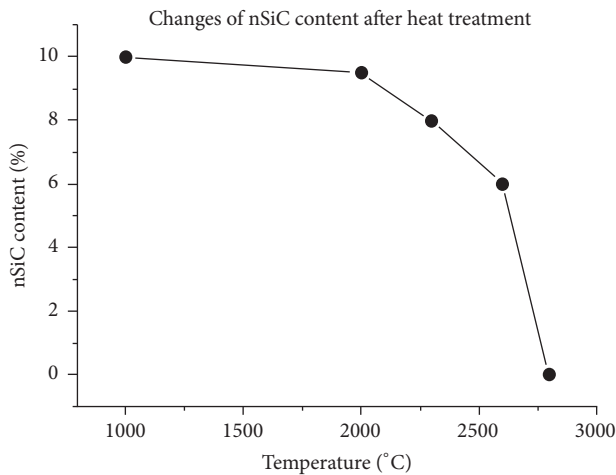| nSiC amount	Carbon phase 1			Carbon phase 2		
	1000°C	2000°C	2800°C	1000°C	2000°C	2800°C
			L_c [nm]			
0	1,3	16,1	19,4	2,0	22,0	43,0
2	1,2	15,6	27,5	1,9	20,9	31,1
6	1,2	17,0	22,7	2,0	25,1	29,4
10	1,12	16,2	21,1	2,0	23,2	27,2

FIGURE 7: Variations of nSiC content in carbon samples after annealing at different temperatures.
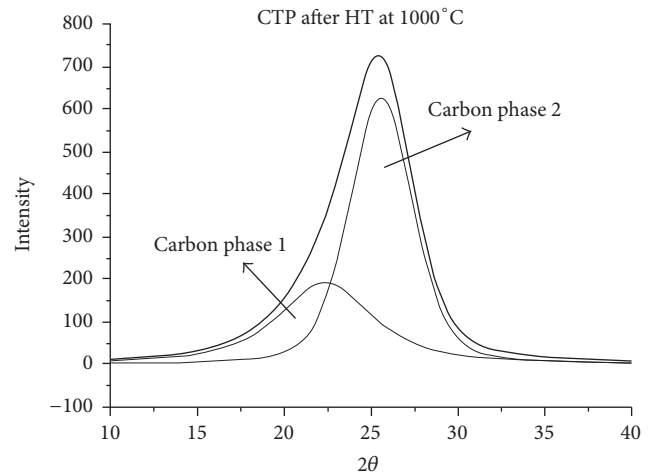

FIGURE 8: XRD of CTP-based samples; (002) peak deconvolution into two separate peaks.

The data collected in Tables 1 and 2, as well as in Figure 8, prove that carbon phase 2 obtained at 2000°C has a more crystalline structure compared to carbon phase 1. The effect of nSiC on the microstructure of both carbon phases is evident. The crystallite sizes of carbon phase 2 increased from 22 nm in a pure carbon phase up to 28.1 nm in a sample containing 8% nSiC. On the contrary, the observed changes in d spacings of the samples obtained at 2000°C are relatively weak. At higher temperature, that is, 2800°C, the crystallite sizes (L_c) and the c-axis spacing (d_{002}) change in a complex way, probably because the temperature is too high, resulting in incongruent decomposition of nSiC and silicon evaporation [25].

4. Conclusions

Deagglomerated SiC nanopowder was mixed with liquid CTP and the suspension was heat-treated in the range from 1000 to 2800°C. CTP-based carbon materials modified with nSiC, depending on the ceramic content and final temperature, differ in their structure and microstructure. Due to the presence of nSiC during carbonization of CTP to 1000°C, the carbon crystallite growth is inhibited. Above 2000°C, the presence of nSiC promotes the growth of crystallites, but the microstructure of carbon samples becomes more heterogeneous in comparison to carbon samples without ceramic nanofiller.
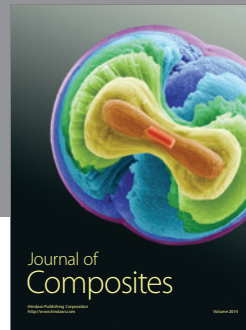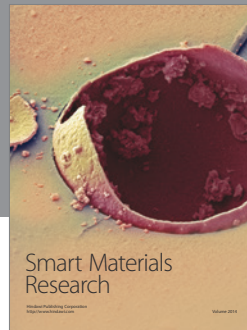
Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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