



AFRL-RY-WP-TR-2012-0250

NOVEL OPTICAL METAMATERIALS AND APPROACHES FOR FABRICATION

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University of Massachusetts Lowell

AUGUST 2012

Final Report

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REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YY) August 2012		2. REPORT TYPE Final		3. DATES COVERED (From - To) 01 August 2007 – 01 November 2008		
4. TITLE AND SUBTITLE NOVEL OPTICAL METAMATERIALS AND APPROACHES FOR FABRICATION				5a. CONTRACT NUMBER FA8718-07-C-0054		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER 62204F		
6. AUTHOR(S) Alkim Akyurtlu, Joel Therrien, and Aaron Bandremer				5d. PROJECT NUMBER 4916		
				5e. TASK NUMBER HA		
				5f. WORK UNIT NUMBER 4916HACM		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Massachusetts Lowell Electrical and Computer Engineering Department 417 Ball Hall 1 University Ave. Lowell, MA 01854				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Sensors Directorate Wright-Patterson Air Force Base, OH 45433-7320 Air Force Materiel Command United States Air Force				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RYHI		
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RY-WP-TR-2012-0250		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.						
13. SUPPLEMENTARY NOTES PAO Case Number: 88ABW-2012-4509, cleared 20 August 2012. Report contains color.						
14. ABSTRACT Techniques for the fabrication of novel optical metamaterials using chemical and biological self- assembly were investigated based on a recently developed material design. The design is for a low-loss and isotropic negative index metamaterial (NIM) for the visible regime based on silicon carbide (SiC) spherical nanoparticles embedded inside of a magnesium diboride (MgB ₂) host. This work offers a solid technical foundation for the continued investigation of metamaterial fabrication using both chemical and biological self-assembly.						
15. SUBJECT TERMS optical, metamaterials, nanoparticles, fabrication						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 24	19a. NAME OF RESPONSIBLE PERSON (Monitor) John S. Derov	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include Area Code) N/A	

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Acknowledgements

X-ray photoelectron spectroscopy (XPS) analysis was performed by Dr. Earl Ada, Manager, Materials Characterization Laboratory, University of Massachusetts Lowell.

Abstract

Techniques for the fabrication of novel optical metamaterials using organic chemistry and biological self-assembly were investigated with the design parameters of 1) silicon carbide nanoparticle size and 2) the distance between them in mind. A controlled surface modification of nanoparticles is, therefore, critical. An 11-carbon alkene with bromine functional end was researched for incorporation into our metamaterial. Bromine functionalization was verified; however, thiol substitution using sodium hydrosulfide was discouraging. Silane chemistry using 3-mercaptopropyltrimethoxysilane was successfully employed to bond reactive thiols to the surface of nanoparticles and glass substrate. A bifunctional maleimide polyethylene glycol acting as a spacer was subsequently investigated for reaction with the thiol groups with inconclusive x-ray photoelectron spectroscopy results at a maleimide reaction concentration of 0.2mM. A maleimide reaction concentration at approximately ten times the initial attempt showed thiolated silicon carbide nanoparticles bound to the surface of maleimide functionalized glass under dark field microscopy. The formation of disulfide bonds between thiol groups of a glass substrate and silicon carbide nanoparticles was achieved at 75°C under oxidizing conditions. Nanoparticles were successfully bonded to the surface of a substrate as seen under dark field microscopy with the disulfide bond formation. Utilizing phage display, we have also identified peptides that bind with nanoparticles and glass substrates. This is a critical step in engineering M13 bacteriophages to self-assemble nanoparticles in an ordered array. We have demonstrated that chemical and biological techniques are viable in the fabrication process.

Summary

Techniques for the fabrication of novel optical metamaterials using chemical and biological self-assembly were investigated based on a recently developed material design. The design is for a low-loss and isotropic negative index metamaterial (NIM) for the visible regime based on silicon carbide (SiC) spherical nanoparticles embedded inside of a magnesium diboride (MgB₂) host. Design parameters of this material are the sizes and fill factor of the SiC nanoparticles. The fill factor defines the distance between the SiC nanoparticles within the host. The main challenge in making such a material lies in the precise placement of the SiC nanoparticles and the avoidance of nanoparticle clustering. Reaction schemes that bond SiC nanoparticles to the surface of a substrate have been identified and verified using analytical chemical techniques and microscopy. Mercaptosilane and reactive thiol chemistry have been successfully employed to bond nanoparticles to substrates. These techniques will be further refined by incorporating spacer molecules such as pegylated maleimide with defined length to allow for the controlled placement of the SiC nanoparticles. Additionally, the novel use of biological self-assembly utilizing phage display has identified a peptide that binds to silicon carbide. This peptide identification will allow for the engineering of phage that will place SiC nanoparticles at defined distances on a patterned substrate. This work offers a solid technical foundation for the continued investigation of metamaterial fabrication using both chemical and biological self-assembly.

Introduction

A novel low-loss and isotropic NIM design for the visible regime based on silicon SiC spherical nanoparticles embedded inside of a MgB_2 host has been reported [1]. A well-controlled surface modification of SiC nanoparticles will be used to fabricate the desired material. We have focused on the use of organic chemistry to bond thiol groups, also called sulfhydryl and mercapto groups, to the surface of siliconcarbide nanoparticles, SiC single crystals, and glass substrates.

To evaluate the chemistry, single crystals of SiC were used as a model substrate. Glass substrates were functionalized to be used as models in the test-bed platform. Thiolated SiC nanoparticles are a good foundation for bonding to a desired surface using chemical linkers. One approach will be the adaptation of methods for the functionalization of silicon nitride (SiN) using alkenes with double functional groups [2]. This approach uses a linear molecule with functional groups on both ends, where the first functional group will bond to the silicon carbide surface while the second functional group bonds to a substrate. To avoid cross-linking, the second functional group (bromine) will be a placeholder that does not react with the silicon carbide. Following attachment to the nanoparticles, a thiol group that bonds to the substrate will replace the bromine. Silane chemistry was also used with more success to bind thiol groups to the surface of our SiC and glass substrates. A bifunctional thiol reactive molecule was evaluated as a linker to our surfaces, as well as a bifunctional pegylated maleimide. In addition, biological self-assembly techniques were evaluated for the “bottom-up” fabrication of the optical metamaterial. This technique employs the use of M13 bacteriophages [3], phages for short, which are viruses that infect bacteria and can be genetically engineered to display peptides of interest on their surface. M13 is a filamentous bacteriophage composed of circular single stranded DNA encapsulated in a coat of the major protein and capped with different minor coat proteins on the ends. Using commercially available combinatorial phage display systems, a library of peptides was screened for high affinity and specificity to silicon carbide nanoparticles. We report on our progress into the fabrication using chemical and biological techniques.

Methods, Assumptions and Procedures

Alkene Functionalization of Silicon Carbide

Silicon carbide single crystals (4H) with dimensions of 5x5x 0.24 mm were used as model substrates to evaluate alkene (1-undecene) functionalization of silicon carbide nanoparticles. The crystals were subjected to an organic contaminant cleaning step with a solution of distilled water, hydrogen peroxide, and ammonium hydroxide (5:1:1) at 65°C for ten minutes. An etching step with 2.5% hydrofluoric acid for two and seven minutes was used to remove the native oxide layer on the crystals and determine if etch time affects the contact angle. The samples were reacted in 0.4M 1-undecene in mesitylene at 165°C for 24 hours to bond the alkene to the surface of the crystals. Contact angle measurements were taken with a Kruss instrument.

Bromine Functionalization of Silicon Carbide

Silicon carbide single crystal (6H) with dimensions of 10x10x0.33 mm was used to bond 1-bromo-11-undecene to the surface. Then, 2.5% HF was used to strip the oxide layer from the wafer. The wafer was subjected to HF etching for 2, 5 and 15 minutes to assess time dependence on the oxide removal step. 0.4 M bromo-undecene was reacted for 24 hours at 165°C with the SiC crystal. X-ray photoelectron spectroscopy (XPS) analysis on a VG Escalab MKII was used to confirm chemical modification. 1 M Sodium hydrosulfide was reacted at 70° Celsius for 12 hours with the bromine functionalized surface to replace the bromine with a reactive thiol group.

Thiol Functionalization with 3-MPTMS

Silane chemistry employing a molecule with a mercapto (thiol) functional end, 3-mercaptopropyltrimethoxysilane (3-MPTMS), was investigated for bonding a reactive thiol to the surface of silicon carbide and glass substrates. The reaction mechanism [4] is detailed in Figure 1.

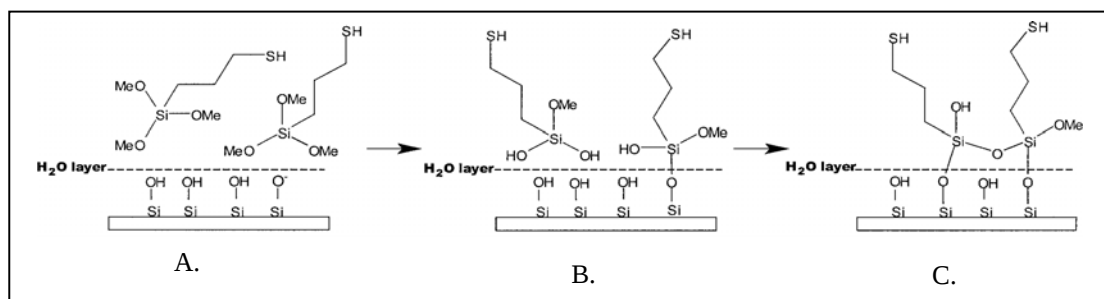


Figure 1: Thiol Functionalization with Mercapto Silane Chemistry. 3-MPTMS molecules in contact with silicon carbide surface (A) react with deprotonated hydroxyls or form silanols by hydrolysis with water from the hydrated surface (water vapor) (B). Silanols react with surface silanols or other other silanols to create a siloxane network (C).

SiC single crystals and glass substrates (microscope slides) were used as models to bond sulfhydryl (SH) groups using vapor deposition. The SiC crystals and glass substrates were cleaned to remove organic contaminants, as above, and suspended by wire in a Pyrex bottle with an open vial containing 0.5 mL of 3-mercaptopropyltrimethoxysilane. The bottle was purged with argon, sealed, and then placed in a 90°C oven for 3 hours. The thiol functionalized silicon (SH-SiC) pieces were rinsed in toluene and acetone and then blown dry in nitrogen. SiC nanoparticles (Acumet, 130 nm) were reacted with the same procedure. Additionally, nanoparticles were placed in the vial of 3-mercaptopropyltrimethoxysilane to assess liquid phase deposition. The nanoparticles were cleaned by five (5) ethanol washings with centrifugation.

We investigated placing a homobifunctional linker molecule that binds thiol on both ends. The reactive group is a maleimide.

Maleimide Functionalization of Thiolated Glass Substrate

Thiol functionalized glass substrates were reacted with bis-maleimide (thiol reactive) functional molecules (Figure 2A) acting as a model linker to attach thiol coated SiC nanoparticles to the glass substrate. A stock solution of BM(PEG)₂, 1-8bis(maleimido)diethylene glycol (Thermo Scientific, Catalog Number: 22336) in dimethyl sulfoxide (DMSO) was prepared at a concentration of 20 millimolar (mM). Twenty (20) microliters (μL) of the stock solution was diluted in 2 mLs of Tris (the organic compound, 'tris(hydroxymethyl)aminomethane') buffered saline containing the glass substrate for a final concentration of 0.2 mM and was reacted at room temperature for 1 hour. The glass substrate was washed with DMSO. The reaction mechanism is detailed in Figure 2B [5].

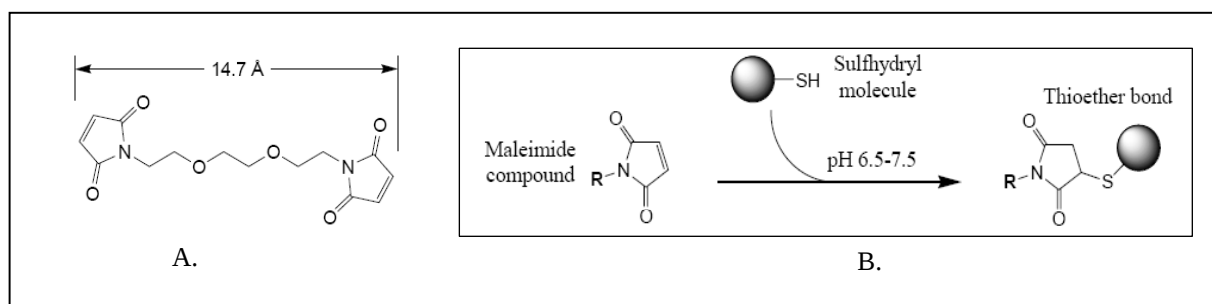


Figure 2: Reaction mechanism of 1-8bis(maleimido)diethylene glycol. Structure of 1-8bis(maleimido)diethylene glycol (A). The reaction of maleimide group with a sulfhydryl (thiol) group (B).

At a later date, 4 mL of a new stock solution was diluted in 50 mL of phosphate buffered saline (pH=6.8) for a final concentration of 1.6 mM and reacted with a thiol functionalized glass substrate at room temperature for 1 hour. Thiol functionalized SiC nanoparticles were reacted with this maleimide glass substrate to assess deposition of nanoparticles.

Disulfide Bond Formation

Thiol groups are self-reactive under oxidizing conditions to form disulfide bonds. We investigated this mechanism for bonding thiolated SiC nanoparticles to thiolated glass substrate. Thiol functionalized glass slide and silicon carbide crystal were independently reacted with thiol functionalized SiC nanoparticles for 13 hours at room temperature under oxidizing conditions. Two series of ethanol, toluene, and acetone washings were performed to remove non-bound nanoparticles. The disulfide bond reaction was continued at 70°C for 20 hours with washing and analysis as above. The samples were analyzed by dark field microscopy. This microscopy method produces images of scattered light from the nanoparticles and neglects directly transmitted light. A brighter image is indicative of nanoparticle deposition.

Simultaneously to the synthetic chemistry investigation into deposition of functional SiC nanoparticles, the novel use of biological techniques to fabricate metamaterials was undertaken. Bacteriophages were screened for affinity to silicon carbide and glass using a phage display library.

Biological Self-Assembly of Bacteriophage

The Ph.D.TM-12 Phage Display Peptide Library Kit (New England BioLabs, Catalog Number: E8110S) was used to select binders to silicon carbide substrate. The phage library was applied to the substrates and incubated at room temperature for 60 minutes. Unbound phage was washed away in a buffer of 50 mM Tris-HCl (pH 7.5)/150 mM NaCl/ 0.1% Tween 20 (a detergent). Bound phage was eluted from the surface of the substrates using an acidic buffer of 0.2 M Glycine-HCl (pH 2.2)/1 mg/ml bovine serum albumin. The eluted phage was immediately neutralized with 1 M Tris-HCl (pH 9.1). The eluted phage was amplified in E.coli, purified and subjected to another round of selections using 0.5% Tween 20 in the wash steps to apply a greater selection pressure. The process as outlined above was carried out for a third round of selection again using the 0.5% Tween 20 wash step. The third round of phage was amplified and sequenced to determine the peptide that binds to silicon carbide. This process was repeated to determine a peptide binder to glass substrate.

Results and Discussion

Prior to organic cleaning, initial contact angles were 77 and 72 degrees on SiC crystal samples 1 and 2, respectively. Post-hydrofluoric acid etching, the contact angles were 75 and 40 degrees. Water contact angles following alkene reaction were 62 and 61 degrees. The change in water contact angle suggests that a surface modification took place and alkenes could be bonded to the surface of the silicon carbide substrate. A double functional, bromo-undecene, molecule was then assessed for bonding to the surface of a silicon carbide model substrate. With a significant change in water contact angle after bromo-undecene reaction, Figure 3 shows that a surface modification took place.

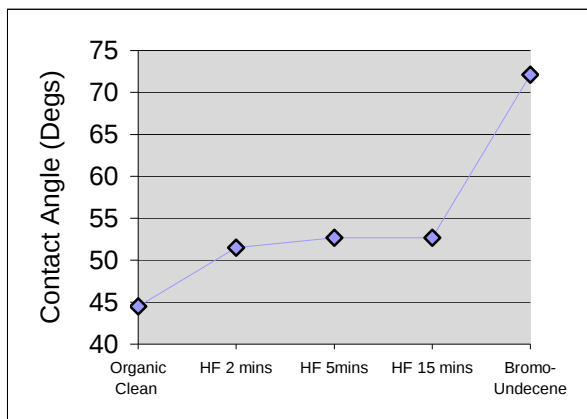


Figure 3: Water Contact Angle. Extended exposure to 2.5% hydrofluoric acid showed no change in contact angle. An increased angle with bromo-undecene functionalization is representative of increased hydrophobicity due to the long chain carbon alkane.

A clear bromine peak is visible at the binding energy value of 70 eV for the 3d electron orbital in Figure 4 after functionalization with bromo-undecene.

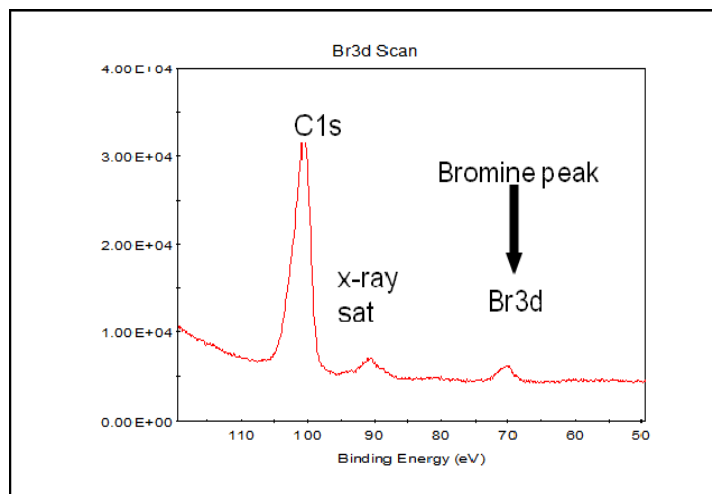


Figure 4: Bromine Functionalization. A bromine peak is shown on the spectra at a binding energy of approximately 70eV. X-ray sat is an x-ray saturation peak after the carbon peak ~100 eV. C1s is the 1s electron orbital of carbon.

The double functional molecule scheme failed when the reaction with sodium hydrosulfide to replace the bromine functional group with the reactive thiol group was not successful. XPS analysis showed no sulfur on the surface of the silicon carbide at a binding energy value of ~226 eV. Background noise is only visible on the spectra at the expected energy value as shown in Figure 5.

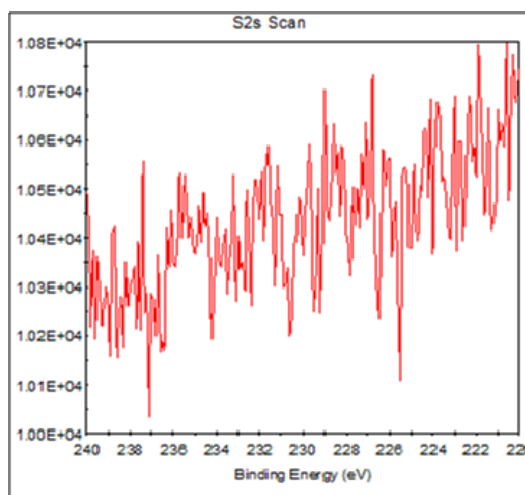


Figure 5: Thiol Functionalization with Sodium Hydrosulfide. Thiol, R-SH S2s, is expected around 225-228 eV. Background noise in spectrum suggests no sulfur is present on the surface.

Sulfur binding energy peaks are visible for the sulfur 2s (S2s) electron orbital and the sulfur 2p (S2p) orbital at 228 eV and 165 eV, respectively in Figures 6A and 6B. Treated glass as compared to the non-treated clean glass had thiol on the surface. Silicon carbide crystal substrate showed the same sulfur binding pattern as compared to non-treated clean SiC substrate (Figures 6C and 6D). A successful thiol functionalization using mercaptosilane was accomplished. This chemistry was applied to SiC nanoparticles to verify bulk particles could be functionalized in addition to a SiC surface.

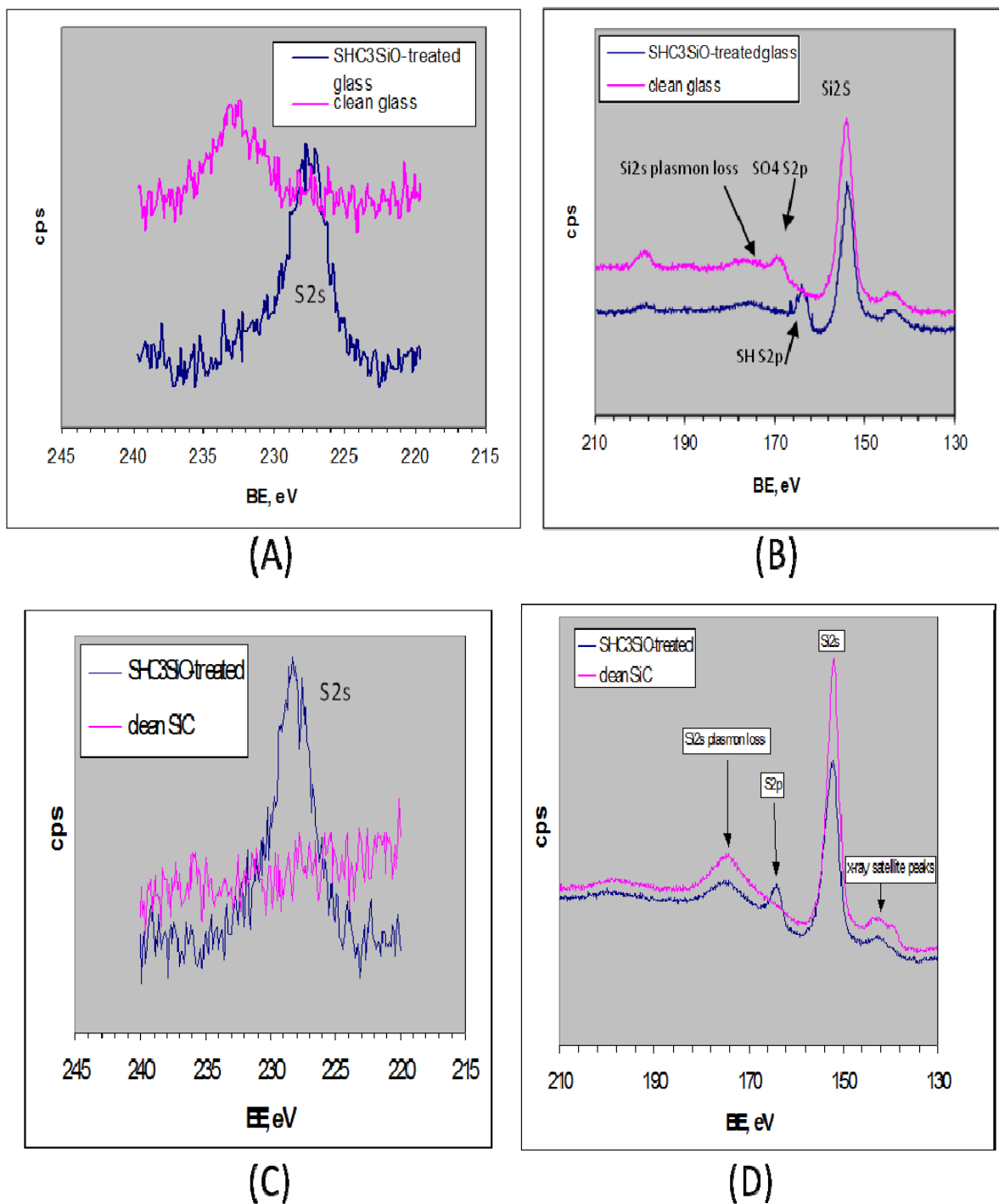


Figure 6: XPS Analysis of the vapor deposition of mercaptosilane on SiC crystal and glass substrate. Glass treated mercaptosilane shows sulfur on the surface (A) and (B). SiC crystal treated mercaptosilane shows sulfur on the surface (C) and (D).

Vapor phase deposition of thiol on SiC nanoparticles was demonstrated as shown in Figures 7A and 7B with sulfur binding energy values of 228 eV and 165 eV for S2s and S2p, respectively. Sulfur of the thiol group is also shown on the surface of the SiC nanoparticles reacted in liquid phase (Figures 7C and 7D). Vapor phase deposition of mercaptosilane showed sulfur on the surface of the SiC crystals and glass slides.

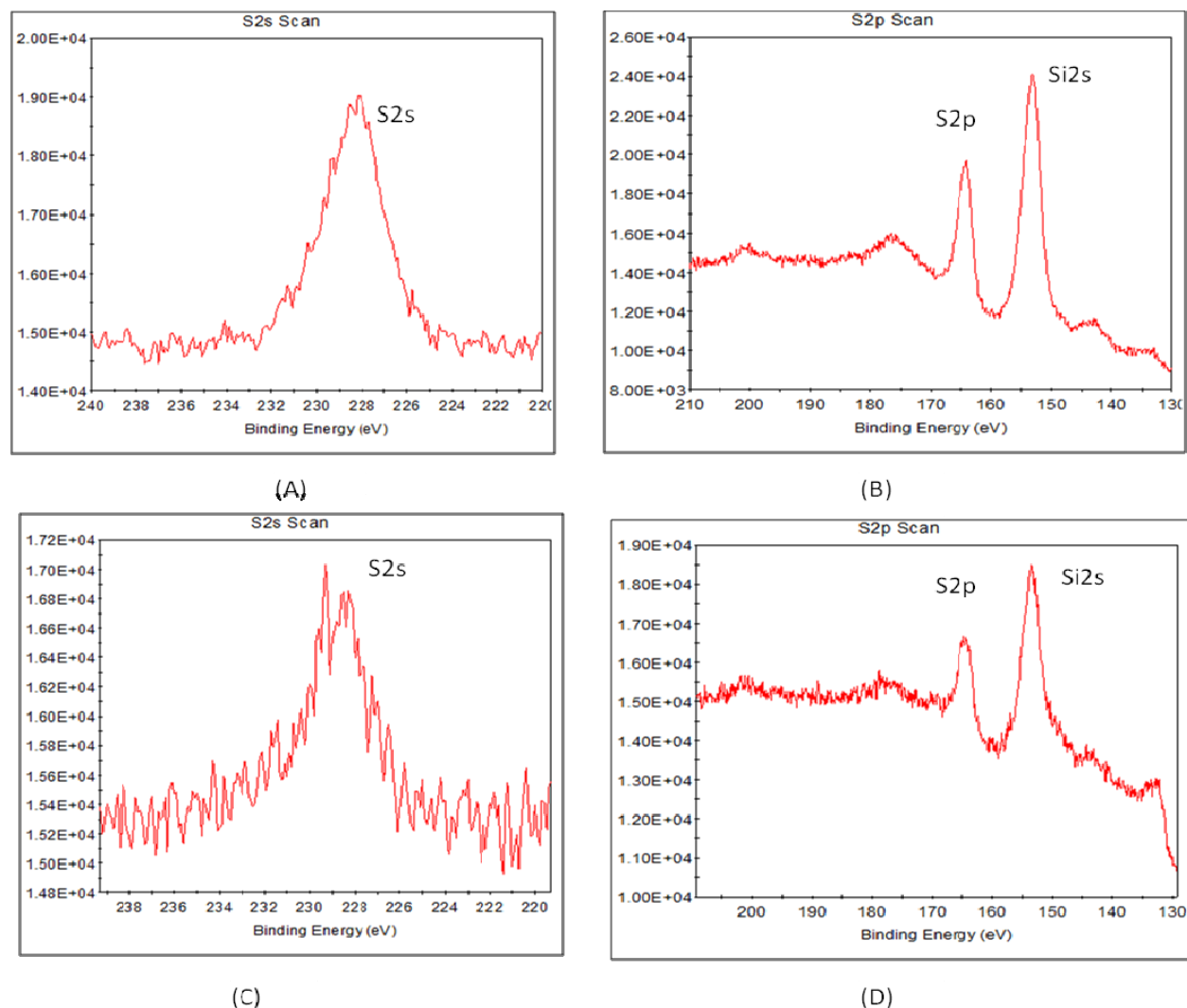


Figure 7: XPS Analysis of the deposition of mercaptosilane on SiC nanoparticles. Vapor phase reaction of mercaptosilane with SiC nanoparticles (A) and (B). Liquid phase reaction of mercaptosilane with SiC nanoparticles (C) and (D).

Maleimide binding with thiol on the surface of a glass substrate was inconclusive at a reaction concentration of 0.2 mM. XPS analysis of the nitrogen 1s electron orbital (N1s) at 400 eV showed a small peak but not significant as compared to background noise (Figure 8).

Reaction conditions were taken from biological chemistry and need to be optimized for our use with inorganic substrates (i.e. silicon carbide and glass). A higher concentration maleimide solution of 1.6 mM (approximately 10 times the previous maleimide concentration) that was reacted with glass substrates and thiol functionalized nanoparticles showed evidence of deposition under dark field microscopy (Figure 9).

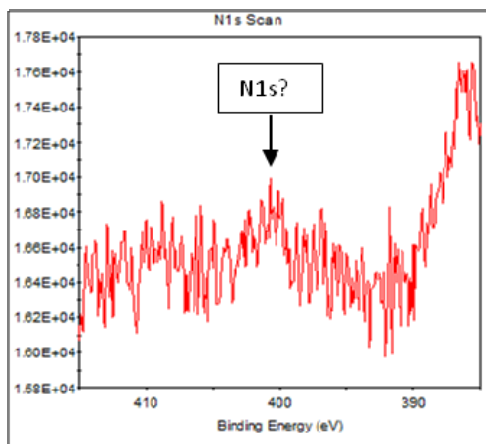


Figure 8: XPS Analysis of maleimide on thiolated glass. N1s signal at 400 eV is not conclusive to prove nitrogen, and thus, maleimide is bound to the surface thiols of the glass substrate. Maleimide reaction concentration was 0.2 mM.

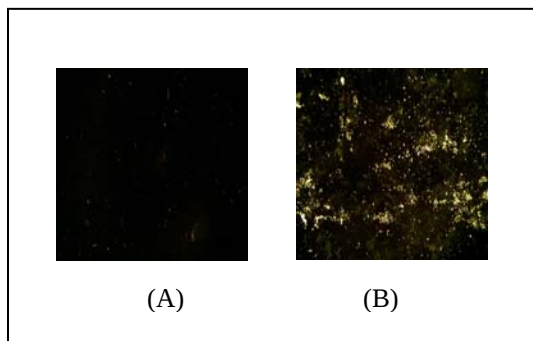


Figure 9: Thiolated SiC nanoparticles bound to maleimide functionalized glass substrate. A higher concentration (1.6 mM) maleimide reaction was performed to functionalized the glass substrate. Dark field microscopy suggests nanoparticles bound to the surface (B). Control glass substrate (A).

Disulfide bonds were formed between thiolated glass and thiolated SiC nanoparticles as demonstrated with dark field microscopy in Figure 10. The images of Figures 10B and 10D are

clearly brighter than the control images in Figures 10A and 10C offering evidence that bound surface nanoparticles scattered light.

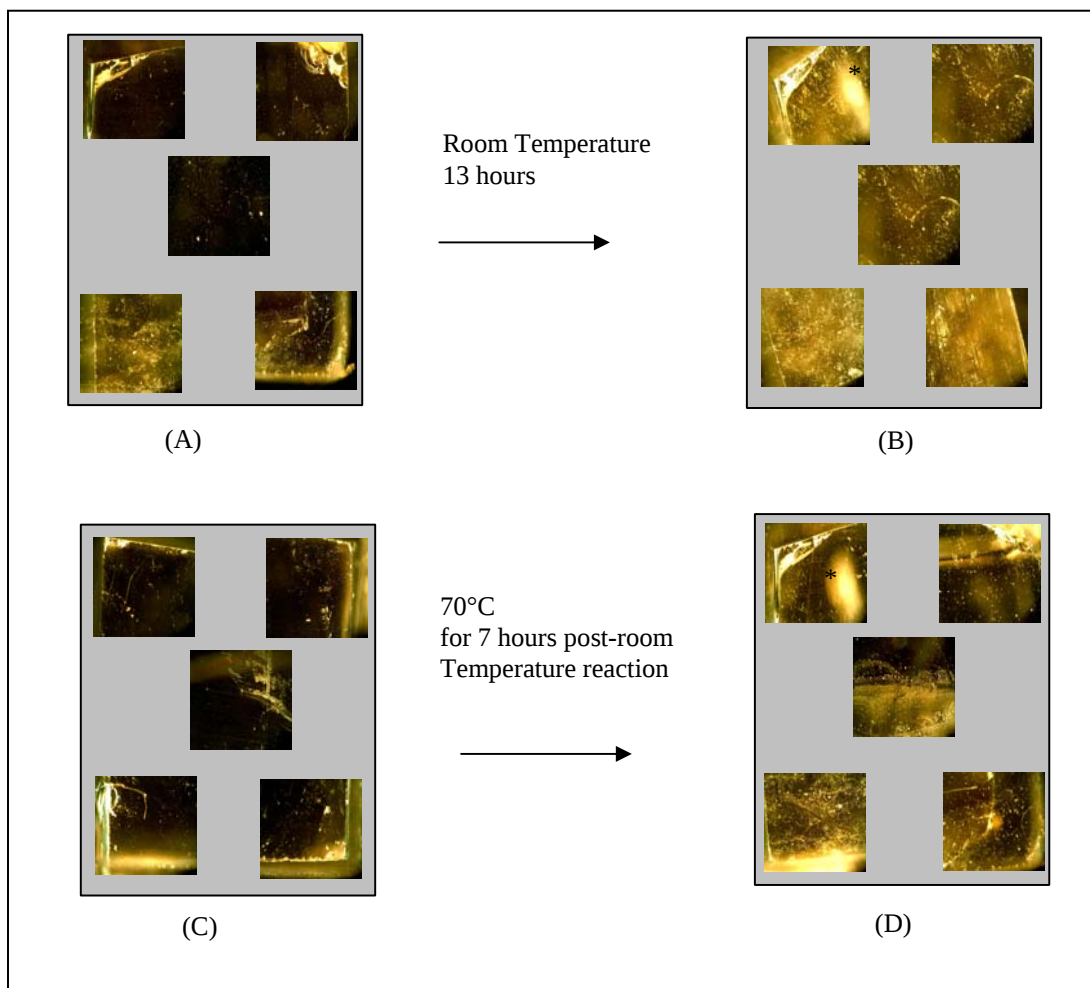


Figure 10: Thiol Functionalized Glass with Bound SiC Nanoparticles. The five images are a representation of the substrate with corners and center images. Control substrates are shown for room temperature glass substrate (A) and high temperature glass substrate reaction (C). (B) and (D) are room and high temperature reactions of glass substrates with thiol SiC nanoparticles. The increased number of bright spots suggests nanoparticle binding to the surface of the surface through a disulfide bond. A scratch was placed on the surface for orientation (*).

To assess non-specific binding of functionalized nanoparticles, a non-thiolated glass substrate was exposed to thiolated nanoparticles under the same conditions. Nanoparticles were not visible under dark field microscopy (Figure 11) providing evidence that functionalized nanoparticles did not bind to a clean glass surface.

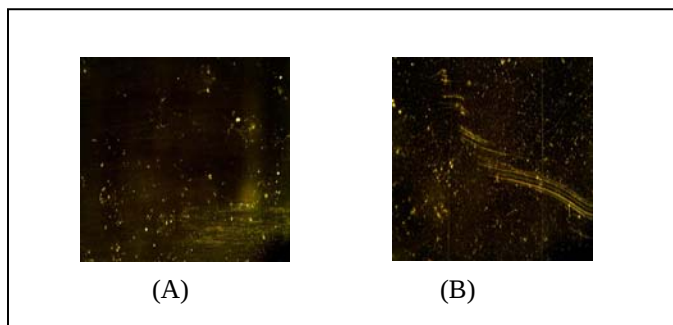


Figure 11: Non-specific Binding of Functionalized nanoparticles not apparent under dark field. Non-functional glass substrate (A). Exposed to thiol SiC nanoparticles (B).

The SiC nanoparticle functionalized glass substrate (Figure 12A) was treated with a strong reducing agent, 2-mercaptoethanol, and imaged with dark field microscopy. A disulfide bond will be reduced under these conditions and deposited nanoparticles will be washed from the substrate (Figure 12B).

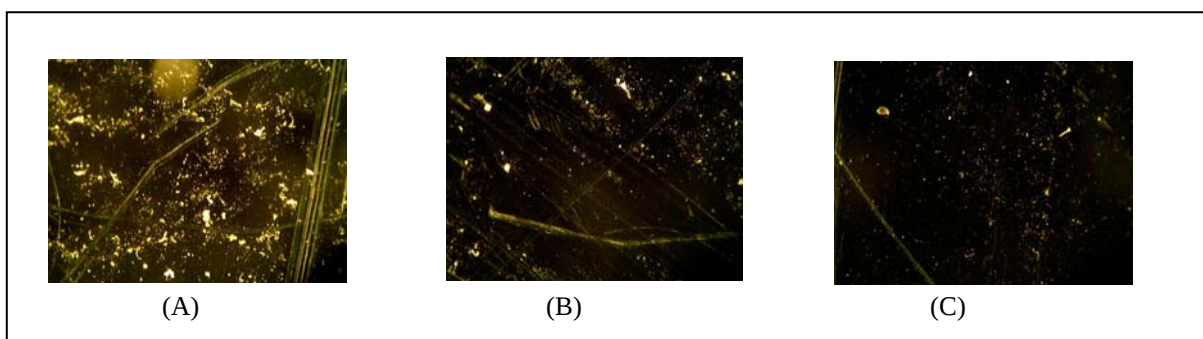


Figure 12: Disulfide bond reduced with 2-mercaptoethanol. SiC nanoparticles disulfide bonded to thiolated glass substrate (A). Glass substrate treated with 2-mercaptoethanol with SiC nanoparticles washed off (B). Clean glass substrate for comparison (C).

Phage display for silicon carbide and glass selected peptides of 12 amino acid length with affinity for glass and SiC, respectively. The peptide for silicon carbide was Asparagine-Proline-Arginine-Histidine-Proline-“unidentified”-Proline-Glycine-Proline-“unidentified”-Histidine-Leucine. The peptide for glass was Asparagine-Proline-Proline-“unidentified”-Histidine-Histidine-Proline-“unidentified”-Histidine-Proline-“unidentified”-Proline. There are two unidentified amino acids in the SiC peptide and three unidentified in the glass peptide due to the heterogeneous nature of the bulk phage solution. Individual phage clones will need to be amplified and sequenced to find the consensus sequence. DNA and amino acid sequence data is

shown in Figure 13.

A.	Silicon Carbide	Amino Acid Position in Phage Peptide											
		1	2	3	4	5	6	7	8	9	10	11	12
	Round 1	AAN	CCN	CCT	CAN	CCG	NNN	CCN	CCG	CCG	NCN	CCN	NCG
	Round 2	NAT	CCN	CNT	CAT	CCG	NCN	CCN	CNG	CCG	NAN	CNT	CNN
	Round 3	NAT	NCG	CGN	CAT	CCG	NCG	CCG	CAG	CCG	CAN	NAT	CTT
	Probably 3	AAT	CCG	CGT	CAT	CCG	NCG	CCG	CAG	CCG	CAN	CAT	CTT
	Amino Acid Sequence	Asn	Pro	Arg	His	Pro	un	Pro	Gln	Pro	un	His	Leu

B.	Glass	Amino Acid Position in Phage Peptide											
		1	2	3	4	5	6	7	8	9	10	11	12
	Round 1	AAN	CNN	CCN	CNN	CCN	NNN	CCN	CCN	CCG	CCN	CCN	CCG
	Round 2	AAN	CCN	CNN	CAN	CCN	CNN	CCN	CNN	CNN	CCN	CCN	CCG
	Round 3	AAN	CCT	NNN	CNN	CAT	CAT	CCG	CAN	CAT	CCT	NCN	CNG
	Probably 3	AAT	CCT	CCT	CAN	CAT	CAT	CCG	un	CAT	CCT	un	CCG
	Amino Acid Sequence	Asn	Pro	Pro	un	His	His	Pro	un	His	Pro	un	Pro

Figure 13: DNA sequence of the three rounds of phage display selection with corresponding amino acids. Silicon carbide (A). Glass (B). “un” is an unidentified amino acid.

Atomic force microscopy was used to image phage bound to silicon carbide crystal substrate (Figure 14).

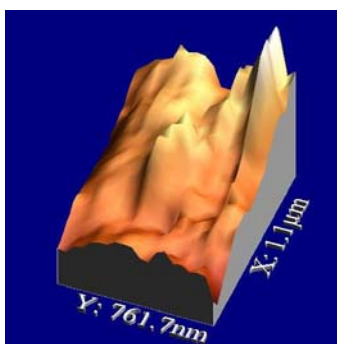


Figure 14: M13 Phage bound to silicon carbide substrate. AFM topography image of several phage on the surface of SiC crystal. The phage appear as the elongated protrusions seen on the flat substrate. AFM scans of clean SiC crystals show no such features.

Conclusions

Different schemes were evaluated for the functionalization of silicon carbide and glass substrates in our efforts into the fabrication of negative index of refraction metamaterials (NIMs). Successes are outlined below.

- Bromine was bound to the surface of silicon carbide.
- Thiol groups were bound to silicon carbide crystal substrates and nanoparticles. This functionalization is a critical step in allowing for placement of nanoparticles as thiol reactive chemistry can be optimized for user-defined placement.
- Thiol groups were bound to glass substrates. Glass prisms are used in NIMs functional testing and binding to glass is critical for evaluation of metamaterials.
- Disulfide bonds were formed between thiol groups of glass substrates and SiC

nanoparticles.

- Thiolated SiC nanoparticles bound to maleimide functionalized glass substrates as evidenced by dark field microscopy
- A first step in the novel use of biological self-assembly was accomplished. Bacteriophages with affinity for silicon carbide were selected.

Recommendations

Further work is warranted to determine reactions that will allow for the placement of nanoparticles at the correct fill factor spacing. We have determined that disulfide bond formation places a layer of nanoparticles on the substrate surface. A dithiol molecule with defined linker between the thiols would act as a spacer molecule allowing for the nanoparticles to be correctly spaced. A lithographic process to create a glass substrate with a defined pattern would act as the base to allow for the nanoparticle bonding to occur. In addition, a bifunctional molecule with silane and maleimide separated by a polyethylene glycol spacer will be investigated once the maleimide reaction is optimized. Biological self-assembly should also be pursued with the engineering of a M13 virus to display both the silicon carbide and glass binding peptides at opposite ends of the virus.

References

1. A. G. Kussow, et al., *Physical Review B*, **76**, 195123, 1-7, 2007.
2. A. Arafat, et al., *JACS*, **126**, 8600-8601, 2004.
3. S. Whaley, et al., *Nature*, **405**, 665-668, 2000.
4. *Journal of Colloid and Interface Science* **254**, 200–203 (2002)
5. Pierce Biotechnology, <http://www.piercenet.com/files/0786dh5.pdf>

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ACRONYM/SYMBOL	DESCRIPTION
μL	microliter
°C	degrees Celsius
3-MPTMS	3-mercaptopropyltrimethoxysilane
AFM	atomic force microscopy
DMSO	dimethyl sulfoxide
DNA sequence nucleotides	A: adenine
	C: cytosine
	G: guanine
	T: thymine
	N: unidentified nucleotide
eV	electron volts
HCl	hydrochloric acid
HF	hydrofluoric acid
M	molar
mm	millimeter
mM	millimolar
NaCl	sodium chloride
NIM	negative index metamaterial
SH	sulfhydryl group
SHC3SiO	mercaptosilane
SiC	silicon carbide
SiN	silicon nitride
Tris	tris(hydroxymethyl)aminomethane
XPS	x-ray photoelectron spectroscopy