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A Review on Recent Patents and Applications of Inorganic Material Binding Peptides

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Abstract: Over the past decade, significant progress has been made in the identification of novel material binding peptides having affinity to a wide range of target materials and their use in nanobiotechnological innovations. These material binding peptides (MBPs), also known as solid/ substance binding peptides (SBPs) can be isolated using combinatorial display technologies such as phage display (PD), surface display (cell, bacterial, yeast, mRNA) exhibit material specific selectivity and affinity towards a range of inorganic and organic nanomaterial surfaces including metals, metal oxides, minerals, semiconductors and biomolecules. MBPs serve as mediators in bringing nanotechnology and biotechnology under one umbrella by linking solid nanoparticles with biomolecules including proteins, bioactive peptide motifs, bifunctional binding peptides, enzymes, antigens and antibody fragments. As the utilization and application of these inorganic binding peptides as molecular connectors, molecular assemblers and material specific synthesizers in nanotechnology has been expanding rapidly, so too has growing commercial interest in patenting such innovations. In this review, we present the past, current and future developments and applications of inorganic MBPs specific to nanomaterials and their applications.

Keywords: Affinity, application, biomolecule, combinatorial peptide display, material binding peptide, mediator, nanotechnology, selectivity.

1. INTRODUCTION

MBPs have attracted considerable interest in the development of innovative nanostructured materials in particular because of their promising and growing applications in nanotechnology. These MBPs are also called inorganic binding peptides (IOBPs) or substrate binding peptides (SUBPs) or solid binding peptides (SBPs) or genetically engineered peptides for inorganics (GEPIs). MBPs are short amino acid peptide sequences that are genetically constructed and show specific affinity to a target material through combinatorial display approaches which include phage display [1-6], cell surface display [7-10], ribosome display [11-14] and mRNA display [15-18] technologies. Although nanomaterials have been designed and produced decades ago, their utilization in nano- or bio-technology is limited due to poor solubility and biocompatibility issues. However, several strategies have been developed to overcome the potential safety concerns and eventually, peptide display technologies came into existence by managing greater control over the nanomaterials without compromising their physical, chemical and functional properties.

G.P Smith, for the first time used phage display technology as a powerful tool to identify ligands for numerous targets in 1985 [1]. From there on, phage or cell surface displayed (7-15mers) libraries have become ubiquitous in selecting and screening peptides having strong affinity towards a range of inorganic material surfaces such as metals (Ag [19-21], Au [22, 23], Pt [24], Pd [25]), metal oxides (SiO_2 [26-30], ZnO [31, 32], TiO_2 [33-35], Fe_2O_3 [36, 37], IrO_2 [38], Al_2O_3 [24, 39], Cu_2O [31]), minerals (calcite, hydroxyapatite, graphite, mica, sapphire) [40-42], semiconductors (CdS, GaN, GaAs and ZnS) [43-45], carbon materials (graphene, carbon nanotubes) [46, 47] and polymer materials [48, 49]. These isolated peptides have many practical applications in biomineralization [32, 50, 51], synthesis and fabrication of inorganic nanomaterials [40, 52-58], immobilization of nanoparticles onto inorganic or organic surfaces and surface functionalization [34, 38, 59-61]. Now, it is starting to be possible to create novel materials using biological linkers to join more than one type of material generating hybrids with unique electronic, mechanical, magnetic or photonic properties [26, 27].

The aim of this paper is to summarize and discuss recent progress in patents on MBPs specifically exploring inorganic nano surfaces like metals, metal oxides, minerals, carbon based materials, polymer based materials, magnetic materials and semiconductors by peptide display strategies and their utilization in the generation of advanced nanomaterials.

In order to get a clear picture on the number of patents present to date relevant to MBPs and their applications, a thorough online search was conducted using the available free national and worldwide databases which include EPO Espacenet, WIPO patent scope, USPTO, Google patent search, Patent lens etc. along with commercial databases including Derwent and Patbase. The key words used to find all the relevant patents were combinatorial/ phage displayed

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peptides, material binding peptides, metal binding peptides (Gold (Au), Silver (Ag), Titanium (Ti), Platinum (Pt), Palladium (Pd), Cobalt, Copper, Nickel, Lead, Cadmium and Aluminum), metal oxide binding peptides (Iron oxide (Fe_2O_3), Lanthanide oxide, Silica or silicon dioxide (SiO_2), Quartz, Zeolites, Zinc oxide (ZnO), Palladium oxide (PdO), Cobalt oxide (CoO), Manganese oxide (MnO_2), Calcium Oxide, Cuprous/ copper oxide (Cu_2O/ CuO), Zirconium oxide (ZrO_2), Tin Oxide (SnO_2), Chromium oxide and Aluminum oxide), mineral binding peptides (Clay, Calcium phosphate, Calcium carbonate and Hydroxyapatite), Carbon based binding peptides (Graphene, Carbon nanotubes, Graphite, Fullerenes and Diamond), Semiconductor binding peptides (Zinc Sulfide, Gallium Arsenide, Cadmium Sulfide, Germanium and combinations), interfacial binding peptides and polymer binding peptides. Both English and American spellings were included in the searches. The initial number of patents found related to material or IOBPs were 981. After reading and excluding irrelevant patents such as organic binding peptides, works published before 2001, repeated patents, documents not in English etc., 51 highly relevant IOBPs patents published from 2001 onwards were selected and analyzed.

2. COMBINATORIAL DISPLAY PROCESS ON NANOMATERIAL SURFACES

The connection between inorganic materials and biomolecules is not new in nature and exists naturally through the process of biomineralization. Through this, complex inorganic nanostructures including metal oxides and minerals are synthesized by certain species like magnetite, an iron oxide (Mms Proteins) in bacteria [62-64], silica (silaffins) in diatoms [65-70], silica (silicatein) in sponges [71, 72] aragonite and calcite (chitin, proteins and polysaccharides) in mollusks [73]. Though artificial processes have been used to reproduce the biominerals or materials their quality is challenging. In order to meet the quality and demand, several research groups started their quest for better alternate routes to produce more efficient, reliable and bulk bionanomaterials using inspiration from nature. This lead to the discovery of novel biomimetic approaches where peptides having affinity towards any target inorganic material can be isolated and practically reproduced using combinatorial peptide libraries such as phage display [1-6], bacterial/ yeast display [7-10], ribosome, mRNA or cDNA display [11-18] and rational design [74-76] as shown in Figure 1.

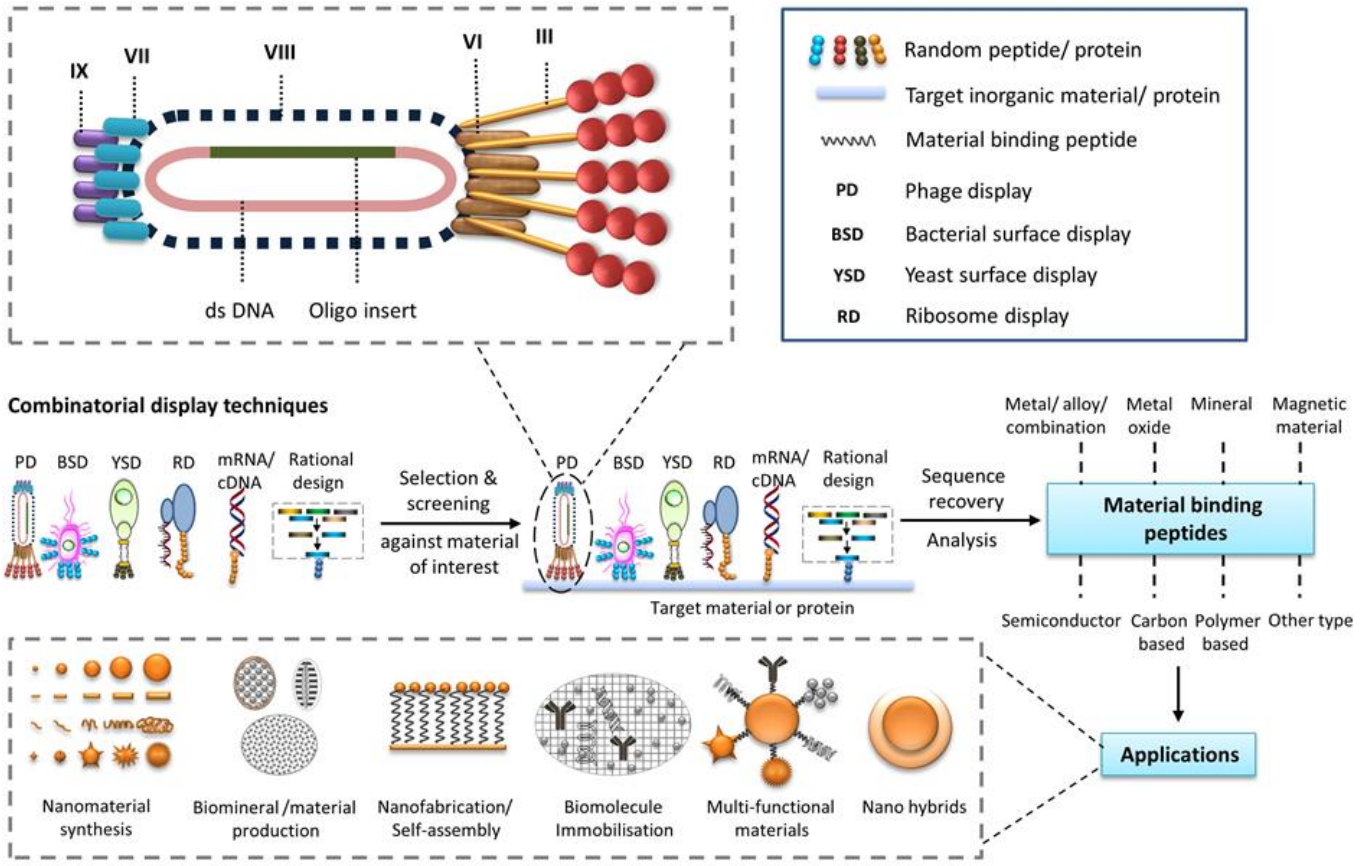

Figure 1: Schematic representation of different types of combinatorial display approaches used for selecting and screening of MBPs and their utilization towards practical applications including nanomaterial synthesis, assembly and fabrication of nanostructures, improving biocompatibility and biomolecule immobilization

A combinatorial phage library consists of peptide, protein and antibody libraries many of which are commercially available. These libraries have been constructed by fusing DNA fragments into the genome of the phage or phagemid, and displaying the peptides on the surface of the phage coat proteins. For example, different types of phage coat proteins including pIII, pVI, pVII, pVIII and pIX have been used in phage libraries to display peptides, proteins and antibodies. as shown in Figure 1. The selection of coat proteins in the phage library depends on the type of display being looked for. For example, pIII phage capsid protein allows for monovalent display while pVIII allows for polyvalent display. A typical combinatorial display approach involves selection, screening and recovery of MBPs using any of the mentioned combinatorial technologies. So far, a range of biomimetic peptides showing specific affinity and molecular recognition for inorganic nanomaterials including metals, metal oxides, minerals, magnetic and semiconductor materials, carbon or polymer based materials have been isolated [19-49]. Further, these material specific peptides have been used for synthesizing simple to complex bio- or nano-materials, mediating the controlled biomineralzation process, directing self-assembly and nanofabrication of ordered structures, facilitating the immobilization of functional biomolecules and for constructing inorganic-inorganic or organic-inorganic nano hybrids [50-61, 77-79].

3. RECENT PATENTS ON INORGANIC MBPS AND THEIR APPLICATIONS

This section summarizes relevant patents on inorganic MBPs and their application towards novel innovations as shown in Tables 1-6. In the patents (WO 078451 A2, US 7905943 B1, US 0172282 A1) Naik and coworkers [80, 81], used the phage display technique to screen and isolate MBPs specific to metals (Ag, Au, Co, Pd, Gd), metal oxides (SiO_2, GeO_2, Co_3O_4, Fe_2O_3, ZnO, SnO_2) and other materials (ruby, carbon nanotubes). These peptides were further used as templates to mediate the controlled synthesis and formation of useful nanostructured materials alongside producing multifunctional bimetallic (gold-palladium) hybrid nanomaterials [81]. In addition to the existing combinatorial phage display approach for identifying novel peptides that are capable of showing high binding to inorganic surfaced nanomaterials, they developed a polymerase chain reaction (PCR)-driven phage display method to isolate peptide sequences specific to nanomaterials, thereby improving the process [82].

In a similar way, many patents have been registered obtaining SBPs having binding affinity towards a range of metals and metal oxides such as gold [83], silver, titanium and silicone [84], silica coated particles [85], titanium oxide and silicon containing compounds [86], titanium and stainless steel [87], iron oxide [88], dysprosium oxide [89] and ceramic materials [90] that utilize the same peptide sequences to initiate and synthesize nanostructures by tuning their size and shape [91]. Also, peptides designed through biomimetic and computational modelling have been used to precipitate stable and well defined titanium oxide nanoparticles of uniquely controlled morphologies including rectangular (KSSKK), spherical (SKSKKKSKSKKK, SKKKKKKKKKS, RRSSSRRSSSRR, RRRSRRRSRRRSRRR and SKKSKKK), flat and fused disks (SKKKKSSKKKKS, KKKSKSKKK, RRRSSRRRSSRRR, SKSKKKSKSKKKSKS and SSKKKSSKKK) and porous sheets (SKKKKKSKKKK, KKSSKKKKKKKKKS, KKKKSSKKKK, SKKSKKKKKKKK and SKKKSKKKK) without the use of high temperatures and pressures [92]. Additionally, these peptides revealed aggregate formation among themselves and the role of secondary structure in controlling morphology [92].

Table 1. **Relevant patents on metal, metal oxide, metal compound or combination binding peptides**

No	Patent number/ Publication or Renewal Years	Patent Title	Inventor/ Assignee/ Applicant	Combinatorial Library Used	Target Inorganic Material of Interest	Reference
1	WO 078451 A2 US 0035223 A1 (2003, 2006)	Method of isolating binding peptides from a combinatorial phage display library and peptides produced thereby	Rajesh Naik, Morley Stone, Daniel Carter/ New Century Pharmaceuticals, Inc. (US)	Phage display (PhD. -12)	Silver, silica, germanium, cobalt and iron oxides	80
2	US 7905943 B1 (2011)	Synthesis of hybrid inorganic nanoparticle structures using peptides	Joseph M. Slocik, Rajesh R. Naik/ The United States of America as Represented by The Secretary of the Air Force (US)	Phage display	Palladium, gold	81
3	US 0172282 A1 US 0176760 A1 (2006, 2008)	Peptide templates for nanoparticle synthesis obtained through PCR-driven phage display method	Rajesh Naik, Morley Stone, Daniel Carter	Phage display (PhD. -12)	Metals (Ag, Au, Co, Pd, Gd), metal oxides (SiO_2, GeO_2, Co_3O_4, Fe_2O_3, ZnO SnO_2), other materials (Ruby,	82

					carbon nanotubes)	
4	US 0280220 A1 US 8088740 B2 (2010, 2012)	Gold binding peptides and shape-and size-tunable synthesis of gold nanostructures	Hor Gil Hur, Jung Ok Kim, Dae Hee Kim, No Sang Myung/ Gwangju Institute of Science and Technology, Gwangju (KR)	Phage display (PhD. -12)	Gold	83
5	WO 010031 A1 US 7498403 B2 (2005, 2009)	Peptides capable of binding to titanium silver silicone	Kiyotaka Shiba, Kenichi Sano/ Japan science and technology agency, Tokyo (JP)	Phage display (C7C, D12)	Silver, titanium, silicon	84
6	US 0158822 A1 WO 080419 A1 (2010)	Peptides that bind to silica coated particles	Fahnestock *et al*./ E.I. du Pont de Nemours and Company, Wilmington, DE (US)	Phage display	Silica	85
7	WO 111832 A1 US 0045917 A1 (2011, 2013)	Method for selecting polypeptide sequence, metal oxide or silicon containing compound binding peptide and use thereof	Akira Wada, Yoshihiro Ito, Takashi Kitajima / Riken (JP)	Phage display	Titanium oxide, silicon containing compounds	86
8	US 0185870 A1 WO 072542 A2 (2003, 2005)	Interfacial biomaterials	Mark W. Grinstaff, Daniel J. Kenan, Elisabeth B. Walsh, Crystan Middleton/ Duke University (US)	Phage display (PhD. -13, 19 X_6PX_6, X_6YX_6, and $SCX_{16}S$ libraries)	Titanium, stainless steel	87
9	US 0158837 A1 WO 080418 A1 (2010)	Iron oxide-binding peptides	Stephen R. Fahnestock, Kristy N. Kostichka, Anju Parthasarathy, Hong Wang/ E.I. Dupont De Nemours and Company (US)	Chemical/ synthetic approach	Iron oxide	88
10	WO 111407 A1 (2015)	Rare earth material-binding peptide and use thereof	Takaaki Hatanaka, Nobuhiro Ishida/ Kabushiki Kaisha Toyota Chuo Kenkyusho (JP)	Phage display (Random T7 library)	Dysprosium oxide	89
11	WO 007723 A1 (2010)	Peptide capable of binding to ceramic material	Hideki Kawamura, Kiyotaka Shiba, Kenji Kashiwagi/ Murata Manufacturing Co., Ltd., Japanese Foundation for Cancer Research (JP)	Phage display (Ph.D. -12 & C7C)	Ceramic and metal or oxide or ions combinations, barium titanate, titanium oxide, zirconium oxide	90
12	US 0100969 A1 (2009, 2016)	Templates for controlling synthesis of nanoparticles into discrete assemblies	Nathanial L. Rosi, Chun-Long Chen/ University of Pittsburgh -- Of the Commonwealth System of Higher Education (US)	Phage display (PhD. -12)	Gold	91
13	US 8834831 B2 (2014)	Controlling morphology of titanium oxide using designed peptides	E. Stote II Robert, Shaun F. Filocamo/ The United States of America as represented by the secretary of the army (US)	Combination of biomimetic and computational models	Titanium oxide	92
14	WO 000493 A2 US 0035245 A1 (2010, 2013)	Inorganic-binding peptides and quality control methods using them	Christelle Vreuls, Cécile Van De Weerdt, Catherine Archembeau, André Renard, Joseph Martial/ Arcelormittal Liege Research, Universite De Liege Interface Entreprises Universite (BE)	Phage display (PhD. -12 & C7C)	Stainless steel, titanium dioxide, zinc oxide	93
15	WO 055980 A2 US 0219504 A1 (2011, 2012)	Composite of a protein comprising zinc oxide-binding peptides and zinc oxide nanoparticles, and use thereof	Nam-Hyuk Cho, Taek-Chin Cheong, Seung-yong Seong, Ji Hyun Min, Jun Hua Wu, Young-Keun Kim/ Snu R&Db Foundation, Korea University Research and Business Foundation (KO)	Combination of peptide library and motif modification	Zinc oxide	94
16	US 0249682 A1 WO 094095 A2 (2005, 2006)	Long lasting waterproof sunscreen comprising metal oxide and peptide conditioner	Janine Buseman-Williams, Xueying Huang, Hong Wang, Gary Whiting/ E.I. Dupont De Nemours and Company (US)	Phage display (Ph. D.-7& 12)	Titanium dioxide, zinc oxide, cerium oxide, iron oxide and combinations	95

17	WO 056511 A2 US 7618816 B2 (2007, 2009)	Metal-binding therapeutic peptides	Desmond Mascarenhas/ Ontherix, Inc. (US)	Combination of cell display, mutations	Metal based compounds and domains	96
18	US 0165225 A1 US 8916376 B2 (2012, 2014)	Metal-binding peptides	Victor G. Stepanov, Yamei Liu, George E. Fox, George W. Jackson, Roger J. McNichols, Weniger/ Biotex, Inc. (US)	Artificial library created (20 mer)	Metal ions, organic molecules, viral particles and biological molecules	97
19	WO 079053 A2 US 8569226 B2 (2009, 2013)	High Affinity metal-oxide binding peptides with reversible binding	Eric Mark Krauland, Stephen Kottmann, Roberto Juan Barbero, Angela Belcher/ Massachusetts Institute of Technology, Cambridge, MA (US)	Yeast surface display, rational design methodology, and genetic engineering	Oxides (sapphire, quartz, thermally grown oxide on silicon, amorphous borosilicate glass) or plasma activated surfaces	98

Vreuls *et al.* invented a method to identify imperfections or non-homogenous conditions on the surface of materials thereby isolating specific nanoparticles from a mixture by using stainless steel (MTWDPSLASPRS), titanium oxide (LNAAVPFTMAGS) and zinc oxide binding peptides (VRTRDDARTHRK) [93]. In a separate patent (US 0219504 A1), Cho and co-workers created a complex protein joining zinc oxide binding peptides and zinc oxide nanoparticles together which resulted in an active agent for delivering drugs *in vivo* by an intracellular mode and helping in cell or MRI imaging [94]. In another patent (US 0249682 A), Williams and co-workers disclosed a sunscreen formulation that is resistant to water and lasts for a long time using peptide derived oxides such as titanium dioxide, zinc oxide, iron oxide, cerium oxide and a combination of nanoparticles alongside liquid as a sunscreen agent [95].

Desmond Mascarenhas in his patent (WO 056511 A2) described a method for treating selective human inflammatory diseases by delivering the metallic binding domain polypeptide linker complex (QCRPSKGRKRGFCW) in conjunction with curcumin and lycopene that showed specific binding to live cells that were under cellular stress resulting in increased cellular uptake, providing diagnostic information and altering a wide range of disease and cellular processes [96]. Alternatively, functionalised biomolecules were produced in cells or organisms by incorporating materials such as metals, toxins and peptides into the genome of cells and such modified cells have been used for isolating targeted molecules within the cells [97]. Furthermore, Krauland *et al.* (WO 079053 A2) engineered two peptides (GKGKGKGKGKGK & GKGKGKGKGKGKASGKGKGKGKGKGK) using a combination of yeast surface display, biopanning approaches, rational design strategy and genetic engineering that exhibit high affinity to metal oxide surfaces (eg. sapphire, quartz etc.) and bind in a reversible manner to plasma activated surfaces (eg. polystyrene, polydimethylsiloxane, polyurethane etc. upon exposure to oxygen plasma) where either of the peptides can selectively be released by exposing the oxide or plasma activated surfaces to high salt conditions and/or changing the electric field. In addition, these peptides when integrated selectively with protein or cells, act as a binding agent towards targeted oxide surfaces, thereby helping in the construction of biosensors [98].

Imamura *et al.* disclosed an invention related to a magnetic–biosubstance complex structure formation, where the biosubstance was immobilized on the carrier present on the magnetic substance. As a result of this, structures containing a carrier can be used as a vehicle for carrying or delivering diagnostic agents, bacteria, cells and drugs, separation and purification of proteins, DNA or RNA, as a carrier for enzyme reaction and for the formation of complex structures could be developed. The structure in the present invention (WO 097416 A1) comprises a magnetic substance, a peptide fragment and/or a gene capable of linking to a magnetic substance, preferably ferrous oxide (Fe_2O_3) binding peptides selected from phage display and a biosubstance containing nucleic acids, proteins, lipids, carbohydrates and combinations thereof, preferably a polyhydroxyalkanoate-synthesizing enzyme [99].

Table 2. Relevant patents on magnetic and semiconductor binding peptides

No	Patent number/ Publication or Renewal years	Patent title	Inventor/ Assignee/ Applicant	Combinatorial library used	Target inorganic material of interest	Reference
20	WO 097416 A1 US 0108123 A1 (2004, 2008)	Magnetic substance-biosubstance complex structure, peptide fragment capable of linking to magnetic substance and gene therefor, and process for structure	Takeshi Imamura, Tetsuya Yano, Tsuyoshi Nomoto, Shinya Kozaki, Tsutomu Honma, Akiko Tsuchitani/ Canon Kabushiki Kaisha (JP)	Phage display (Ph.D. -12)	Iron oxide (Fe_2O_3)	99
21	US 0148380 A1 US 8372949 B2 (2003, 2013)	Molecular recognition of materials	Angela M. Belcher (US)	Phage display library (7-12 a.a fused to p3	Semiconductor and magnetic material combinations (GaN,	100

				protein)	ZnS, CdS, Fe_3O_4, Fe_2O_3, CdSe, ZnSe and $CaCO_3$)	
22	WO 026590 A2 US 0003629 A9 (2003, 2012)	Biological control of nanoparticle nucleation, shape and crystal phase	Angela Belcher, Richard Smalley, Esther Ryan, Seung-Wuk Lee/ Board of Regents, The University of Texas System (US)	Phage display (Ph.D. -12, C7C)	Metal oxides (Fe_3O_4, Fe_2O_3 and $CaCO_3$) Semiconductors (GaAs, InP, ZnS, CdS, CdSe, and ZnSe)	101
23	WO 029431 A2 US 0300605 A1 (2003, 2011)	Nanoscaling ordering of hybrid materials using genetically engineered mesoscale virus	Angela M. Belcher, Seung-Wuk Lee/ Board of Regents, University of Texas System (US)	Phage display (PhD. -7& 12)	Semiconductors (GaN, CdS, FeS, and ZnS, CdSe, ZnSe)	102
24	WO 033488 A2 (2004)	Peptide mediated synthesis of metallic and magnetic materials	Angela M. Belcher, Brian Reiss, Chuanbin Mao, Daniel Solis/ Board of Regents, University of Texas System (US)	Phage display (PhD. -12)	Metal materials including magnetic materials (e.g., Co, CoPt $SmCo_5$, or FePt)	103
25	WO 037856 A2 US 0264166 A1 (2005, 2012)	Multifunctional biomaterials as scaffolds for electronic, optical, magnetic, semiconducting, and biotechnological applications	Angela M. Belcher, Beau R. Peelle, Ki Tae Nam/ MIT, Board of Regents, The University of Texas System (US)	Phage display (M13 pf1, fd1, TMV)	Semiconductors (ZnS and CdS) Metals (Au)	104
26	WO 036992 A2 EP 1545202 A2 (2004, 2005)	Fabricated biofilm storage device	Angela M. Belcher, Seung-Wuk Lee, Brent L. Iverson, Soo-Kwan Lee/ Board of Regents, University of Texas System (US)	Phage display (PhD. -12)	Semiconductors (GaAs, and ZnS) indium tin oxide (ITO), metal, metal alloy, mineral, or combinations of streptavidin BPs	105
27	WO 067683 A2 US 8846190 B2 (2005, 2014)	Inorganic nanowires	Angela M. Belcher, Chuanbin Mao, Daniel J. Solis/ Board of Regents, The University of Texas System (US)	M13 bacteriophage display	Semiconductor, metallic, metal oxide and magnetic or mixtures	106

Table 3. Relevant patents on carbon based MBPs

No	Patent number/ Publication or Renewal years	Patent title	Inventor/ Assignee/ Applicant	Combinatorial library used	Target inorganic material of interest	Reference
28	US 0309126 A1 (2014)	Peptide binding to graphitic materials and phage including same	Hyunjung Yi, Ki Young Lee, Ki Young Lee, Chaun Jang, Joonyeon Chang and Joonyeon Chang/ Korea Institute of Science and Technology, seoul (KR)	M13 phage display (p8 peptide library)	Graphite, graphene, carbon nanotube, fullerene	107
29	WO 102020 A2 US 0028316 A1 (2003, 2011)	Carbon nanotube binding peptides	Anand Jagota, Steven Raymond Lustig, Siqun Wang, Hong Wang/ E. I. Du Pont De Nemours and Company (US)	Phage, bacterial and yeast display	Carbon nanotube	108
30	US 0156688 A1 US 9029168 B2 (2012, 2015)	Use and making of biosensors utilizing antimicrobial peptides for highly sensitive biological monitoring	Michael C. McAlpine, Manu Sebastian Mannoor/ The Trustees of Princeton University (US)	Phage display and chemical modification	Graphene, microbial and bacterial cells	109

Angela M. Belcher's group obtained many patents describing the selection and screening of IOBPs or viruses using phage display libraries and genetic engineering methods for varied materials including magnetic and semiconductor nanomaterials, and their utilization towards a range of applications [US 0148380 A1, WO 026590 A2, WO 029431 A2, WO 033488 A2, WO 037856 A2, WO 036992 A2, WO 067683 A2]. As illustration, the examples include, a method for selecting peptides containing one or more sequences having specific affinity for one or more magnetic or semiconducting crystal materials like GaN, ZnS, CdS, Fe_3O_4, Fe_2O_3, CdSe, ZnSe and $CaCO_3$ [100], controlled

nanoparticle synthesis including the desired target nanoparticle size, shape, growth and crystal phase by using the same phage or virus displayed nanoparticle binding peptides [101] and directing the assembly and fabrication of magnetic or semiconducting nanoscale hybrid materials mediated by genetically engineered mesoscale virus or phage displayed peptides [102, 103]. Additionally, these peptide or virus equipped multifunctional biomaterials have been used as templates or scaffolds for magnetic, electronic, optical and semiconducting applications [104], as well as for designing biofilm storage devices and nanowires [105, 106]. All the patents from this group describe a range of phage displayed or virus modifications that show specific binding to nanomaterial structures, as well as forming novel hybrid structures in the presence of modified biomaterials for specific binding. For instance, the polypeptide and oligomeric amino acid sequences can be expressed anywhere on the surface of the virus particles or coat proteins including pIII, pVI, pVII, pVIII and pIX and in the genome of the virus itself or at more than one site for modification of specific binding units. i.e. the ends of the polypeptide or virus particle can be altered to show specific recognition to an initial target material, whereas the genome of the virus can be manipulated to show specific affinity towards a second target material. In this process, multiple sites on the virus nanoparticles can be modified and utilized as scaffolds or templates for designing nanowires and novel devices [100-106].

Carbon based MBPs include graphene, fullerene and single or multi-walled carbon nanotubes. In separate inventions, two separate patents (US 0309126 A1 and WO 102020 A2) were issued for selecting peptides that were found to have specific binding interaction for a variety of graphitic materials such as graphene, highly oriented pyrolytic graphite, graphite alone and fullerenes [107] and for carbon nanotubes [108]. Moreover, these graphitic or carbon nanotube binding peptides have been used for application towards designing sensing devices to detect microorganisms. For example, a method for preparing sensors has been disclosed (US 0156688 A1), in which the sensing device was built by immobilising the antimicrobial peptide motifs having definite binding affinity for targets including *E.coli*, gram +ve or -ve bacteria, viruses, pathogens, fungi and varied cancer cells which can be read out upon changes in the electrical conductivity of the system [109].

Table 4. Relevant patents on mineral binding peptides

No	Patent number/ Publication or Renewal years	Patent title	Inventor/ Assignee/ Applicant	Combinatorial library used	Target inorganic material of interest	Reference
31	WO 117564 A2 US 7749957 B2 (2007, 2010)	Clay-binding peptides and methods of use	Steven Dale Ittel, Scott D. Cunningham, Pierre E. Rouviere, Stephen R. Fahnestock, John P. O'Brien, Eberhard Schneider, Gregor Schurmann, Peter Wagner/ E.I. du Pont de Nemours and Company, Wilmington (US)	Phage display (PhD. -7& 12) and mRNA display (p27 mer)	Clay	110
32	US 7754680 B2 (2010)	Peptides for binding calcium carbonates and methods of use	Scott D. Cunningham, Steven Dale Ittel, John P. O'Brien, Pierre E. Rouviere / E.I. du Pont de Nemours and Company, Wilmington, DE (US)	Phage display (PhD. -7& 12) and mRNA display (p27 mer)	Calcium carbonates	111
33	WO 062776 A2 US 8022040 B2 (2006, 2011)	Hydroxyapatite-binding peptides for bone growth and inhibition	Carolyn R. Bertozzi, Jie Song, Seung-Wuk Lee/ The Regents of the University of California (US)	Phage display (Ph. D.-7& 12, C7C)	Hydroxyapatite(HAp)	112
34	WO 166626 A1 US 0152672 A1 (2012, 2016)	Reagents and methods for treating dental disease	Mehmet Sarikaya, Martha Somerman, Candan Tamerler-Behar, Hanson Fong, Hai Zhang, Mustafa Gungormus/ University of Washington (US)	Phage display (PhD. -12, C7C)	Hydroxyapatite	113
35	US 0070200 A1 (2010)	Method and system for designing polypeptides and polypeptide-like polymers with specific chemical and physical characteristics	Mehmet Sarikaya, Candan Tamerler-Behar, Ersin Emre Oren, Vaikuntanath V. Samudrala (US)	Phage display (Ph.D.-12), bacterial cell surface display (FliTrx)	Hydroxyapatite, quartz and gold	114

Similarly, mineral based MBPs for clay, calcium phosphate or calcium carbonate, hydroxyapatite and other materials have been identified. A number of patents were granted for peptides having specific binding affinity for a variety of minerals including clay [110], calcium carbonate [111] and hydroxyapatite materials [112-114]. Additionally,

these mineral recognising peptides have been utilized for regenerating or inhibiting the growth of bone under controlled biomineralization conditions [112] and for curing dental diseases [112]. For example, Bertozzi *ed.* filed a patent for the identification of hydroxyapatite binding peptides which are similar to the type I collagen sequence $(Gly\text{-}Pro\text{-}Hyp)_X$, a crucial material of extracellular matrices of native bone; with these sequences then being used as a template for synthesizing implantable bone by attaching a biocompatible and biodegradable substrate in mammals [112]. In contrast, Sarikaya *et.al.* developed a method for curing dental diseases and initiated dental mineralisation by constructing a recombinant polypeptide complex comprising phage displayed amelogenin and heterologous polypeptide containing substances derived from collagen, dentin, statherin, osteocalcin, enamilin and/or inorganic polypeptides and their affinity tags and markers [113]. In another patent (US 0070200 A1), he described a method and system for developing polypeptides which were initially characterized based on their specific affinities, physical and chemical properties for target inorganic substances and then applied those characterizations computationally to generate a polypeptide-scoring function resulting in the identification of further polypeptide sequences for additional applications in areas such as electronics, nanomedicine and nanotechnology [114].

Table 5. Relevant patents on polymer binding peptides

No	Patent number/ Publication or Renewal years	Patent title	Inventor/ Assignee/ Applicant	Combinatorial library used	Target inorganic material of interest	Reference
36	US 0185870 A1 WO 072542 A2 (2003)	Interfacial biomaterials	Mark W. Grinstaff, Daniel J. Kenan, Elisabeth B. Walsh, Crystan Middleton/ Duke University (US)	Phage display (PhD. -13, 19 X_6PX_6, X_6YX_6, and $SCX_{16}S$ libraries)	Polystyrene, polyurethane, polycarbonate, polyglycolic acid.	87
37	WO 035612 A2 US 0113741 A1 (2004, 2010)	Composition, method and use of bi-functional biomaterials	Angela M. Belcher, Christine J. Schmidt, Kiley P. H. Miller, Archit Sanghvi/ Board of Regents, The University of Texas Systems (US)	Phage display (Ph.D. -12)	Polypyrrole doped with chlorine (PPyCl) and poly lactic acid-co-glycolic acid (PLGA))	115
38	WO 033482 A2 US 0084618 A1 (2004, 2012)	Phenolic binding peptides	Christopher Murray, Pilar Tijerina, Franciscus Van Gastel/ Danisco US Inc., Palo Alto, CA (US)	Phage display (PhD-7& 12, C7C)	Phenolic compounds	116
39	US 0141628 A1 US 7906617 B2 (2007, 2011)	Polyethylene binding peptides and methods of use	Scott Cunningham, David Lowe, John O'Brien, Hong Wang, Antoinette Wilkins/ E.I. du Pont de Nemours and Company, Wilmington, DE (US)	Phage display (PhD-7& 12)	Polyethylene	117
40	US 0265431 A1 US 7858581 B2 (2007, 2010)	PMMA binding peptides and methods of use	Scott Cunningham, David Lowe, John O'Brien, Hong Wang, Antoinette Wilkins / E.I. du Pont de Nemours and Company, Wilmington, DE (US)	Phage display (PhD-7& 12)	Polymethylmethacrylate	118
41	US 0310495 A1 (2010)	Peptides having affinity for poly (benzyl methacrylate-co-methacrylic acid) potassium salt copolymers and methods of use	Eberhard Schneider, Gregor Schurmann, Peter Wagner, Hong Wang, Gordon Mark Cohen/ E. I. Du Pont De Nemours and Company (US)	mRNA and phage display	Poly (benzyl methacrylate -co-methacrylic acid) potassium salt copolymers	119
42	WO 018964 A2 US 0178390 A1 (2009, 2013)	System comprising bacteriophages and particles that contain active substances	Stefanie Eiden, Axel Eble, Martin Weiss, Daniel Gordon Duff, Olaf Bork, Holger Egger, Bastian Budde, Sascha Plug/ Bayer Technology Services Gmbh	Phage display (PhD. -12, gpIII, gpVII)	Polycarbonate and polyurethane surfaces	120
43	WO 065573 A1 US 0279894 A1 (2009, 2010)	Bacteriophages and coating material for surfaces	Stefanie Eiden, Axel Eble, Bastian Budde, Sascha Plug, Peter Krüger/ Bayer Technology Services Gmbh,	Phage display (PhD. -12, gpIII, gpVIII)	Polyurethane surfaces	121

			Bayer Material science			

A variety of synthetic polymers were displayed that link biological and non-biological surfaces resulting in the identification of polymer binding peptides and their utilization in generating unique functional nanomaterial surfaces. Synthetic and copolymer surfaces include polystyrene, polyurethane, polymethylmethacrylate, polycarbonate, polyurethane, polyglycolic acid, phenolic compounds and combinations of other nanomaterials thereof. A few patents were registered for selecting peptides or proteins found to interact specifically with polymer surfaces including polystyrene, polyurethane, polycarbonate, polyglycolic acid and combinations with metal or oxide nanomaterials [87], polypyrrole doped with chlorine and poly lactic acid-co-glycolic acid [115], phenolic compounds [116], polyethylene [117], polymethylmethacrylate [118], poly (benzyl methacrylate-co-methacrylic acid) potassium salt copolymers [119] and polycarbonate and polyurethane surfaces [120, 121]. Moreover, these polymer binding peptides along with proteins of bacteriophages have been utilized for the prolonged release of drugs [120] and as an active coating material for developing corrosion resistant surfaces [121].

Table 6. Relevant patents on other MBPs

No	Patent number/ Publication or Renewal years	Patent title	Inventor/ Assignee/ Applicant	Combinatorial library used	Target inorganic material of interest	Reference
44	WO 048399 A2 US 0364584 A1 (2004, 2014)	Skin or hair binding peptides	Giselle G. Janssen, Christopher J. Murray, Deborah S. Winetzky/ Danisco Us Inc.	Phage display (Ph.D. 7& 12, C7C)	Hair and Skin	122
45	US 0222609 A1 WO 126641 A1 (2006, 2007)	Peptide-based body surface colouring reagents	John O'Brien, Hong Wang, Ying Wu/ E. I. Du Pont De Nemours and Company (US)	Phage display (Ph.D. -12)	Hair, nail, teeth, gums, skin, and tissues of the oral cavity.	123
46	US 0107614 A1 WO 057463 A2 (2005, 2008)	Peptide-based conditioners	Stephen Fahnestock, John O'Brien, Hong Wang/ E. I. Du Pont De Nemours and Company (US)	Phage display (Ph.D. 7 & 12)	Hair, nail, gums, oral cavity tissues and skin	124
47	WO 028503 A1 US 7759460 B2 (2006, 2010)	Peptide-based body surface reagents for personal care	Xueying Huang, John P. O'brien, Hong Wang, Ying Wu/ E. I. Du Pont De Nemours and Company (US)	Phage display (Ph.D. 7& 12)	Hair, Nail and Skin	125
48	US 0247590 A1 WO 117709 A2 (2010)	Peptide-based systems for delivery of cosmetic agents	Douglas Robert Anton, Susan Daly, Robert J. Bianchini, Hong Wang, Pierre E. Rouviere, Scott D. Cunningham, Stephen R. Fahnestock, Tanja Maria Gruber/ Johnson & Johnson, E. I. Du Pont De Nemours and Company (US)		Human hair, skin and nail.	126
49	WO 015163 A1 US 0183373 A1 (2009, 2011)	Recombinant peptide production using a cross-linkable solubility tag	Albert W. Alsop, Qiong Cheng, Linda Jane Decarolis, Stephen R. Fahnestock, Tanja Maria Gruber, Pierre E. Rouviere/ E. I. Du Pont De Nemours and Company (US)	Phage, ribosome and mRNA display	Hair, skin, nail, teeth, cellulose, polymer and clay.	127
50	US 0141629 A1 US 7709601 B2 (2007, 2010)	Nylon binding peptides and methods of use	Scott Cunningham, David Lowe, John O'Brien, Hong Wang, Antoinette Wilkins/ E.I.du Pont de Nemours and Company, Wilmington, DE (US)	Phage display (Ph.D. -7 &12)	Nylon agents (pharmaceuticals, markers, colorants, conditioners and fragrances)	128
51	WO 079479 A2 US 0231251 A9 (2001, 2013)	Methods for selective targeting	Giselle G. Janssen, Christopher J. Murray, Deborah S. Winetzky David A. Estell, Pilar	Phage display (Ph.D. -7-12)	Selected fabrics, stains, soil, pigments, skin, hair, cytokines and	129

			Tijerina, Yiyou Chen/ Genencor International, Inc.		receptors	
52	US 7332356 B2 (2004)	Fluorescent dye binding peptides	Garry Nolan, Michael Rozinov/ The Board of Trustees For The Leland Stanford Junior University (US)	Phage display (Ph.D.-12)	Fluorophore dyes (Fluorescein, oregon green 514, rhodamine red and texas red)	130

In the same way, a separate class of MBPs were also reported where one or more compounds binds to different specific targets under the presence of anti-targets. In simple terms, a peptide that binds specifically to compound A has been identified using compound B as an anti-target and compound B binding peptides in the presence of anti-target compound A. The compounds include coloring, conditioning, cosmetic and personal care reagents that are directly involved in improving the properties of keratin, a key component in skin, hair, nails and teeth. Various patents have been published where peptides having higher affinity for human body surfaces such as skin, hair, nail, teeth, pigment, gum or oral cavity; nylon agent and fluorophore dyes were selected and identified using phage, ribosome and mRNA libraries [122-130]. Although peptide based products have useful applications, their long lasting behavior remains a challenge. In order to improve the durability for these products, two or more agent binding peptides have been used alongside linkers [123-127]. Further, these body surface binding proteins or peptides have been used in day to day applications such as hair or nail coloring reagents [123], conditioners for hair or skin [124], personal care products for skin, teeth and associated pigments [125], as cosmetic delivery agents [126], recombinant peptide production [127] and for developing markers, fragrances, pharmaceutical products, selective fabrics and fluorophore dyes [128-130].

CONCLUSION

Biomimetic MBPs have emerged as a new frontline in the design of novel nanomaterials with improved/ controlled physical and chemical properties without affecting the structural or functional activities of the nanomaterials themselves which can be realized from the above discussion of recent literature and patents. Although combinatorial display technologies are firstly for selecting and identifying biomolecules against almost any material of interest and further towards generating more efficient and reliable peptide based nanostructures, the accuracy of molecular recognition for inorganic materials as a target and then translating practical (*in vitro*, *in vivo* or *ex vivo* and *in silico*) applications into product specific commercial success is still challenging unlike the situation where organic molecules are the targets of interest.

CURRENT & FUTURE DIRECTIONS

The unique binding ability/nature of peptide libraries to select and screen specific material of interest, particularly inorganic materials has created much interest and potential to reach a wider scientific community which may ultimately lead to the development of even more novel bio- or nano-materials. However, these libraries still possess drawbacks. These include their ability to bind to non-specific undesired targets [131, 132], under representation of the desired sequences and their properties due to having bias towards peptide/ protein position, composition, and expression [133] or pH and interaction specific intrinsic bias [30], thus many target specific strong MBPs are not found during the phage display process. Additionally, another important factor to consider is the limited fundamental understanding of peptide-material interactions which is a major bottle neck for generating peptide based inorganic nanomaterials with improved biostability/ compatibility, solubility and functionality and increased physico-chemical properties. In advancing our understanding of peptide mineral interactions a clear understanding of the solution behavior of both the peptide and the mineral is needed before the interaction of the two can be understood. As examples, in our research we have shown that by careful study of the particular properties of the material itself, for example silica [29, 30, 134] and ZnO [57, 135, 136] we can show that the size of particles [29, 30, 134] and charge/ functionality on particles [30, 137] have clear effects on the binding of small peptides to minerals as well as the route by which a material is formed [57, 135, 136] by moderating peptide mineral interaction.

Further, although, online databases are easily available for specific organic MBPs such as antimicrobial and anticancer peptides, no specific databases have been designed for inorganic MBPs obtained from distinct classes of combinatorial display techniques. We propose that such databases, with all the experimental and computational information relating to the different classes of nanomaterials and libraries should be built. These databases will find solutions for bias problems and improve our understanding of biomolecule-inorganic material interactions which will lead in turn to the development of smart nanomaterials and slowly reduce the sole dependence on *in vitro* display technologies to take this approach forward as is presently the case.

LIST OF ABBREVIATIONS

MBPs = Material binding peptides

SBPs = Solid binding peptides

IOBPs = Inorganic binding peptides

GEPIs = Genetically engineered peptides for inorganics

PD = Phage display

BSD = Bacterial surface display

YSD = Yeast surface display

RD = Ribosome display

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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