Journal of Nanoparticle Research (2006) 8: 193–213 DOI 10.1007/s11051-005-9034-9

Perspectives

The seminal literature of nanotechnology research

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Received 21 February 2005; accepted in revised form 19 August 2005

Key words: nanotechnology, nanoscience, nanotubes, quantum dots, nanoparticles, nanomaterials, selfassembly, citation analysis, citation-assisted background, literature survey, literature review

Abstract

A generally weak area in research papers, reports, and reviews is the complete identification of seminal background documents that formed the building blocks for these papers. A method for systematically determining these seminal references is presented. Citation-assisted background (CAB) is based on the assumption that seminal documents tend to be highly cited. Application of CAB to the field of nano-technology research is presented. While CAB is a highly systematic approach for identifying seminal references, it serves as a supplement and is not a substitute for the judgment of the authors

Introduction

Research is a method of systematically exploring the unknown to acquire knowledge and understanding. Efficient research requires awareness of all prior research and technology that could impact the research topic of interest, and builds upon these past advances to create discovery and new advances. The importance of this awareness of prior art is recognized throughout the research community. It is expressed in diverse ways, including requirements for Background sections in journal research articles, invited literature surveys in targeted research areas, and required descriptions of prior art in patent applications.

For the most part, development of Background material for any of the above applications is relatively slow and labor intensive, and limited in scope. Background material development usually involves some combination of manually sifting through outputs of massive computer searches, manually tracking references through multiple generations, and searching one's own records for personal references. The few studies that have been done on the adequacy of Background material in documents show that only a modest fraction of relevant material is included (e.g., MacRoberts & MacRoberts, 1989, 1996; Liu, 1993).

Typically missing from standard Background section or review article development, as well as in the specific examples cited above, is a systematic

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approach for identifying the key documents and events that provided the groundwork for the research topic of interest. The present paper presents such a systematic approach for identifying the key documents, called citation-assisted background (CAB), and applies it to the area of nanotechnology research.

For nanotechnology specifically, the burgeoning global interest has been accompanied by numerous surveys and reviews of the technical literature. There are numerous books (e.g., Bhushan's Handbook of Nanotechnology (Bhushan, 2004); Goddard's Handbook on Nanoscience, Engineering, and Technology (Goddard, 2002); Freitas' multi-volume set on nanomedicine (Freitas, 1999, 2003); see Appendix 1 of (Kostoff et al., 2005b) for more complete listing of Reference Books), review articles (e.g., Kricka's multi-lingual survey of nanotechnology books and patents (Kricka & Fortina, 2002); Simon's review of the science and potential applications of nanotechnology (Simon, 2005)), and reports (e.g., The Royal Society's comprehensive review on nanoscience and nanotechnologies (Dowling et al., 2004); Colton's indepth review of nanoscale measurements and manipulation (Colton, 2004)) that cover various sub-sets of nanotechnology.

Every published research review on nanotechnology typically covers a limited subset of the technology rather than the total discipline. None of these published reviews has the spatial and temporal breadth of coverage of the present paper, none uses a query of the extent and complexity of the present paper, and none uses the systematic approach described here to insure that all highly cited articles related to the discipline of interest are identified. In a paper published in the present issue (Kostoff et al., 2005a), we used text mining techniques to query the open literature to uncover the infrastructure of nanotechnology publications. In the present paper, we describe a systematic approach to insure that all highly cited seminal articles related to nanotechnology are identified. The technique is use to demonstrate the utility of the CAB approach.

Concept description

The CAB concept (Kostoff & Shlesinger, 2005) identifies the seminal Background documents for a

research area using citation analysis. CAB rests on the assumption that a seminal document for a specific research area will typically have been referenced positively by a substantial number of people who are *active researchers in that specific area*. Implementation of the CAB concept then requires the following steps:

- The research area of interest must be defined clearly
- The documents that define the area of interest must be identified and retrieved
- The references most frequently used in these documents must be identified and selected
- These critical references must be analyzed, and integrated in a cohesive narrative manner to form a comprehensive Background section or separate literature survey

These required steps are achieved in the following manner.

- 1. The research topic of interest is defined clearly by the researchers who are documenting their study results. For example, consider the topic of nanotechnology. In a recent text mining study of nanotechnology (Kostoff et al., 2005a), the topical area was defined to include development and use of techniques to study physical phenomena and construct structures in the physical size range of 1–100 nanometers (nm), as well as the incorporation of these structures into applications.
- 2. The topical definition is sharpened further by the development of a literature retrieval query. In the text mining study mentioned above (Kostoff et al., 2005a), the literature retrieval query was based on the following keywords (*denotes the wildcard used in most search engines):

"NANOPARTICLE* OR NANOTUB* OR NANOSTRUCTURE* OR NANOCOMPOS-ITE* OR NANOWIRE* OR NANOCRYSTAL* OR NANOFIBER* OR NANOFIBRE* OR NANOSPHERE* OR NANOROD* OR NANOTECHNOLOG* OR NANOCLUSTER* OR NANOCAPSULE* OR NANOMATERIAL* OR NANOFABRICAT* OR NANOPOR* OR NANOPARTICULATE* OR NANOPHASE OR NANOPOWDER* OR NANOLITHOGRAPHY OR NANO-PARTICLE* OR NANODEVICE* OR NANODOT* OR NANOINDENT* OR NANOLAYER* OR NANOSCIENCE OR NANOSIZE* OR NANOSCALE* OR ((NM OR NANOMETER* OR NANOMETRE*) AND (SURFACE* OR FILM* OR GRAIN* OR POWDER* OR SILICON OR DEPOSITION OR LAYER* OR DEVICE* OR CLUSTER* OR CRYSTAL* OR MATERIAL* OR ATOMIC FORCE MICROSCOP* OR TRANSMISSION ELECTRON MICROSCOP* OR SCANNING TUNNELING MICROSCOP*)) OR QUAN-TUM DOT* OR QUANTUM WIRE* OR ((SELF-ASSEMBL* OR SELF-ORGANIZ*) AND (MONOLAYER* OR FILM* OR NANO* OR QUANTUM* OR LAYER* OR MULTI-LAYER* OR ARRAY*)) OR NANOELEC-TROSPRAY* OR COULOMB BLOCKADE* OR MOLECULAR WIRE*".

- 3. The query is entered into a database search engine, and documents relevant to the topic are retrieved. In the nanotechnology text mining study mentioned above, 21,474 documents were retrieved from the Web version of the Science Citation Index (SCI) for the year 2003. The SCI was used because it is the only major research database to contain references in a readily extractable format.
- 4. These documents are combined to create a separate database, and all the references contained in these documents are extracted. Identical references are combined, the number of occurrences of each reference is tabulated, and a table of references and their occurrence frequencies is constructed. In the nanotechnology text mining study, 308,961 separate refer-

ences were extracted and tabulated. Table 1 contains the ten highest frequency (most cited) references extracted from the nanotechnology database.

Two frequencies are computed for each reference, but only the first is shown in Table 1. The frequency shown in the rightmost column is the number of times each reference was cited by the 21.474 records in the retrieved database only. This number reflects the importance of a given reference to the specific discipline of nanotechnology. The second frequency number (not shown) is the total number of citations the reference received from all sources in all years after publication, and reflects the importance of a given reference to all the fields of science that cited the reference. This second number is obtained from the citation field or citation window in the SCI. In CAB, only the first frequency is used, since it is topic-specific. Using the first discipline-specific frequency number obviates the need to normalize citation frequencies for different disciplines (due to different levels of activity in different disciplines), as would be the case if total citation frequencies were used to determine the ordering of the references.

Concept implementation

To identify the total candidate references for the Background section, a table similar in structure to Table 1, but containing all the references from the retrieved records, is constructed. A threshold frequency for selection can be determined by arbitrary inspection (i.e., a Background section consisting of

Table 1. Most highly cited documents

Author	Year	Source	Vol	Page	#Cit
Iiiima S	1991	Nature	V354	P56	730
Alivisatos AP	1996	Science	V271	P933	249
Kresge CT	1992	Nature	V359	P710	213
Thess A	1996	Science	V273	P483	196
Murray CB	1993	J Am Chem Soc	V115	P8706	194
Ulman A	1996	Chem Rev	V96	P1533	191
Morales AM	1998	Science	V279	P208	177
Tans SJ	1998	Nature	V393	P49	174
Oregan B	1991	Nature	V353	P737	173
Huang MH	2001	Science	V292	P1897	170

150 key references is arbitrarily selected). The first author has found a dynamic selection process more useful. In this dynamic process, references are selected, analyzed, and grouped based on their order in the citation frequency table until the resulting Background is judged sufficiently complete by the Background developers.

To insure that the influential documents published both long ago and very recently are included, the following total process is used. The reference frequency table is ordered by inverse frequency, as above, and a high value of the selection frequency threshold is selected initially. Documents with citations above this frequency are tagged. Then, the table is re-ordered chronologically. The early historical documents with citation frequencies substantially larger than those of their contemporaries are selected, as are the extremely recent documents with citation frequencies substantially larger than those of their contemporaries. By contemporaries, it is meant documents published in the same time frame, not limited to the same year (see next paragraph for examples of how we implement 'same time frame'). Then, the dynamic selection process defined above is applied to the early historical references, the intermediate time references (those falling under the high frequency threshold), and the extremely recent references (approximately 2 years or less).

Table 2 contains the final references selected for the nanotechnology Background survey. The first reference listed, Faraday's 1857 paper, had many more (over 50% more) citations (15) than any paper published in the 1800s, up to Maxwell-Garnett's paper in 1904. Specifically, from 1805 to 1901, the next most cited paper had nine citations. In turn, Maxwell-Garnett's paper had many more (over 250% more) citations (23) than any published previously, or those published until Mie's paper in 1908. Specifically, from 1871 to 1907, the next most cited paper had nine citations. This is a graphic example of how we interpret a paper's having substantially more citations than its contemporaries. We do not constrain ourselves with a numerical threshold, but rather interpret the total citation pattern within a given time frame.

These results were examined by the authors of the present document. They judged that all papers in the table were relevant for a Background section, or review paper. Due to space considerations, not all papers listed will be included in the historical narrative shown in the Seminal Nanotechnology Documents section.

There are a number of technical attributes (e.g., technical themes, relation to 2003 nanotechnology documents, level of development, etc) and infrastructure attributes (e.g., author institution, author country, journal, language) that can be assigned to each document above. Temporal trends in these attributes can be tracked, and their evolution evaluated. Such a detailed evaluation was beyond of the scope of the present study. However, one sub-set was examined for demonstration purposes.

Examination of Table 2 shows that Science and Nature magazines are well represented in recent years. It was desired to quantify their representation. The frequency of appearance of Nature and Science articles in the total list of cited documents (with citation frequency of three and above) was examined. Table 3 contains the relevant data.

Four time bands were examined, and the highly cited papers in Science and Nature, as well as all cited publications with a threshold frequency of three, were assigned to the appropriate time bands. Because of the low citations received by papers published in 2002 and 2003 (when the data were recorded), the highly cited publications for these 2 years were under-represented. The absolute decrease in highly cited publications for the fourth band (1999–2003) should be ignored, and only the relative performance of Science and Nature to the other journals considered.

In the 1980s and 1990s, Nature and Science combined contained a substantial fraction of the most cited documents, and in the last decade, Science appears to be the clear leader. In this decade, Science contains about 2–3% of total cited nanotechnology publications (with a threshold frequency of three), but over 40% of the most highly cited publications. Reasons for Science's large fractional increase of most highly cited publications in the post-1993 time bands are unclear.

Seminal nanotechnology documents

The intellectual heritage of a discipline can be represented by identifying, and relating, the significant documents, people, and events that have had major influences on the development of the discipline.

First Author	Year	Source	Vol	Page	#Cit
Faraday M	1857	Philos T Roy Soc Lon	V147	P145	15
Maxwellgarnett JC	1904	Philos T Roy Soc Lon	V203	P385	23
Mie G	1908	Ann Phys	V25	P377	53
Stoney GG	1909	P Roy Soc Lond A Mat	V82	P172	33
Scherrer P	1918	Gottinger Nachrichte	V2	P98	16
Fowler RH	1928	P Roy Soc Lond A Mat	V119	P173	43
Fock V	1928	Z Phys	V47	P446	20
Bruggeman DAG	1935	Ann Phys-Leipzig	V24	P636	37
Brunauer S	1938	J Am Chem Soc	V60	P309	56
Avrami M	1939	J Chem Phys	V7	P1103	24
Avrami M	1940	J Chem Phys	V 8	P212	17
Avrami M	1941	J Chem Phys	V9	P177	23
Stoner EC	1948	Philos T Roy Soc A	V240	P599	46
Neel L	1949	Ann Geophys	V5	P99	32
Lamer VK	1950	J Am Chem Soc	V72	P4847	18
Barrett EP	1951	J Am Chem Soc	V73	P373	68
Turkevich J	1951	Discuss Faraday Soc	P55		32
Williamson GK	1953	Acta Metall	V1	P22	27
Parratt LG	1954	Phys Rev	V95	P359	31
Meiklejohn WH	1956	Phys Rev	V102	P1413	21
Landauer R	1957	IBM J Res Dev	V1	P223	26
Kissinger HE	1957	Anal Chem	V29	P1702	25
Wohlfarth EP	1958	J Appl Phys	V29	P595	19
Sauerbrey G	1959	Z Phys	V155	P206	50
Fano U	1961	Phys Rev	V124	P1866	22
Lifshitz IM	1961	J Phys Chem Solids	V19	P35	20
Judd BR	1962	Phys Rev	V127	P750	27
Ofelt GS	1962	J Chem Phys	V37	P511	25
Simmons JG	1963	J Appl Phys	V34	P1793	21
Wagner RS	1964	Appl Phys Lett	V4	P89	102
Hohenberg P	1964	Phys Rev B	V136	P864	54
Kohn W	1965	Phys Rev A	V140	P1133	5/
Stober W	1968	J Colloid Interf Sci	V26	P62	64
Rietveld HM	1969	J Appl Crystallogr	V2	P65	22
Kogelnik H	1969	Bell Syst Tech J	V48	P2909	22
Tuinstra F	1970	J Chem Phys	V 53	P1126	22
Kern W	1970	RCA Rev	V 31	P18/	26
Johnson KL	19/1	P Roy Soc Lond A Mat	V 324	P301	30
Demas JIN	19/1	J Phys Chem-US	V / 5	P991 D4270	20
Jonnson PB	1972	Phys Rev B	V0 V229	P4370	54
Fujishima A	1972	Nature	V 238	P3/	23
A vincent A	19/3	Cham Phys Sci	V241 V20	P20 P277	51
Aviralli A	1974	Vray Diffraction Dro	V 29	F2//	J4 19
	19/4	Dhya Latt A	¥154	D225	40
Givergizev El	1975	Phys Lett A L Cruct Crowth	V 34 V 21	P223	32 25
Shannon BD	1975	A ata Crystallogr A	V 31 V 22	F 20 D751	23 47
Monkhorst HI	1970	Dhue Dev D	V 32 V13	F / J1 D5188	47
Ashcroft NW	1970	Solid State Physics	v 15	1 5100	43
Cullity BD	1078	Flements Xray Diffra	P102		50
Wagner CD	1979	HDB Xray Photoelectr	1 102		92 ΔΛ
Mott NF	1979	FI FOT Processes NONC			44
RARD AI	1979	Electrochemical Meth			+2 51
Ceperley DM	1080	Phys Rev Lett	V45	P566	J1 19
Cepency Divi	1900	T HYS ICV Lett	v + J	1 500	40

Table 2. Seminal documents selected for inclusion in background

Τ	able	2.	Continued

First Author	Year	Source	Vol	Page	#Cit
Sagiv J	1980	J Am Chem Soc	V102	P92	35
Vosko SH	1980	Can J Phys	V58	P1200	34
Sze SM	1981	Physics Semiconducto			91
Perdew JP	1981	Phys Rev B	V23	P5048	67
Richter H	1981	Solid State Commun	V39	P625	34
Arakawa Y	1982	Appl Phys Lett	V40	P939	82
Gregg SJ	1982	Adsorption Surface A			66
Lee PC	1982	J Phys Chem-US	V86	P3391	39
Ando T	1982	Rev Mod Phys	V54	P437	36
Bohren CF	1983	Absorption Scatterin			58
Nuzzo RG	1983	J Am Chem Soc	V105	P4481	45
Brus LE	1984	J Chem Phys	V80	P4403	70
Kroto HW	1985	Nature	V318	P162	93
Ziegler JF	1985	Stopping Range Ions			62
Sing KSW	1985	Pure Appl Chem	V57	P603	58
Binnig G	1986	Phys Rev Lett	V56	P930	66
Brus L	1986	J Phys Chem-US	V90	P2555	60
Porter MD	1987	J Am Chem Soc	V109	P3559	100
Tang CW	1987	Appl Phys Lett	V51	P913	89
Yablonovitch E	1987	Phys Rev Lett	V58	P2059	77
Allen MP	1987	Computer Simulation			46
Lee C	1988	Phys Rev B	V37	P785	71
Yoshizawa Y	1988	J Appl Phys	V64	P6044	58
Bain CD	1989	J Am Chem Soc	V111	P321	93
Gleiter H	1989	Prog Mater Sci	V33	P223	73
Henglein A	1989	Chem Rev	V89	P1861	66
Canham LT	1990	Appl Phys Lett	V57	A1046	98
Burroughes JH	1990	Nature	V347	P539	94
Vanderbilt D	1990	Phys Rev B	V41	P7892	79
Sheikbahae M	1990	IEEE J Quantum Elect	V26	P760	63
Iijima S	1991	Nature	V354	P56	730
Oregan B	1991	Nature	V353	P737	173
Ulman A	1991	Intro Ultrathin Orga			135
Kresge CT	1992	Nature	V359	P710	213
Beck JS	1992	J Am Chem Soc	V114	P10834	143
Oliver WC	1992	J Mater Res	V 7	P1564	142
Hamada N	1992	Phys Rev Lett	V68	P1579	121
Tenne R	1992	Nature	V360	P444	93
Ebbesen TW	1992	NATURE	V358	P220	77
Mintmire JW	1992	Phys Rev Lett	V68	P631	77
Saito R	1992	Appl Phys Lett	V60	P2204	70
Murray CB	1993	J Am Chem Soc	V115	P8706	194
Iijima S	1993	Nature	V363	P603	108
Bethune DS	1993	Nature	V363	P605	93
Nazeeruddin MK	1993	J Am Chem Soc	V115	P6382	90
Becke AD	1993	J Chem Phys	V98	P5648	89
Usuki A	1993	J Mater Res	V 8	P1179	86
Kojima Y	1993	J Mater Res	V 8	P1185	76
Brust M	1994	J Chem Soc Chem Commun	P801		151
Martin CR	1994	Science	V266	P1961	143
Colvin VL	1994	Nature	V370	P354	79
Deheer WA	1995	Science	V270	P1179	128
Chopra NG	1995	Science	V269	P966	99
Kreibig U	1995	Optical Properties M			91

Table 2. Continued

First Author	Year	Source	Vol	Page	#Cit
Hoffmann MR	1995	Chem Rev	V95	P69	86
Hagfeldt A	1995	Chem Rev	V95	P49	84
Alivisatos AP	1996	Science	V271	P933	249
Thess A	1996	Science	V273	P483	196
Ulman A	1996	Chem Rev	V96	P1533	191
Dresselhaus MS	1996	Sci Fullerenes Carbo			123
Giannelis EP	1996	Adv Mater	V 8	P29	118
Treacy MMJ	1996	Nature	V381	P678	102
Mirkin CA	1996	Nature	V382	P607	100
Li WZ	1996	Science	V274	P1701	88
Alivisatos AP	1996	J Phys Chem-US	V100	P13226	80
Dai HJ	1996	Nature	V384	P147	73
Decher G	1997	Science	V277	P1232	161
Dillon AC	1997	Nature	V386	P377	136
Journet C	1997	Nature	V388	P756	111
Rao AM	1997	Science	V275	P187	108
Tans SJ	1997	Nature	V386	P474	104
Wong EW	1997	Science	V277	P1971	94
Han WQ	1997	Science	V277	P1287	90
Reed MA	1997	Science	V278	P252	78
Cullis AG	1997	J Appl Phys	V82	P909	74
Nie SM	1997	Science	V275	P1102	74
Morales AM	1998	Science	V279	P208	177
Tans SJ	1998	Nature	V393	P49	174
Saito R	1998	Physical Properties			146
Ren ZF	1998	Science	V282	P1105	145
Bruchez M	1998	Science	V281	P2013	134
Chan WCW	1998	Science	V281	P2016	120
Loss D	1998	Phys Rev A	V57	P120	110
Frisch MJ	1998	Gaussian 98 Revision			106
Wildoer JWG	1998	Nature	V391	P59	103
Zhao DY	1998	Science	V279	P548	101
Martel R	1998	Appl Phys Lett	V73	P2447	101
Liu J	1998	Science	V280	P1253	90
Chen J	1998	Science	V282	P95	89
Zhao DY	1998	J Am Chem Soc	V120	P6024	82
Odom TW	1998	Nature	V391	P62	79
Smith BW	1998	Nature	V396	P323	76
Xia Y	1998	Angew Chem Int Edit	V37	P550	71
Caruso F	1998	Science	V282	P1111	71
Fan SS	1999	Science	V283	P512	133
Hu JT	1999	Accounts Chem Res	V32	P435	132
Nikolaev P	1999	Chem Phys Lett	V313	P91	84
Bimberg D	1999	Quantum Dot Heterost			83
Dekker C	1999	Phys Today	V52	P22	76
Lebaron PC	1999	Appl Clay Sci	V15	P11	76
Chen J	1999	Science	V286	P1550	76
Kataura H	1999	Synthetic Met	V103	P2555	73
Liu C	1999	Science	V286	P1127	71
Sun SH	2000	Science	V287	P1989	161
Kong J	2000	Science	V287	P622	142
Alexandre M	2000	Mat Sci Eng R	V28	P1	130
Peng XG	2000	Nature	V404	P59	115
Collins PG	2000	Science	V287	P1801	84

Table	2.	Continued

First Author	Year	Source	Vol	Page	#Cit
Joachim C	2000	Nature	V408	P541	77
Templeton AC	2000	Accounts Chem Res	V33	P27	77
Murray CB	2000	Annu Rev Mater Sci	V30	P545	74
Duan XF	2000	Adv Mater	V12	P298	73
Huang MH	2001	Science	V292	P1897	170
Pan ZW	2001	Science	V291	P1947	166
Bachtold A	2001	Science	V294	P1317	114
Duan XF	2001	Nature	V409	P66	100
Huang MH	2001	Adv Mater	V13	P113	89
Puntes VF	2001	Science	V291	P2115	88
Cui Y	2001	Science	V291	P851	70
Cui Y	2001	Science	V293	P1289	68
Baughman RH	2002	Science	V297	P787	82
Gudiksen MS	2002	Nature	V415	P617	62
Huynh WU	2002	Science	V295	P2425	60
Oconnell MJ	2002	Science	V297	P593	55
Hirsch A	2002	Angew Chem Int Edit	V41	P1853	49
Park J	2002	Nature	V417	P722	49
Georgakilas V	2002	J Am Chem Soc	V124	P760	49
Xia YN	2003	Adv Mater	V15	P353	38
Duan XF	2003	Nature	V421	P241	23
Wu XY	2003	Nat Biotechnol	V21	P41	15

Table 3. Total and highly cited publications vs. time (\geq 3 cites)

		TIME BAND –	years	
	1984–1988	1989–1993	1994–1998	1999–2003
Total publications	1609	3870	10,949	18,517
Nature publications	31	109	264	344
Nature/total publications	0.0192666	0.0281654	0.0241118	0.0185775
Total highly cited publications	12	25	46	36
Nature highly cited publications	1	8	11	6
Nature/total highly cited publications	0.0833333	0.32	0.2391304	0.1666667
Total publications	1609	3870	10,949	18,517
Science publications	15	137	370	389
Science/total publications	0.0093226	0.0354005	0.033793	0.0210077
Total highly cited publications	12	25	46	36
Science highly cited publications	0	0	20	15
Science/total highly cited publications	0	0	0.4347826	0.4166667

Some influences can be quantified; others are evaluated more subjectively. One of the metrics used as a proxy for influence is the number (and quality) of citations to particular documents and/ or events. With use of CAB, this section identifies the key historical documents that served as the building blocks for present-day nanotechnology. These documents are the references extracted from the records retrieved from the SCI database by the keyword search (shown in the Introduction), using a systematic rigorous approach to identify references that have had significant influence on the development of nanotechnology.

Most of the references used for this section were identified as highly cited from the documents *in the retrieved database only* (\sim 21,000 documents out of \sim 30,000 accessed by the SCI in 2003). They therefore represent the broader nanotechnology

community's views on seminal papers, and go beyond the experiences or biases of any one person or small group. Due to space constraints, only about 150 of the most cited documents were analyzed and included in this Seminal Nanotechnology Documents section. In future literature surveys for Background, or for stand-alone reviews, the authors strongly recommend that a systematic approach to defining seminal papers be used, such as the method presented here.

As stated in the Concept Description section, nanotechnology has two components: (1) development and use of techniques to study physical phenomena, and (2) construction of structures in the nanoscale size range or smaller. The first component has been ongoing for many decades, while the second component has come to the forefront within the last two decades. The following intellectual heritage reflects this division in time. The first section traces the nanoscience heritage of nanotechnology from the early 20th century to the late 1980s. At the latter time, instruments were becoming experimentally available that allowed scanning and probing at the nanoscale level. These instruments offered the promise of being able to manipulate/measure these small structures, and were not limited to observing at the macroscopic level as ensemble averages, as had been done previously. Since about 1985, these advanced instruments were becoming commercially available, and this time period can be viewed as the transition to modern nanotechnology. The second section in the heritage traces the modern development of what can be termed nanotechnology.

Early nanoscience development – pre 1985

The ability to conduct present-day nanotechnology required the advancement of many technical disciplines. For example, interpretation of the Scanning Tunneling Microscope (STM) scans requires knowledge of the electronic structure of the material being scanned, and required a century of electromagnetic research to arrive at the present level of understanding. The first section describes some of this historical advancement, under the caveats about generational citation mentioned above. For ease of comprehension, the historical papers are categorized into solid state electronic structure, optics/spectroscopy, surfaces/films/layers, instrumentation and materials. These four categories were generated by visual inspection of the historical records.

Solid state electronic structure/properties

Determination of electronic structure in materials has been of long-term interest, for determining bulk and surface material properties, and especially for designing magnetic recording media. An early study focused on explaining the electron emission from metals using the Fowler-Nordheim model for current densities and tunneling currents. although its extension to other materials such as semiconductors is questionable (Fowler & Nordheim, 1928). Later came the effective medium approach, designed to address the inhomogeneous media in which different phases are randomly distributed in the form of grains of an arbitrary shape, size, and orientation (Bruggeman, 1935). One of the first post-WW2 advances in magnetic recording showed that the magnetization reversal of a single-domain nanoparticle can be described by the Stoner-Wohlfarth model (Stoner & Wohlfarth, 1948). This was followed shortly by the theory of thermal remnent magnetization in an ensemble of identical noninteracting single domain uniformly magnetized particles (Neel, 1949).

A decade later saw origination of the densityfunctional theory (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), which was effective in describing the ground state of finite many electron systems, and was later extended to excitation spectra also. The late 1960s produced the Rietveld method for profile refinement method of nuclear and magnetic structures, which employed directly the profile intensities obtained from step-scanning measurements of the neutron powder diagram (Rietveld, 1969). Another major advance in determining structure and electronic properties of nanocrystals was Raman spectra of graphite (Tuinstra & Koenig, 1970). Raman spectra from single crystals of graphite and other graphitic materials showed one single line for single graphite crystals, and another single line for the other materials. The Raman intensity of this band is inversely proportional to the crystallite size, and allows an estimate of the crystallite size in the surface layer of any carbon sample.

Mossbauer-effect measurements showed that the noncolinear spin arrangement in ultrafine ferrimagnetic crystallites differs from the Néel type found in large crystallites, and led to the proposal that the ions in the surface layer are inclined at various angles to the direction of the net moment (Coey, 1971). Shortly thereafter, a molecular electronic device (rectifier), consisting of a single molecule that would demonstrate almost ideal diode characteristics in passing current preferentially in one direction, was proposed (Aviram & Ratner, 1974).

Subsequently, the Monkhorst–Pack method was used for Brillouin-Zone integrations, to analyze the electronic structure of materials (Monkhorst & Pack, 1976). At the same time, determination of effective ionic radii provided a useful capability for computing crystal structures (Shannon, 1976). Demonstration of field emission devices with high emission current density attained in metal tip arrays (Spindt et al., 1976) laid the groundwork for applications as electron emitters in flat panel displays, attracting many subsequent investigations.

The first important application of the quantum many-body algorithm (now known as the Quantum Diffusion Monte Carlo method, or quantum DMC) to electronic structure calculations used a stochastic method to calculate ground-state of the electronic gas (Ceperley & Alder, 1980). It was then applied to determine the properties of electron gases at intermediate densities. Shortly thereafter, a simple formula for the exchangecorrelation energy per electron resulted from selfinteraction correction to density-functional approximations for many-electron systems, an important quantity in electronic structure calculations (Perdew & Zunger, 1981). At the same time, a further advance in Raman diagnostics occurred through the one phonon Raman-spectrum in microcrystalline silicon, in which the spatial correlation model was developed to explain the modification of the Raman spectra of crystals by the introduction of disorder (Richter et al., 1981). In parallel, a seminal book on underlying physics and operational characteristics of all major bipolar, unipolar, special microwave, and optoelectronic devices (Sze, 1981) was published.

A norm-conserving form of model pseudopotentials to treat the electron-ion interaction (Kleinman & Bylander, 1982) advanced ionic core description for density-functional theory. An extensive review of surface-enhanced spectroscopy (Moskovits, 1985) was followed by two seminal papers on the electronic structure of semiconductors, emphasizing electron-electron and electron-hole interactions in small semiconductor crystallites, including the size dependence of the lowest excited electronic state, and electronic wave-functions in semiconductor clusters (Brus. 1984, 1986). Improvement to Kohn's densityfunctional theories with gradient corrections for exchange correlation, using a semi-empirical exchange-correlation functional containing localspin-density, gradient, and exact-exchange terms, was demonstrated on 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 total atomic energies of first- and second-row systems, and performed significantly better than previous functionals with gradient corrections only (Becke, 1993). A connected system of programs for performing semi-empirical, ab initio, and densityfunctional molecular orbital (MO) calculations (Gaussian 98) became available 5 years later (Frisch et al., 1998).

Optics/*spectroscopy*

Optical properties of thin films and other nanostructures are important for diagnostic purposes, for luminescent probe applications, and for photonic band gap materials. An effective dielectric constant was proposed for a medium consisting of a dispersion of conducting particles much smaller than the wavelength of light to predict the colors that would be observed (Maxwell Garnett, 1904). Perhaps the initial breakthrough relating the optical extinction of light by an isolated spherical particle to size and frequency was the classical electrodynamics analysis of the extinction cross-section (Mie, 1908). Much later came publications of optical absorption intensities of rareearth ions (Judd, 1962) and intensities of crystal spectra of rare earth ions, the latter including an expression for the oscillator strength of a transition between different levels (Ofelt, 1962).

Lithographic fabrication of materials with visible stop bands is quite challenging. One class of materials that offers a unique solution to this problem is colloidal crystals, where one relies on the tendency of submicron dielectric spheres to spontaneously self-assemble into ordered arrays. Demonstrated controlled growth of monodisperse silica spheres in micron size range (Stober et al., 1968) allowed the change in optical transmission spectrum to be determined as a function of the thickness of the colloidal crystal. Later, optical constants (including dielectric constants) of noble

metals were published (Johnson & Christy, 1972), along with optical properties of solids, the latter emphasizing intrinsic optical properties and photoelectric emission (Wooten, 1972).

Another optics-based application of potential interest to nanotechnology is photolytic-based catalysis. A critical demonstration of electrochemical photolysis of water at a TiO₂ semiconductor electrode (Fujishima & Honda, 1972) consisted of an n-type semiconducting TiO₂ (rutile) electrode exposed to sunlight and connected to a platinum electrode, leading to hydronium-ion and gaseous oxygen formation at the negative electrode. Nanostructures have played important roles in improving the lasing characteristics of semiconductor lasers. For example, three-dimensional quantum confinement of electrons with quantum dots was proposed, along with the application of quantum dots to semiconductor lasers, and it predicted significant improvement of temperature sensitivity to the threshold current (Arakawa & Sakaki, 1982).

Surfaces, films and layers

Measuring the properties of thin films has been a major component of nanotechnology research since its inception, but with far greater scientific insight post 1960. One of the early studies measured the tension of metallic thin films deposited by electrolysis (Stoney, 1909). Three decades later, it was shown that the surface area of a (ceramic) powder can be calculated from the N2-isotherm (Brunnauer et al., 1938). By the analysis of the adsorption curves, the volume is determined, which corresponds to the quantity of nitrogen necessary for a monomolecular layer. From this value, the specific surface of the sample can be determined. This paper is seminal for introducing methods to determine the presence of an adsorbed molecular monolayer.

A significant feature of nanomaterials is the presence of a high surface to volume ratio (S/V), as noted previously. Study of pure materials for significant times under the high S/V conditions becomes problematical, even under relatively high vacuum conditions. The entrance of even small amounts of air into the vacuum chamber results in almost instant oxidation of the material at the surface. To circumvent this oxidation problem, researchers have used the noble metals extensively, starting with examination of the nucleation and

growth processes in the synthesis of colloidal gold (Turkevich et al., 1951).

A thin layer on a substrate will produce oscillations in the reflectivity related to the layer's thickness, and the distance between adjacent fringes gives an indication of layer thickness. An interference pattern is created when more than one layer is present. A major step forward occurred with publication of the Parratt formula for giving the reflectivity relation between the layers, using recursive solution (Parratt, 1954). Measuring the film mass is also critical for thin film analyses, and a variety of methods can be used. One unique approach showed that the frequency shift of a quartz crystal resonator is directly proportional to the added mass (Sauerbrey, 1959), and was the first step in the use of the quartz crystal microbalance to measure very small quantities of surface films. Further advances on physical adsorption isotherms came through generalization of the Langmuir isotherm, which model assumes monolayer adsorption on a homogeneous surface, in order to extend the description for multilayer adsorption (Sing et al., 1985).

Instrumentation

The transition from nanoscience to nanotechnology took a major step forward in the early 1980s, with the invention of the first STM in 1981 (Binnig et al., 1982), followed by the invention of the atomic force microscope (AFM) in 1986. Both probes provide information about the outermost surface, give very accurate height measurements, and are very good for planar surfaces. In the STM, the tunneling currents measured vary exponentially with the tip-surface distance, and in the AFM, the force variations between a cantilevered tip and the surface are influenced by surface height variations. Interestingly, the only one of Binnig's papers to receive significant citations in the present database is the 1986 paper on AFM (Binnig et al., 1986).

Materials

The value of nanoscale materials is becoming more appreciated with the passage of time. A series of papers on the kinetics of phase transformation driven by nucleation and growth kinetics, containing the Avrami equation, related the transformed fraction to the extended fraction (Avrami, 1939, 1940, 1941). Another important nanotechnology materials area is understanding porosity at the nanoscale level, for eventual filtering and separation applications. A major advance occurred with the development of the BJH model for determination of pore volume and area distributions in porous substances, using computations from nitrogen isotherms (Barrett et al., 1951).

One of the earliest post-war major advances was the use and appropriate interpretation of X-ray diffractometry to examine microstructures. Diffraction pattern line broadening can be caused by both small grain size and/or internal strain, and separation of the two effects by a quantitative analysis was shown using a plot according to the Williamson-Hall method (Williamson & Hall, 1953). This was followed by the first and second editions of a classic book on X-ray diffraction procedures for polycrystalline and amorphous materials (Klug & Alexander, 1954, 1974), and further followed by a methodology that allowed phase transition activation energies to be estimated from the temperature of maximum reaction rate and heating rate (Kissinger, 1957). Subsequently came a Vapor-Liquid-Solid mechanism to describe the growth of whiskers without dislocations, in which a drop of liquid at the tip of a whisker controls growth (Wagner & Ellis, 1964). Atoms from the vapor preferentially condense into, or are transported along, the crystal surface to the liquid droplet and then crystallize into the growing whisker tip.

Modern nanotechnology development – post 1985

Based simply on the publication counts identified by the keyword search used in this paper, modern nanotechnology development has proceeded along two major technology thrusts: *nanotubes* and the *other nanotechnologies*. This reflects the keen interest in the remarkable properties of carbon nanotubes that has led to many publications. *Nanotubes* can be bifurcated further into development, mainly growth and deposition issues, and into applications, mainly for field emission. The *other nanotechnologies* split into many different focal areas, including surface quantum dot layers, lasers and optical emissions from nanostructures, film and layer deposition on substrates, nanomaterial magnetics, nanostructure metallurgy, precious metal nanoparticles, and polymer-based nanocomposites. The background and evolution of these developments will now be addressed.

Nanotubes

The basis of nanotube development is the pioneering paper on C-60 - buckminsterfullerene, which identified the unique carbon atomic structures of that class of carbon materials (Kroto et al., 1985). Specific nanotube development started about 6 years later with a very highly cited paper on the production of helical microtubules of graphitic carbon using an arc-discharge evaporation method (Iijima, 1991). It was shortly followed by synthesis of graphitic nanotubes in gram quantities, using a variant of the standard arcdischarge technique for fullerene synthesis under a helium atmosphere (Ebbesen & Ajayan, 1992); electronic-structure of chiral graphene tubules (Saito et al., 1992); calculation of the electronic structure of a fullerene tubule using a first-principles, self-consistent, all-electron Gaussian-orbital based local-density-functional approach (Mintmire et al., 1992); and electronic transport variation predictions for carbon microtubules (Hamada et al., 1992).

The next year saw the emergence of single shell carbon nanotubes of 1-nm diameter (Iijima & Ichihashi, 1993), and cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls (Bethune et al., 1993). Then, synthesis of pure boron nitride nanotubes (Chopra et al., 1995), large-scale synthesis of aligned carbon nanotubes (Li et al., 1996), production of single-wall nanotubes by condensation of a laser-vaporized carbon–nickel–cobalt mixture and their selfassembly into ropes (Thess et al., 1996), and a comprehensive book on the science of fullerenes and carbon nanotubes (Dresselhaus et al., 1996) followed shortly thereafter.

Development toward more useful material quantities included: large-scale production of single-walled carbon nanotubes (SWNT) by the electric-arc technique (Journet et al., 1997); synthesis of large arrays of well-aligned carbon nanotubes on glass (Ren et al., 1998); conversion of single-wall fullerene nanotubes from nearly endless, highly tangled ropes into short, open-ended pipes that behave as individual macromolecules (Liu et al., 1998); a readily scalable purification process capable of handling SWNT material in large batches, including progress in scaling up SWNT production by the dual pulsed laser vaporization process, thereby enabling the production of gram per day quantities of highly pure SWNT (Rinzler et al., 1998); encapsulated C-60 in carbon nanotubes (Smith et al., 1998), on atomic structure and electronic properties of single-walled carbon nanotubes (Odom et al., 1998); solution properties of single-walled carbon nanotubes (Chen et al., 1998); electronic structure of atomically resolved carbon nanotubes (Wildoer et al., 1998); paralleled by a book on physical properties of carbon nanotubes (Saito et al., 1998).

The following year saw publication of optical properties of SWNTs (Kataura et al., 1999), synthesis of nanowires and nanotubes (Hu et al., 1999), and gas-phase catalytic growth of SWNT from carbon monoxide (Nikolaev et al., 1999). More recently, catalytic growth of zinc oxide nanowires by vapor transport (Huang et al., 2001a) was followed by room temperature UV nanowire nanolasers (Huang et al., 2001b).

Subsequently, synthesis of semiconductor nanowire superlattices from group III-V and group IV materials was demonstrated, where the superlattices are created within the nanowires by repeated modulation of the vapour-phase semiconductor reactants during growth of the wires (Gudiksen et al., 2002). At the same time, structure-assigned optical spectra of SWNT was demonstrated, where spectrofluorimetric measurements on SWNT isolated in aqueous surfactant suspensions have revealed distinct electronic absorption and emission transitions for more than 30 different semiconducting nanotube species. By combining these fluorimetric results with resonance Raman data, each optical transition has been mapped to a specific nanotube structure. Optical spectroscopy can thereby be used to rapidly determine the detailed composition of bulk SWNT samples, providing distributions in both tube diameter and chiral angle (Bachilo et al., 2002). Later, a comprehensive review described current research activities that concentrate on one-dimensional (1D) nanostructures-wires, rods, belts, and tubes-whose lateral dimensions fall anywhere in the range of 1-100 nm, emphasizing 1D nanostructures that have been synthesized in relatively copious quantities using chemical methods (Xia et al., 2003).

Nanotube applications

Seminal applications papers start to appear in the mid-1990s, about 4 years after the initial nanotube announcement referenced above. A carbon nanotube field emission electron source (Deheer et al., 1995) and an enhancement of field emission of electrons from individually mounted carbon nanotubes when the nanotube tips are opened by laser evaporation or oxidative etching (Rinzler et al., 1995) were described, followed by observations of exceptionally high Young's modulus for individual carbon nanotubes (Treacy et al., 1996) and use of carbon nanotubes as nanoprobes in scanning probe microscopy (Dai et al., 1996). The following year saw hydrogen storage in singlewalled nanotubes (Dillon et al., 1997), electrical transport measurements on individual single-wall nanotubes that demonstrate genuine quantum wire behavior (Tans et al., 1997), and synthesis of gallium nitride nanorods through a carbon nanotube-confined reaction (Han et al., 1997).

Applications in 1998 included a three-terminal switching field-effect transistor consisting of one semiconducting SWNT connected to two metal electrodes (Tans et al., 1998), single- and multiwall carbon nanotube field-effect transistors (Martel et al., 1998), and carbon nanotube quantum resistors (Frank et al., 1998). Further applications included carbon nanotubes as molecular quantum wires (Dekker, 1999), carbon nanotube intramolecular junctions (Yao et al., 1999), a fully sealed, high-brightness carbon-nanotube fieldemission display (Choi et al., 1999), and Luttingerliquid behavior in carbon nanotubes based on a better approximation to one-dimensional electron transport in conductors (Bockrath et al., 1999).

Demonstrations in 2000 included extreme oxygen sensitivity of electronic properties of carbon nanotubes (Collins et al., 2000) and SWNTs as chemical sensors (Kong et al., 2000). Subsequent seminal applications included: logic circuits with field-effect transistors based on single carbon nanotubes (Bachtold et al., 2001); indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices (Duan & lieber, 2001); logic gates and computation from assembled nanowire building blocks (Huang et al., 2001c); use of nanowires as building blocks to assemble semiconductor nanodevices (Cui & Lieber, 2001); boron-doped silicon nanowire nanosensors for highly sensitive and selective detection of biological and chemical species (Cui et al., 2001); and noncovalent sidewall functionalization of SWNT for protein immobilization for biological and chemical sensing applications (Chen et al., 2001), in parallel with a survey of carbon nanotube applications (Baughman et al., 2002).

Quantum dots

While the concept of quantum dots was advanced by Arakawa in 1982, as discussed in the historical section, the earliest quantum dots were fabricated successfully in 1986 by an indirect method, the post-growth lateral patterning of the 2D quantum wells (Reed et al., 1986). Synthesis of semiconductor nanocrystallites based on pyrolysis of organometallic reagents by injection into a hot coordinating solvent (Murray et al., 1993) followed about a half-decade later. In turn, it was followed by vertically self-organized InAs quantum box islands on GaAs(100), demonstrating that the driving force for such vertically self-organized growth is the interacting strain fields induced by the islands that give rise to a preferred direction for In migration (Xie et al., 1995), and InAs/GaAs pyramidal quantum dots, emphasizing strain distribution, optical phonons, and electronic-structure (Grundmann et al., 1995).

The next year saw properties of semiconductor fragments consisting of hundreds to thousands of atoms with bulk bonding geometry (Alivisatos, 1996a), size-dependent properties and physical chemistry of semiconductor nanocrystals (Alivisatos, 1996b), as well as shell filling and spin effects in a few electron quantum dot (Tarucha et al., 1996). It was followed by: quantum dot bioconjugates for ultrasensitive nonisotopic detection (Chan & Nie, 1998); a universal set of one- and two-quantum-bit gates for quantum computation using the spin states of coupled single-electron quantum dots (Loss & DiVincenzo, 1998); Kondo effect in a single-electron transistor (Goldhaber-Gordon et al., 1998); a tunable Kondo effect in quantum dots, where a dot can be switched from a Kondo system to a non-Kondo system as the number of electrons on the dot is changed from odd to even, and the Kondo temperature can be tuned by means of a gate voltage as a single-particle energy state nears the Fermi energy (Cronenwett et al., 1998); and semiconductor nanocrystals as fluorescent biological labels (Bruchez et al., 1998).

In 1999, a seminal book on the principles and phenomena of quantum dot heterostructures (Bimberg, 1999) was published, followed by demonstration that control of the growth kinetics of the II-I semiconductor cadmium selenide can be used to vary the shapes of the resulting particles from a nearly spherical morphology to a rod-like one (Peng et al., 2000), and then by triggered single photons from a quantum dot (Santori et al., 2001). A later demonstration showed in vivo imaging of quantum dots encapsulated in phospholipid micelles. Specifically, when conjugated to DNA, the nanocrystal-micelles acted as in vitro fluorescent probes to hybridize to specific complementary sequences (Dubertret et al., 2002). Still later, immunofluorescent labeling of cancer marker Her2 and other cellular targets with semiconductor quantum dots (QD) was demonstrated, indicating that QD-based probes can be very effective in cellular imaging and offer substantial advantages over organic dyes in multiplex target detection (Wu et al., 2003).

Optics/spectroscopy

Significant papers on the emission, transmission, reflection, and absorption in the optical spectrum for the purposes of diagnosis, detection, display, and communication start with organic electroluminescent diodes (Tang & Vanslyke, 1987) and inhibited spontaneous emission in solid-state physics and electronics, where strong diffraction effects can inhibit the propagation of electromagnetic waves of certain frequencies in systems that exhibit periodic dielectric properties (Yablonovitch, 1987). Light-emitting-diodes based on conjugated polymers, with electroluminescence generated from polymers where single and double bonds alternate in the main chain (Burroughs et al., 1990), were then described, followed by conversion of light to electricity by cis-x2bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (ii) charge-transfer sensitizers (x=Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline TiO₂ electrodes (Nazeeruddin et al., 1993).

Other light-emitting-diodes made from cadmium selenide nanocrystals and a semiconducting polymer were shown subsequently (Colvin et al., 1994), followed by a review of interfacial electron transfer reactions in colloidal semiconductor solutions, and thin films and their application for solar light energy conversion and photocatalytic water purification (Hagfeldt & Gratzel, 1995), as well as a book on optical properties of metal clusters (Kreibig & Vollmer, 1995).

Later came structural and luminescence properties of porous silicon (Cullis et al., 1997), followed by diameter-selective Raman scattering from vibrational modes in carbon nanotubes (Rao et al., 1997) and semiconductor nanocrystals as fluorescent biological labels (Bruchez et al., 1998).

Surfaces, films and layers

At the same time that positioning of single atoms with a scanning tunneling microscope (Eigler & Schweizer, 1990) was demonstrated, construction of first principles pseudopotentials with possible application to first row and transition metal systems (Vanderbilt, 1990) was an important electronic structures landmark, as was demonstration of dye-sensitized colloidal titanium dioxide thin films for efficient and cheap solar cells (Oregan & Gratzel, 1991), and a text on ultrathin organic films (Ulman, 1991). The following year saw ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism (Kresge et al., 1992), as well as a new family of mesoporous molecular sieves prepared with liquid-crystal templates (Beck et al., 1992), and polyhedral and cylindrical structures of tungsten disulfide (Tenne et al., 1992).

A review of the formation and structure of selfassembled monolayers covered organized molecular assemblies, penetration-controlled reactions, Langmuir–Blodgett monolayers, surface-confined monolayers, long-chain surfactants, phase probe molecules, aqueous permanganate interaction, transform infrared-spectroscopy, chemically adsorbed monolayers, and ray photoelectronspectroscopy (Ulman, 1996), and was followed by nanoassemblies of layered polymeric composites (Decher, 1997).

A demonstration of direct-write "dip-pen" nanolithography to deliver collections of molecules in a positive printing mode, where molecules are delivered from an AFM tip to a solid substrate of interest via capillary transport (Piner et al., 1999) was a substantive advance in nanolithography, and was followed by monolayer protected cluster molecules (Templeton et al., 2000), and synthesis of semiconducting oxides by evaporation of commercial metal oxide powders at high temperatures (Pan et al., 2001).

Magnetics

While a substantial number of articles are published in nanotechnology magnetics, relatively few are cited highly, compared to some of the other sub-fields. Whether this is due to the more concentrated focus of the discipline, or the more applied nature, or some other factors, is not clear.

In 1988, a huge magnetoresistance was discovered in (001)Fe/(001)Cr superlattices prepared by molecular beam epitaxy, and ascribed this giant magnetoresistance to spin-dependent transmission of the conduction electrons between Fe layers and Cr layers (Baibich et al., 1988). Also that year, new Fe-based soft magnetic-alloys composed of ultrafine grain-structure (Yoshizawa et al., 1988) were described. Later, self-oriented regular arrays of carbon nanotubes and their field emission properties (Fan et al., 1999) were shown, followed by synthesis of monodisperse iron-platinum nanoparticles and ferromagnetic iron-platinum nanocrystal superlattices (Sun et al., 2000), and more recently by demonstrating a simple approach for controlling the colloidal synthesis of anisotropic cadmium selenide semiconductor nanorods can be extended to the size-controlled preparation of magnetic cobalt nanorods as well as spherically shaped nanocrystals (Puntes et al., 2001).

Materials

An improved technique to determine hardness and elastic modulus using load and displacement sensing indentation experiments (Oliver & Pharr, 1992) was soon followed by demonstration of mechanical-properties of nylon 6-clay hybrid, emphasizing tensile, flexural, impact, and heat distortion tests (Kojima et al., 1993). A few years later, nanobeam mechanics, including elasticity, strength, and toughness of nanorods and nanotubes (Wong et al., 1997) were described, and followed by the synthesis of semiconductor nanowires combining laser ablation cluster formation and vapor–liquid–solid growth (Morales & Lieber, 1998).

Nanowires, powders, and catalysts

A review of small-particle research, emphasizing physicochemical properties of extremely small colloidal metal and semiconductor particles (Henglein, 1989) was followed by silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers (Canham, 1990), as well as a classic book on the physics and chemistry of sol-gel processing (Brinker & Scherer, 1990).

A membrane-based synthetic approach to nanomaterials (Martin, 1994) was followed by synthesis of thiol derivatized gold nanoparticles in a two phase liquid-liquid system (Brust et al., 1994). Later, fabrication of a highly ordered metal nanohole array (platinum and gold) by a two-step replication of the honeycomb structure of anodic porous alumina (Masuda & Fukuda, 1995) was followed shortly by a DNA-based method for rationally assembling gold nanoparticles into macroscopic materials (Mirkin et al., 1996). A study on general synthesis of compound semiconductor nanowires provided a rational and predictable intellectual framework as well as corresponding methodologies for the synthesis of a broad range of nanowire materials with controlled chemical compositions. physical dimensions, and electronic and optical properties (Duan et al., 2000).

Polymers/nanocomposites

Synthesis of nylon 6-clay hybrid (Usuki et al., 1993) showed that montmorillomite cation exchanged for 12-aminolauric acid was swollen by epsilon-caprolactam to form a new intercalated compound. Design and synthesis of polymer nanocomposites with layered silicates (Gianellis, 1996) provoked much interest, and was followed in a couple of years by triblock copolymer syntheses of mesoporous silica with periodic 50-300 angstrom pores (Zhao et al., 1998), and nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures (Zhao et al., 1998). Subsequently, a paper was published on the syntheses, properties and (future) applications of polymer-layered silicate nanocomposites (Alexandre & Dubois, 2000).

Summary and conclusions

In summary, modern day nanotechnology achievements are based on the confluence of (1) research results and discoveries from diverse disciplines such as Solid State Electronic Structure, Optics/Spectroscopy, Surfaces/Films/Layers, Instrumentation, Materials, and Magnetics, and (2) technology developments including Lasers, Computers, and High Vacuum, dating back to the early twentieth century, and more recently the development of surface probe microscopes such as STMs and AFMs. CAB, supplemented by high quality human judgment, helps document these discoveries and display the sequencing among these achievements. For nanotechnology, Science and Nature have become the journals of choice for the most highly cited papers, with Science becoming the clear leader in the past decade.

In this paper, we described the geneology of the seminal papers that accelerated nanotechnology research and development. The CAB technique proved to be very comprehensive in identifying what the authors perceived to be the seminal papers in nanotechnology, and allowed a technical narrative to be constructed linking these technical achievements and breakthroughs over time. Since the data obtained were temporal, CAB allowed interesting time-dependent effects to be observed, such as the changes in fraction of highly cited papers being published in Nature/Science.

Limitations of the source databases prevented greater use of the full power of CAB. The SCI version available to the authors provided only first author name, source, year, and volume/issue for journal paper references downloaded en masse. For those references that were contained in the SCI as full records, the full record could have been downloaded manually. For references not accessed by the SCI, the data would have to be re-constructed manually from other sources to be part of the analytical database.

Once complete historical records had been obtained, Reference Mining, the retrospective analog of Citation Mining (Kostoff et al., 2001), could be performed on the historical database to obtain a wide variety of bibliometric and technical taxonomy results. For example, the full author fields could be clustered to identify key researchers such as Smalley and Lieber who were instrumental in nanotechnology development but may not have been first authors on many papers. Additionally, if sponsor information were obtained (laboriously) for each record, then a Hindsight-type of retrospective analysis (Sherwin & Isenson, 1967) could be performed for nanotechnology using the complete text and numerical data contained within the full record. Such analysis would provide some quantitative and qualitative indicators of the environment associated with these advances.

Future nanotechnology CAB studies should extract more technical and infrastructure attributes from the seminal papers, and examine the trends over time. The CAB output provides a structure for such analyses.

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