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Nanomaterials with enzyme-like characteristics (Nanozymes): next-generation artificial enzymes

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Table S1. Timeline for the development of natural and artificial enzymes.

Year	Events	Reference
1877	The term "enzyme" was coined by Wilhelm Kuhne.	
1926	The enzyme urease was crystallized and determined to be a protein by James B. Sumner.	1, 2
1946	James B. Sumner won Nobel Prize in Chemistry "for his discovery that enzymes can be crystallized".	
1965	Cyclodextrin inclusion compounds were used to imitate enzymes.	3, 4
1967-1968	The idea of an RNA molecule with enzymatic properties was proposed by Carl R. Woese, Francis H. C. Crick and Leslie E. Orgel.	5-7
1970	The term "artificial enzyme" was coined by Ronald Breslow.	8
1971	Polymer with enzyme-like activity (synzyme) was reported by Irving M. Klotz.	9
1972	Molecularly imprinted polymers were invented by Günter Wulff and Irving M. Klotz.	10, 11
1982	The term "ribozyme" was coined by Thomas R. Cech.	12
1982-1983	The ribozymes were discovered by Sidney Altman and Thomas R. Cech.	12, 13
1986	Catalytic antibodies were invented by Peter G. Schultz and Richard A. Lerner.	14, 15
1989	Sidney Altman and Thomas R. Cech won Nobel Prize in Chemistry "for their discovery of catalytic properties of RNA".	
1992	The first artificial RNAzyme was selected.	16
1993	DNA cleavage induced by fullerene derivatives.	17
1994	The first DNAzyme was selected.	18
1996-1997	Fullerene derivatives as superoxide dismutase mimic.	19, 20
2004	Nano gold as RNase mimic. The term "nanozyme" was coined.	21
2004	Nano gold as oxidase mimic	22
2005	Nano ceria as superoxide dismutase mimic.	23
2007-2008	Ferromagnetic nanoparticles as peroxidase mimic.	24, 25
2009-2010	Nano ceria as catalase and oxidase mimic.	26, 27
2011	Nano V_2O_5 as haloperoxidase mimic	28

Note: The protein crystal image was adopted with permission from reference 2. Copyright (1926) American Society for Biochemistry and Molecular Biology. The cyclodextrin inclusion complex was adopted with permission from reference 4.

References:

1. J. B. Sumner, *J. Biol. Chem.*, 1926, **70**, 0097-0098.
2. J. B. Sumner, *J. Biol. Chem.*, 1926, **69**, 435-441.
3. F. Cramer and W. Kampe, *J. Am. Chem. Soc.*, 1965, **87**, 1115-1120.
4. N. Hennrich and F. Cramer, *J. Am. Chem. Soc.*, 1965, **87**, 1121-1126.
5. C. R. Woese, *The Origins of the Genetic Code*; Harper and Row: New York, 1967.
6. F. H. C. Crick, *J. Mol. Biol.*, 1968, **38**, 367-379.
7. L. E. Orgel, *J. Mol. Biol.*, 1968, **38**, 381-393.
8. R. Breslow and L. E. Overman, *J. Am. Chem. Soc.*, 1970, **92**, 1075-1077.
9. I. M. Klotz, G. P. Royer and I. S. Scarpa, *Proc. Natl. Acad. Sci. U. S. A.*, 1971, **68**, 263-264.
10. G. Wulff and A. Sarhan, *Angew. Chem.-Int. Edit.*, 1972, **11**, 341-342.
11. Takagish.T and I. M. Klotz, *Biopolymers*, 1972, **11**, 483-491.
12. K. Kruger, P. J. Grabowski, A. J. Zaug, J. Sands, D. E. Gottschling and T. R. Cech, *Cell*, 1982, **31**, 147-157.
13. C. Guerriertakada, K. Gardiner, T. Marsh, N. Pace and S. Altman, *Cell*, 1983, **35**, 849-857.
14. S. J. Pollack, J. W. Jacobs and P. G. Schultz, *Science*, 1986, **234**, 1570-1573.
15. A. Tramontano, K. D. Janda and R. A. Lerner, *Science*, 1986, **234**, 1566-1570.
16. T. Pan and O. C. Uhlenbeck, *Biochemistry*, 1992, **31**, 3887-3895.
17. H. Tokuyama, S. Yamago, E. Nakamura, T. Shiraki and Y. Sugiura, *J. Am. Chem. Soc.*, 1993, **115**, 7918-7919.
18. R. R. Breaker and G. F. Joyce, *Chem. Biol.*, 1994, **1**, 223-229.
19. L. L. Dugan, J. K. Gabrielsen, S. P. Yu, T. S. Lin and D. W. Choi, *Neurobiol. Dis.*, 1996, **3**, 129-135.
20. L. L. Dugan, D. M. Turetsky, C. Du, D. Lobner, M. Wheeler, C. R. Almli, C. K. F. Shen, T. Y. Luh, D. W. Choi and T. S. Lin, *Proc. Natl. Acad. Sci. U. S. A.*, 1997, **94**, 9434-9439.
21. F. Manea, F. B. Houillon, L. Pasquato and P. Scrimin, *Angew. Chem.-Int. Edit.*, 2004, **43**, 6165-6169.
22. M. Comotti, C. Della Pina, R. Matarrese and M. Rossi, *Angew. Chem.-Int. Edit.*, 2004, **43**, 5812-5815.
23. R. W. Tarnuzzer, J. Colon, S. Patil and S. Seal, *Nano Lett.*, 2005, **5**, 2573-2577.
24. L. Z. Gao, J. Zhuang, L. Nie, J. B. Zhang, Y. Zhang, N. Gu, T. H. Wang, J. Feng, D. L. Yang, S. Perrett and X. Yan, *Nature Nanotech.*, 2007, **2**, 577-583.
25. H. Wei and E. Wang, *Anal. Chem.*, 2008, **80**, 2250-2254.
26. A. Asati, S. Santra, C. Kaittanis, S. Nath and J. M. Perez, *Angew. Chem.-Int. Edit.*, 2009, **48**, 2308-2312.
27. T. Pirmohamed, J. M. Dowding, S. Singh, B. Wasserman, E. Heckert, A. S. Karakoti, J. E. S. King, S. Seal and W. T. Self, *Chem. Commun.*, 2010, **46**, 2736-2738.
28. R. André, F. Natálio, M. Humanes, J. Leppin, K. Heinze, R. Wever, H.-C. Schröder, W. E. G. Müller andW. Tremel,, *Adv. Funct. Mater.*, 2011, **21**, 501-509.
29. R. C. Spitale, R. Volpini, M. V. Mungillo, J. Krucinska, G. Cristalli and J. E. Wedekind, *Biochemistry*, 2009, **48**, 7777-7779.