纳米颗粒对大型蚤毒性效应的研究进展

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摘要 随着纳米颗粒的广泛生产和使用, 其生物毒性效应已成为环境研究领域的一个热点和前沿. 大型蚤作为一种模式生物, 广泛应用于纳米颗粒的毒性检测. 本文综述了典型纳米颗粒对大型蚤毒性的研究进展, 包括急性毒性、慢性毒性和生物累积, 分析了主要致毒机理, 并展望了需进一步加强的研究方向.

关键词 纳米材料, 水生生物, 生态效应, 生物累积, 纳米毒理学

纳米颗粒是指任一维度在1~100 nm的颗粒^[1], 截至2016年已经有超过1800种人工纳米颗粒问世(www.nanotechproject.org). 由于其特殊的小尺寸效应、表面效应、量子尺寸效应和宏观量子隧道效应等, 纳米颗粒正日益广泛地应用于工业、农业、生活等众多领域^[2]. 在其生命周期的各个阶段, 纳米颗粒都难免进入水环境, 从而可能影响水生生态系统. 大量研究表明, 纳米颗粒对水生生物具有一定的毒性效应^[3~7]. 大型蚤在食物链中居于初级生产者(例如绿藻)与次级消费者(例如斑马鱼)之间, 对水生食物链中物质平衡和能量循环起重要作用. 由于大型蚤对有毒物质非常敏感^[8], 美国国家环境保护局于1978年将其确定为毒性测试模式生物, 经济合作与发展组织(OECD)建立了大型蚤毒性试验的标准方法OECD 202^[9]和OECD 211^[10], 我国也在1991年建立了有毒物质对大型蚤急性毒性的实验方法^[11]. 因此, 大型蚤也是评估纳米材料水生生物毒性的一种很好的模式生物, 并已被大量研究. 但是, 由于纳米颗粒种类繁多^[12~15]、实验条件不同^[16~19]等原因, 现有研究结果往往存在一定的差异或争议, 亟需系统分析比较相关研究结果, 明确共识及差异所在, 以更好地开展进

一步研究工作. 为此, 在文献综述基础上, 本文阐述了纳米颗粒对大型蚤的急性毒性、慢性毒性、致毒机理以及大型蚤对纳米颗粒的生物累积作用, 最后分析了当前纳米颗粒对大型蚤毒性效应研究存在的问题及需进一步加强的研究方向.

1 纳米颗粒对大型蚤的急性毒性

纳米颗粒的急性毒性效应是用于分析其毒性大小的基本数据, 主要研究大型蚤的活动受抑制率或者死亡率, 常使用6~24 h的幼蚤进行实验, 实验时长一般为24 h或者48 h. 急性毒性实验的指标主要包括最大无影响浓度(no observed effect concentration, NOEC)、最低有效浓度(lowest observed effect concentration, LOEC)、半数有效浓度(50% effect concentration, EC₅₀)和半数致死浓度(50% lethal concentration, LC₅₀)等. 表1列出了典型纳米颗粒对大型蚤急性毒性的研究结果. 由表可以看出, 各种纳米颗粒对大型蚤的急性毒性有显著的剂量效应关系.

1.1 金属基纳米颗粒

金属基纳米颗粒主要包括金属单质和金属氧化

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表1 纳米颗粒对大型蚤的急性毒性效应^{a)}Table 1 The acute toxicity of nanoparticles to *Daphnia magna*

种类	粒径(nm)	实验水质	纳米颗粒毒性	溶出离子毒性	文献
PVP-AgNPs	40±10	重组水	24 h-EC ₅₀ <500 µg/L	48 h-EC ₅₀ =0.68 µg/L	[20]
PVP-AgNPs	57.6±1.2	M4	48 h-EC ₅₀ =121 µg/L	48 h-EC ₅₀ =1.10 µg/L	[21]
PVP-AgNPs	79.7±1.1	SM7	48 h-LC ₅₀ =2.0 µg/L	48 h-LC ₅₀ =0.57 µg/L	[22]
AgNPs-L	123.9±1.3	SM7	48 h-LC ₅₀ =28.7 µg/L	48 h-LC ₅₀ =1.1 µg/L	[22]
AgNPs-S	65.3±1.1	SM7	48 h-LC ₅₀ =1.1 µg/L		[22]
Cit-AgNPs	15.5±3.59	重组水	24 h-LC ₅₀ =48.6 µg/L	24 h-LC ₅₀ =1.7 µg/L	[23]
Cit-AgNPs	40	MHRW	24 h-LC ₅₀ =4.30 µg/L	24 h-LC ₅₀ =0.81 µg/L	[24]
AgNPs	20	SM7	24 h-LC ₅₀ =28.7 µg/L	48 h-LC ₅₀ =2.51 µg/L	[25]
AgNPs	3~8	ASTM	24 h-LC ₅₀ =11.41 µg/L 48 h-LC ₅₀ =11.02 µg/L	24 h-LC ₅₀ =1.36 µg/L 48 h-LC ₅₀ =1.05 µg/L	[26]
AgNPs	60	RHW	72 h-LC ₅₀ =10.1 µg/L	72 h-LC ₅₀ =1.3 µg/L	[27]
MUDA-AuNPs	10	M7	24 h-LC ₁₀ =0.73 mg/L	—	[28]
MUDA-AuNPs	30	M7	24 h-LC ₁₀ =2.1 mg/L	—	[28]
Cit-AuNPs	30	M7	24 h-LC ₁₀ >10 mg/L	—	[28]
AuNPs	10±1	MHW	24 h-LC ₅₀ =0.05 mg/L, 48 h-LC ₅₀ =0.02 mg/L	—	[29]
AuNPs	21	重组水	48 h-LC ₅₀ =70 mg/L	48 h-LC ₅₀ =2 mg/L	[30]
CuNPs	50	STM	48 h-LC ₅₀ =93 µg/L	—	[31]
CS-nZVI	254	无菌水	48 h-EC ₅₀ =795.2 mg/L	—	[32]
BS-nZVI	211	无菌水	48 h-EC ₅₀ =873.6 mg/L	—	[32]
nZVI	80~120	合成水	96 h-EC ₅₀ =0.5 mg/L	96 h-EC ₅₀ =1 mg/L(Fe ²⁺) 96 h-EC ₅₀ =15 mg/L(Fe ³⁺)	[33]
nZnO	27.2±6.7	MHRW	24 h-LC ₅₀ =22.2 mg/L	24 h-LC ₅₀ =1.28 mg/L	[34]
nZnO	21	ISO	48 h-EC ₅₀ =1.9 mg/L		[35]
nZnO	43	STM	48 h-LC ₅₀ =0.99 mg/L	48 h-LC ₅₀ =1.01 mg/L	[36]
nZnO	50~70	重组水	24 h-LC ₅₀ =3.2 mg/L, NOEC=0.5 mg/L	24 h-LC ₅₀ =6.1 mg/L NOEC=2.0 mg/L	[37]
nZnO	5.6	M4	48 h-EC ₅₀ =1.1 mg/L	—	[38]
nZnO	5.6	池塘水	48 h-EC ₅₀ =13.4 mg/L	—	[38]
nCuO	31±12.8	重组水	48 h-EC ₅₀ =4.0 mg/L, 48 h-NOEC=0.5 mg/L	48 h-EC ₅₀ =0.07 mg/L	[39]
nCuO	大约30	重组水	24 h-LC ₅₀ =3.2 mg/L, NOEC=0.5 mg/L	24 h-LC ₅₀ =0.17 mg/L NOEC=0.1 mg/L	[31]
nCuO	30~50	MHW	48 h-EC ₅₀ =1.09 mg/L	48 h-EC ₅₀ =0.06 mg/L	[40]
nCuO	30~40	ISO	48h-EC ₅₀ =22 mg/L	48 h-EC ₅₀ =0.06 mg/L	[41]
nCr ₂ O ₃	20.16±3.72	ISO	48h-EC ₅₀ =6.79 mg/L	48 h-EC ₅₀ =3.24 mg/L	[42]
nAl ₂ O ₃	5~10	重组水	24 h-LC ₅₀ =3.6 mg/L	24 h-LC ₅₀ =12.04 mg/L	[43]
nAl ₂ O ₃	80	重组水	48 h-EC ₅₀ =114.3 mg/L, 48 h-LC ₅₀ =162.4 mg/L	—	[44]
nFe ₂ O ₃	6.0	TMAOH	48 h-LC ₅₀ =23.10 g/L	—	[45]
nFe ₃ O ₄	6.0	TMAOH	48 h-LC ₅₀ =0.23 mg/L	—	[45]
ASC-nFe ₃ O ₄	5.2±0.4	M7	96 h-EC ₅₀ =50.7 mg/L	—	[46]
Cit-nFe ₃ O ₄	5.2±0.4	M7	96 h-EC ₅₀ =68.4 mg/L	—	[46]
DEX-nFe ₃ O ₄	5.2±0.4	M7	96 h-EC ₅₀ =27.9 mg/L	—	[46]
PVP-nFe ₃ O ₄	6.1±0.6	M7	96 h-EC ₅₀ >100 mg/L	—	[46]
nTiO ₂	345	河水	48 h-LC ₅₀ =27.8 mg/L	—	[47]
nTiO ₂	358	ISO	48 h-LC ₅₀ =19.3 mg/L	—	[47]
nTiO ₂	<25	河水	48 h-EC ₅₀ =8.26 mg/L(光照)	—	[48]

续表1

种类	粒径(nm)	实验水质	纳米颗粒毒性	溶出离子毒性	文献
nTiO ₂	<25	河水	48 h-EC ₅₀ =27.45 mg/L(黑暗)	-	[48]
nTiO ₂	10	COMBO	48 h-LC ₅₀ =7.75 mg/L	-	[49]
nTiO ₂	7.5	TMAOH	48 h-LC ₅₀ =16 mg/L	-	[45]
nTiO ₂	15	重组水	48 h-EC ₅₀ =1.30 mg/L	-	[50]
nTiO ₂	25	重组水	48 h-EC ₅₀ =3.15 mg/L	-	[50]
nTiO ₂	32	重组水	48 h-EC ₅₀ =3.44 mg/L	-	[50]
nCeO ₂	6.5	TMAOH	48 h-LC ₅₀ =12 mg/L	-	[45]
LPC-SWCNTs	2	重组水	96 h-LC ₂₀ =10 mg/L	-	[51]
MWCNTs	10~20	河水	96 h-LC ₅₀ =4 mg/L	-	[52]
GN	0.76	SM7	48 h-LC ₄₀ =16 mg/L	-	[53]
THF-C ₆₀	10~200	RHW	48 h-LC ₅₀ =0.8 mg/L	-	[54]
CdSe/ZnS QDs	1.6	ASTM	48 h-EC ₅₀ =389.3 μg/L	-	[55]
CdSe/ZnS QDs	2~5	重组水	48 h-EC ₅₀ =3.87 mg/L	48 h-EC ₅₀ =1.21 mg/L(Zn ²⁺) 48 h-EC ₅₀ =1.46 mg/L(Cd ²⁺)	[56]
Cd QDs	3.24	重组水	48 h-EC ₅₀ =67.4 μg/L	48 h-EC ₅₀ =34.1 μg/L	[57]
Cd QDs		MHW	48 h-EC ₅₀ =70.4 μg/L		[58]
Cd QDs		MHW	48 h-EC ₅₀ =17.3 μg/L(UV-B)		[58]

a) 负载物质: L, 乳酸盐; S, 十二烷基苯磺酸钠; PVP, 聚乙烯吡咯烷酮; Cit, 柠檬酸盐; MUDA, 巯基烷酸; LPC, 溶血磷脂酰胆碱; THF, 四氢呋喃; ASC, 抗坏血酸盐; DEX, 聚葡萄糖; CS, 化学合成; BS, 生物合成. 培养基: M4, Elendt M4培养基; M7, Elendt M7培养基; SM7, 简化的M7培养基; MHRW, 中等硬度重组水; ASTM, 美国材料与试验协会培养基; RHW, 重组硬质水; STM, 标准测试培养基; ISO, 国际标准化组织测试水; TOMAH, 氢氧化四甲铵培养基; MHW, 中等硬度水; COMBO, COMBO培养基

物, 由于种类繁多, 应用广泛, 其毒性效应研究也相对较多, 主要集中在纳米银(AgNPs)、纳米金(AuNPs)、纳米铜(CuNPs)、纳米二氧化钛(nTiO₂)、纳米氧化铜(nCuO)、纳米氧化锌(nZnO)、纳米三氧化二铝(nAl₂O₃)、纳米三氧化二铬(nCr₂O₃)等. 从表1可以看出, 48 h的毒性效应会略高于24 h, 但差异不大^[26,29]; 理论上LC₅₀数值应该会大于EC₅₀, 但较少有文献进行有针对性的比较. Zhu等人^[44]使用六种不同纳米颗粒, 结果为LC₅₀大于EC₅₀, 例如nAl₂O₃的48 h-EC₅₀为114.3 mg/L, 而48 h-LC₅₀为162.4 mg/L. 不同金属基纳米颗粒对大型蚤产生的急性毒性效应差异较大, 例如, AgNPs的LC₅₀/EC₅₀在1.1~500 μg/L; AuNPs的LC₅₀在0.02~70 mg/L; CuNPs的48 h-EC₅₀为93 μg/L; nZnO的LC₅₀/EC₅₀在0.99~22.2 mg/L; nCuO的LC₅₀/EC₅₀在1.09~22 mg/L; nCr₂O₃的48 h-EC₅₀为6.79 mg/L; nAl₂O₃的LC₅₀/EC₅₀在3.6~162.4 mg/L; nTiO₂的48 h-LC₅₀/EC₅₀在1.30~27.8 mg/L. 铁基纳米颗粒的急性毒性相对较低, 如两种表面改性纳米零价铁(nZVI)的48h-EC₅₀分别为795.2和873.6 mg/L^[32], 纳米三氧化二铁(nFe₂O₃)的48 h-LC₅₀为23.10 g/L^[45];

但也有毒性相对较高的研究报道, 如裸露nZVI的96 h-EC₅₀为0.5 mg/L^[33]; 纳米四氧化三铁(nFe₃O₄)的48 h-LC₅₀为0.23 mg/L^[45]. 不同粒径的同种纳米颗粒对大型蚤的急性毒性也存在一定的差异. Clément等人^[50]研究了15, 25和32 nm的3种不同粒径nTiO₂对大型蚤的急性毒性, 发现毒性随着粒径减小而增大. 表面负载MUDA的10 nm AuNPs的24 h-EC₁₀为0.73 mg/L, 其毒性效应约是30 nm AuNPs(24 h-EC₁₀为2.1 mg/L)的3倍^[28]. Li等人^[30]发现21 nm AuNPs的48 h-LC₅₀为70 mg/L, 然而Lee等人^[29]研究表明10 nm AuNPs的48 h-LC₅₀仅为0.02 mg/L, 两者毒性检测结果相差数千倍, 虽然两个研究培养基不同, 前者为MHW(水质硬度中等的培养基), 后者是重组水, 但Lee等人^[29]认为这个毒性差异主要由粒径不同引起. 综上可知, 粒径较小的纳米颗粒往往具有更大的毒性, 其原因可能是尺寸较小的纳米颗粒更容易穿越细胞膜, 进入细胞, 进而引起更大的急性毒性效应.

纳米颗粒应用过程中往往需要在其表面引入极性功能团或负载有机大分子以抑制其团聚, 这些极性物质或大分子有机物往往能显著影响金属基纳米

颗粒对大型蚤的毒性效应。例如, Skjolding等人^[28]研究发现, 表面负载Cit的AuNPs(30 nm)对大型蚤的48 h-EC₁₀大于10 mg/L, 而相同粒径的MUDA-AuNPs的24 h-EC₁₀仅为2.1 mg/L; Zhao和Wang^[22]测定PVP, 乳酸盐(L)和十二烷基苯磺酸钠(S)3种不同表面负载的AgNPs(粒径分别为79.7, 123.9, 65.3 nm)对大型蚤的急性毒性, 其48 h-LC₅₀分别为2.0, 28.7和1.1 μg/L, 当然这其中的毒性差异也可能和纳米颗粒的粒径有关; Baumann等人^[46]研究了DEX, ASC和Cit 3种不同负载物对nFe₃O₄(5.2 nm)毒性的影响, 发现其96 h-EC₅₀分别27.9, 50.7和68.4 mg/L. 由于极性官能团和有机大分子的引入可以改变纳米颗粒表面性质, 影响其团聚、溶解等物理化学行为, 从而抑制或增强其与大型蚤的直接或间接作用, 因此毒性实验需要充分考虑纳米颗粒表面负载物的影响。

Wiench等人^[38]比较了M4培养基和池塘水中nZnO对大型蚤的急性毒性, 发现纳米颗粒在池塘水中的毒性显著较低(48 h-EC₅₀分别为1.1, 13.4 mg/L), 并指出其原因可能是由于水体中溶解性有机碳与纳米颗粒相结合, 从而降低了纳米颗粒的毒性. Gao等人^[17]在研究AgNPs和CuNPs在萨旺尼河(SR)水样中对大型蚤的急性毒性时, 同样发现纳米颗粒在SR水中毒性比在超纯水中小, 并且毒性随SR水中总有机碳含量增加而降低. 其他相关研究^[59,60]同样指出, 水中天然有机质负载于纳米颗粒表面可以降低纳米颗粒的毒性. 但是, 真实水体成分复杂, 水样中纳米颗粒对水生生物的表现毒性效应是多种水质指标综合作用的结果, 而非由某一两种因素决定^[61]. 因此, 还需加强探究真实水体中纳米颗粒的毒性效应, 以科学评估其真实环境风险。

1.2 碳纳米材料和量子点

碳纳米材料主要包括单壁碳纳米管(SWCNTs)、多壁碳纳米管(MWCNTs)、石墨烯(GN)、富勒烯(C₆₀)、纳米金刚石(ND)等. 已有较多文献报道了不同碳纳米材料对大型蚤的急性毒性效应. Mendonça等人^[62]认为ND可以在大型蚤体内积蓄并干扰大型蚤生长繁殖; Lovern等人^[63]发现C₆₀可以加快大型蚤的心脏跳动和运动频率, 从而影响其捕食等生理活动. 一些课题组定量研究了碳纳米材料对大型蚤的急性毒性效应. Roberts等人^[51]报道了溶血磷脂酰胆碱分散悬浮SWCNTs(LPC-SWCNTs)对大型蚤的96 h-LC₂₀为10

mg/L, 96 h-LC₁₀₀为20 mg/L; Edgington^[52]指出MWCNTs对大型蚤的96 h-LC₅₀为4 mg/L; Fan等人^[53]发现当GN浓度为16 mg/L时, 大型蚤死亡率为40%; Zhu等人^[54]研究表明四氢呋喃(THF)分散悬浮的C₆₀对大型蚤的48 h-LC₅₀为0.8 mg/L. 碳纳米材料用途广泛, 其环境安全性得到了广泛的关注, 特别是其生物毒性效应也被越来越多地发现报道. 除大型蚤外, 相关研究还表明碳纳米管(CNTs)对非洲爪蟾^[64]、罗非鱼^[65]和小球藻^[66]等具有一定的毒性效应; MWCNTs, 氧化石墨烯(GO)和还原氧化石墨烯(RGO)都能对斑马鱼胚胎产生毒性^[67]. 因此, 在开发应用碳纳米材料时, 需要加强其生物毒性效应研究。

量子点(QDs)是一类新兴纳米材料, 由于其独特的性质和组成, 已经在一些领域得到应用. 已有文献研究了QDs对大型蚤的急性毒性. 结果表明, 在合成过程中添加的稳定配体、无机壳(例如ZnS)都会影响QDs性质^[68], 进而影响其对大型蚤的毒性效应. 例如, CdSe/ZnS QDs 这种常见的量子点, 由于合成方法不同, 其对大型蚤的毒性效应相差巨大(48 h-EC₅₀分别为3.87和389.3 μg/L)^[55,56]. 同时, 有研究发现QDs的毒性效应受到实验过程中光照的影响, 如UV-B会显著增加Cd QDs对大型蚤的毒性, 使其48 h-EC₅₀从70.4 μg/L下降到17.3 μg/L^[58]; Lee等人^[57]研究表明Cd QDs在无光照条件下的48 h-EC₅₀为67.4 μg/L, 间接地佐证了UV-B可以改变Cd QDs的毒性. 此外, Kušić和Leszczynska^[69]发现CdSe/ZnS会改变有机污染物(如苯酚、甲苯、邻苯二酚等)对大型蚤的毒性效应. 但从总体上看, 目前关于QDs对大型蚤的毒性研究较少, 鉴于其特殊的理化性质, 研究QDs的急性毒性效应具有重要的实际意义。

2 纳米颗粒对大型蚤的慢性毒性

一些纳米颗粒可以长期存在于水环境之中, 使得水生生物受到持续暴露风险; 同时, 进入水生生物体内的纳米颗粒可以在体内进行累积并长时间残留, 进而对水生生物产生持续影响, 因此需要研究纳米颗粒对水生生物的长期慢性毒性. 表2总结了典型纳米颗粒对大型蚤的慢性毒性研究结果. 目前, 关于纳米颗粒对大型蚤慢性毒性的实验方法主要参照OECD 211^[10], 毒性指标主要包括: LC₅₀, 存活率、首次繁殖个数、首次繁殖时间、子代繁殖总数、蜕皮次数、母蚤体长、重量等. 多数慢性毒性实验研究时长

表2 纳米颗粒对大型蚤的慢性毒性效应

Table 2 The chronic toxicity of nanoparticles to *Daphnia magna*

纳米颗粒	暴露时长(d)	实验水质	暴露浓度	研究结果	文献
AgNPs	21	ISO	0.1~1.0 $\mu\text{g/L}$	大型蚤体长显著减小, 对幼蚤毒性作用强	[42]
AgNPs	21	M7	0.25~1.6 $\mu\text{g/L}$	首次繁殖时间延迟, 繁殖总数减少, 体长下降	[70]
AgNPs	21	SM7	50~500 $\mu\text{g/L}$	体长下降, 繁殖总数下降	[25]
AgNPs	21	M7	5~60 $\mu\text{g/L}$	低浓度, 繁殖总数增加. 高浓度, 繁殖总数下降, 死亡率随浓度升高而增加	[71]
nTiO ₂	21	重组水	0.01~100 mg/L	大型蚤子代繁殖数目比死亡率更敏感	[43]
nTiO ₂	21	MHW	0.5~10 mg/L	怀孕比例下降	[72]
nZnO	21	重组水	5~500 $\mu\text{g/L}$	繁殖总数下降	[73]
nZnO	21	ISO	0.0024~0.16 mg/L	21 d-EC ₁₀ =0.030 mg/L, 浓度增加繁殖总数减少	[74]
nCuO	21	ISO	0.037~1.438 mg/L	21 d-EC ₁₀ =0.546 mg/L, 浓度增加, 大型蚤体长显著减小, 高浓度繁殖率显著下降	[75]
nCuO	21	ISO	0.9~7.8 mg/L	低浓度子代繁殖数目增加, 体长显著性下降	[41]
nCu ₂ O	30	河水	10 $\mu\text{g/L}$	体长下降, 繁殖间隔时间增大	[76]
MWCNTs	21	RHW	0.5~5 mg/L	干重减小, 繁殖率明显低于空白	[77]
MWCNTs	21	RHW	0.125~1.0 mg/L	高浓度繁殖率明显低于空白, 低浓度繁殖率与空白无区别	[77]
MWCNTs	14	MHRW	1.7~5.4 mg/L	14d-LC ₅₀ =4.3 mg/L, 繁殖总数下降, 体长没有显著性影响	[78]

为21 d, 但是根据大型蚤自身生长繁殖以及实验环境条件的不同, 实验时长也有采用14 d^[78]或者30 d^[76].

由表2可以看出, 目前慢性实验研究主要集中在纳米颗粒对大型蚤的生长和繁殖的影响. AgNPs可导致大型蚤体长变短、繁殖时间推迟、繁殖总数下降等^[42,70]. Zhao等人^[25]研究发现经过21 d暴露于50 $\mu\text{g/L}$ AgNPs的大型蚤, 与在空白的SM7培养基(简化的M7培养基, 保留了主要成分, 去掉了微量元素)中培养的大型蚤相比, 其体长由 3.35 ± 0.04 mm减小到 3.13 ± 0.06 mm, 同时子代繁殖总数由 73.6 ± 9.3 个下降到了 57.8 ± 5.9 个. Wang等人^[76]同样发现, 与SM7培养基中大型蚤相比, 在33.3 mg/L nCu₂O悬浮液中暴露30 d后的大型蚤, 其体长从 3.08 ± 0.08 mm减少到 1.91 ± 0.08 mm, 繁殖总数从169个下降到62个. Kim等人^[72]在研究nTiO₂对大型蚤繁殖能力时发现, 当nTiO₂的浓度为0.5和1 mg/L时, 大型蚤能分别在第8 d和第13 d使产蛋率回到正常水平; 当暴露浓度高于1.5 mg/L时, 大型蚤的产蛋率不能恢复; 当暴露浓度达到10 mg/L时, 大型蚤的生殖能力显著下降, 基本丧失繁殖能力. Wang等人^[43]研究结果也表明当大型蚤长期暴露在高浓度nTiO₂时, 子代繁殖数目会受到影响. 相关研究同样发现nZnO也能明显抑制大型蚤的繁殖^[73,74], 且大型蚤繁殖总数随着纳米颗粒浓度的增加而逐渐越小^[74]. 除此之外, MWCNTs也被发现

对大型蚤具有慢性毒性效应, Stanley等人^[78]研究发现, MWCNTs长期暴露会引起大型蚤死亡(14 d-LC₅₀为4.3 mg/L), 并降低繁殖总数, 但对其体长没有显著影响; Alloy和Roberts^[77]研究同样发现高浓度(1.0 mg/L)下MWNTs会显著抑制大型蚤的繁殖率, 但低浓度(0.125 mg/L)下无显著影响. 综上所述, 高浓度纳米颗粒会抑制大型蚤的生长和繁殖力.

少量研究发现纳米颗粒在低浓度条件下可以促进大型蚤的繁殖. 例如Rossetto等人^[41]在研究低浓度nCuO(7.8 mg/L)对大型蚤的慢性毒性时发现, nCuO不仅没有抑制大型蚤的繁殖, 反而增加了其子代数; Sakka等人^[71]同样发现低浓度AgNPs(6.4 $\mu\text{g/L}$)暴露组的大型蚤繁殖数目高于空白组, 并且认为其原因是低浓度纳米颗粒可以促进幼蚤的孵化. 然而这方面的报道还较少, 缺少充足数据进行对比, 而且不同研究间结论存在矛盾, 例如其他研究中, 同样甚至更低浓度的nCuO(0.037~1.438 mg/L)^[75]和AgNPs(0.25~1.6 $\mu\text{g/L}$)^[42,70]不能促进大型蚤繁殖. 因此, 今后需要探究更多纳米颗粒低浓度长期暴露对大型蚤繁殖能力的影响.

实际环境中, 纳米颗粒的生物效应是长期的, 低浓度纳米颗粒在短期内可能不会造成大型蚤死亡, 但是可能会逐步抑制大型蚤生理活动, 最终影响大型蚤的生长和繁殖. 目前, 关于纳米颗粒对大型蚤的

毒性研究多数集中于急性毒性测试, 缺乏足够的慢性毒性实验数据支撑和沿食物链积累、传递的基础数据, 因此今后加强研究纳米颗粒对大型蚤的慢性毒性更具实际意义。

3 大型蚤对纳米颗粒的生物累积作用

研究水生生物对纳米颗粒的生物累积作用对理解纳米颗粒的生态效应具有重要意义。一般使用大型蚤体内负荷量/累积量(body burden)或者富集系数(bioconcentration factors, BCF)来表示其对纳米颗粒的生物累积作用。纳米颗粒进入大型蚤体内及细胞的途径如图1所示。纳米颗粒进入水环境之后可以分散悬浮在水中, 通过饮水经大型蚤口腔进入其体内(图1, 途径①)^[91]; 纳米颗粒因自身团聚或与水中胶体/微生物异相团聚形成粒径较大的颗粒物, 可以被大型蚤误食或摄食作用而进入其肠道(图1, 途径②)^[91~96]; 而附着在大型蚤体表的小粒径纳米颗粒单体也可通过皮肤直接进入其细胞或体内(图1, 途径③)^[97]。

表3列出了有关大型蚤对纳米颗粒生物累积作用的研究结果, 大部分研究仅分析了若干不同浓度下大型蚤对纳米颗粒的累积量。由于不同研究所采用的纳米颗粒浓度差异较大($1\sim 100\times 10^3\text{ }\mu\text{g/L}$), 因此难以根据生物累积量来比较大型蚤对不同纳米颗粒的

累积能力, 但在较高暴露浓度时, 生物累积量均可达到 $\mu\text{g/mg}$ 级别, 如 0.04 nmol/L AuNPs暴露48 h后, 大型蚤体内Au的累积浓度高达 $242.9\pm 23.2\text{ }\mu\text{g/mg}$ ^[85]。少数研究报道了大型蚤对纳米颗粒的生物富集系数, nCuO的富集系数(24 h-BCF=28 L/kg)相对较小^[82], 而P25 TiO₂的富集系数(12 h-BCF)高达 $1.18\times 10^5\text{ L/kg}$ ^[84], 由此可见大型蚤对不同纳米颗粒的累积能力差异很大。对同一种纳米颗粒, 大型蚤生物累积量一般随纳米颗粒浓度和暴露时间增加而增加。纳米颗粒的表面负载物也会影响大型蚤的生物累积作用, 如3种不同表面负载的AgNPs(PVP-AgNPs, AgNPs-L, AgNPs-S)之间的生物累积量差异可达10倍以上^[90], 其原因是AgNPs-S和AgNPs-L是网状结构, 相比于PVP-AgNPs, 更利于大型蚤吸收; 不同表面负载的量子点间的生物富集量也有显著差异, 带负电的量子点更有利于大型蚤的吸收^[86,87]。

大型蚤可以通过自身净化作用将进入体内的部分纳米颗粒排出体外, 排出速率一般小于累积速率, 随纳米颗粒种类而变化(表3)。例如, Skjolding等人^[28]研究发现, 大型蚤对两种AuNPs的累积速率都大于其净化速率, 实验结束后, 仍有大量AuNPs残留在大型蚤体内。Zhu等人^[84]发现大型蚤对nTiO₂(1 mg/L)经过3.72 h的累积作用就可以达到最大累积量的一半, 但经过74.52 h才能排出最大累积量的一半。除金属

图1 环境中的纳米颗粒进入(a)大型蚤体内和(b)细胞途径示意图

Figure 1 Routes for nanoparticles entering body (a) and cell (b) of daphnia

表3 大型蚤对纳米颗粒的生物累积作用^{a)}

Table 3 Bioaccumulation of nanoparticles by *Daphnia magna*

纳米颗粒	暴露时长(h)	实验水质	浓度(μg/L)	生物累积量	生物累积速率	文献
Carbonate-AgNP	48	SM7	500	22.9 mg/g,	—	[25]
AgNPs-L	48	ISO	1, 1000	142±25 μg/g, 6618±3784 μg/g	—	[79]
PVP-AgNPs	48	ISO	1, 1000	13.4±1.4 μg/g, 475±172 μg/g	—	[79]
AgNPs-S	48	ISO	1, 1000	22.2±2.8 μg/g, 2791±347 μg/g	—	[79]
AgNPs	48	重组水	50	3.4 mg/g	—	[80]
AgNPs	12	重组水	10	300 μg/g	—	[80]
ZnO	48	河水	500	42.8±0.2 μg/g	累计速率=4.8 μg/(g h)	[81]
ZnO	48	ISO	1.78×10 ³	4.23±2.51 μg/mg	—	[79]
CuO	48	MHRW	13.35×10 ³	62.09±11.26 μg/mg	—	[82]
CuO	24	MHRW	1	59.52±1.51 μg/kg, 24 h-BCF=28 L/kg	—	[82]
Cu ₂ O	72	河水	2×10 ³	439 μg/g(立方体), 641 μg/g(八面体)	—	[83]
P25 TiO ₂	12	重组水	0.1×10 ³	BCF=5.66×10 ⁴ L/kg	T _{1/2} 吸收=3.87 h T _{1/2} 排出=26.72 h	[84]
P25 TiO ₂	12	重组水	1×10 ³	BCF=1.18×10 ⁵ L/kg	T _{1/2} 吸收=3.72 h T _{1/2} 排出=74.52 h	[84]
AuNPs	48	MHW	0.04 ^{b)}	242.9±23.2 μg/mg	—	[85]
MUDA-AuNPs	24	M7	500	16.1 ± 10.3 μg/mg	吸收系数=4112 L/(kg h) 排出系数=0.26/h	[28]
Cit-AuNPs	24	M7	500	1.2 ± 0.76 μg/mg	吸收系数=339 L/(kg h) 排出系数=0.10/h	[28]
Al ₂ O ₃	24	重组水	100×10 ³	15±5 ng/只	—	[51]
COOH-Cd QDs	24	MHW	8 ^{b)}	259.17 RFU/20只蚤	35.4%残留	[86]
NH ₂ -Cd QDs	24	MHW	8 ^{b)}	150.01 RFU/20只蚤	15.8%残留	[86]
PEG-Cd QDs	24	MHW	8 ^{b)}	95.17 RFU/20只蚤	12.9%残留	[86]
QEI-CdSe/ZnS QDs	24	MHW	100	1460±50 μg/g	排出系数=0.0057/h	[87]
QSA-CdSe/ZnS QDs	24	MHW	100	1014±99 μg/g	排出系数=0.0079/h	[87]
QSH-CdSe/ZnS QDs	24	MHW	100	584±81 μg/g	排出系数=0.0189/h	[87]
CNTs	48	M7	0.4×10 ³	63±15 μg/mg	—	[88]
GN	24	重组水	100	3.7 μg/mg	54%残留	[89]
GN	24	重组水	250	7.4 μg/mg	36%残留	[89]
聚苯乙烯微球	12	重组水	2	0.055 ng/只	—	[90]

a) Carbonate, 碳酸盐; PEG, 聚乙二醇; QEI, 聚乙烯亚胺; QSA, 含胺组聚合物; QSH, 含酸基聚合物; RFU, 相对荧光强度. b) 浓度单位为nmol/L

基纳米颗粒外, 也有少数文献研究了大型蚤对碳纳米材料的净化作用, Guo等人^[89]发现大型蚤不能将进入体内的GN完全排放, 经过24 h净化后, 仍有54%(暴露浓度100 μg/L)和36%(暴露浓度250 μg/L)的GN残留在体内. Petersen等人^[88]同样指出进入大型蚤体内的CNTs在实验过程中不能完全被排出, 并且残存的CNTs会黏附在大型蚤肠道内, 与藻细胞(食物)形成团聚体, 影响大型蚤对藻细胞的消化吸收.

综上所述, 大型蚤可以通过饮水、摄食、皮肤吸

收等途径累积纳米颗粒, 但进入体内的纳米颗粒难以被完全排出. 因此, 今后需要进一步研究纳米颗粒在大型蚤体内的形态转化、长期慢性毒性、代际转移及食物链迁移等, 以全面评估纳米颗粒的生物生态效应.

4 纳米颗粒对大型蚤的致毒机理

4.1 纳米颗粒自身毒性

纳米颗粒可以通过物理吸附作用黏附于大型蚤

身体表面^[88],例如触角、皮肤、表壳等,对其产生物理损伤. Lewinski等人^[98]研究发现CdSe/ZnSe量子点可大量附着在大型蚤外壳、触角、附器部分等,进而抑制其活动. nTiO₂也被发现可以附着在大型蚤外壳,形成稳定的“壳层”,影响大型蚤蜕皮^[99]. 除此之外,被大型蚤误食进入其肠道的纳米颗粒(如MWCNT^[100])可以形成团聚体,堵塞肠道,影响大型蚤的正常摄食,进而产生毒性效应. 摄食进入体内的纳米颗粒由于具有大的比表面积,很容易通过配位作用、氢键作用、疏水性作用、静电作用等吸附在细胞膜表面,与膜上生物大分子作用而干扰细胞膜上正常的信号传递过程,由此导致细胞功能异常^[33,55]. 一些纳米颗粒甚至可以改变细胞膜通透性,溶解磷脂双分子层,导致形成纳米小洞或者细胞膜破裂,或者堵塞细胞膜上的各种离子通道,影响营养物质的吸收和排泄物的外排,进而影响生物体的正常生理过程^[97]. 此外,纳米颗粒还可以通过膜孔(图1,途径④)、内吞作用(图1,途径⑤)或者通过细胞膜破损处(图1,途径⑥)等方式进入到细胞内,进一步通过氧化损伤或与胞内生物大分子直接反应等干扰细胞正常的代谢功能,影响大型蚤的生理过程. 由于具有高的比表面积和表面活性,一些纳米颗粒物能产生活性氧(ROS),通过氧化脂质而损伤细胞、使蛋白质变性、损伤DNA的结构与表达等,进而影响细胞内正常的新陈代谢作用,对大型蚤产生急性毒性效应^[101~105];同时纳米颗粒进入大型蚤细胞后也可以直接与DNA作用,造成基因损伤. Tang等人^[106]研究发现Cd QDs, Zn QDs和CdSe/ZnS QDs 3种量子点均会影响大型蚤的基因表达. Ambrosone等人^[68]也发现QDs的存在影响基因表达,甚至使得染色体断裂. Azevedo等人^[107]指出nZnO会直接与DNA作用,造成DNA损伤,同时还会抑制DNA修复. 纳米颗粒能改变线粒体的生物能学,影响线粒体膜通透性,或者影响二磷酸腺苷(ADP)、三磷酸腺苷(ATP)的合成^[108];纳米颗粒还会影响细胞增殖与细胞凋零^[109]. 这些都会对大型蚤造成负面效应. 目前关于纳米颗粒对基因影响的研究相对较少,今后需进一步加强,以更深入地了解纳米颗粒的致毒机理,从而找出缓解毒性的方法.

4.2 金属基纳米颗粒释放有毒金属离子

金属基纳米颗粒往往具有高活性,在水环境中易被氧化,并溶解释放出金属离子,而金属离子的毒

性通常高于纳米颗粒本身(表1). 例如,AgNPs^[20~27], AuNPs^[30], nZnO^[34], nCuO^[31,39~41], nCr₂O₃^[42], CdSe/ZnS QDs^[56], Cd QDs^[57]等对大型蚤的急性毒性均远小于其溶解释放的金属离子毒性. 因此,很多学者认为金属基纳米颗粒对水生生物(包括大型蚤)的急性毒性来自于其溶解释放的金属离子. 纳米颗粒释放出来的金属离子与带负电的细胞膜通过库伦引力作用,吸附在细胞膜上,并可通过对应的离子通道(图1,途径⑦),进入细胞内,破坏细胞骨架或者抑制合成酶的活性,使细胞失活,产生离子毒性^[110]. 同时,金属离子可以改变细胞膜结构或者积累在细胞质中,直接影响细胞功能^[111]. 这些金属离子还可通过竞争作用抑制Na⁺/K⁺-ATP的活性^[112],从而影响细胞对Na⁺^[113,114], Ca²⁺/Mg²⁺^[115,116]等有益金属离子的吸收,从而影响大型蚤的生理活动. 金属离子也可以诱导产生ROS^[117],直接引起DNA损伤或者抑制DNA复制/分裂^[118]. 然而,并非所有的金属离子毒性都强于其纳米颗粒,例如有研究发现Al³⁺对大型蚤的急性毒性弱于nAl₂O₃^[43], nZVI的毒性强于其释放的Fe²⁺/Fe³⁺^[33]. 此外,对同种纳米颗粒,不同研究也可能得出完全不同的结论,例如, Poynton等人^[34]指出Zn²⁺对大型蚤的毒性强于nZnO; Xiao等人^[36]的研究结果表明Zn²⁺与nZnO的毒性相当; Heinlaan等人^[37]则发现Zn²⁺的毒性小于nZnO. 因此,迄今关于纳米颗粒释放金属离子在表现纳米毒性效应中的贡献还存在较大争议,有待深入研究,培养基的组成和纳米颗粒的粒径、形貌、表面负载物等都会影响金属离子的释放过程和存在形态,因而影响其毒性效应.

4.3 纳米颗粒与其他化合物形成有毒复合物

一些纳米颗粒本身无毒性,但会与一些有机化合物(包括其分散剂)反应,形成有毒副产物. Spohn等人^[119]发现C₆₀和其分散剂THF本身对大型蚤均没有显著毒性,但是C₆₀会与THF反应生成γ-丁内酯等副产物,这些副产物对大型蚤具有一定的毒性效应,洗掉副产物后,THF-C₆₀对大型蚤不再具有毒性. 纳米颗粒与环境中有毒重金属离子和有机污染物相互作用后可能对水生生物(包括大型蚤)产生复合毒性效应,这是当前纳米颗粒生物生态效应研究领域的一个前沿方向.

不同类型纳米颗粒对大型蚤的具体致毒机理往往不同,可能由单一途径决定,也可能是多种途径共

同作用的结果. 纳米颗粒可以通过物理作用直接影响大型蚤的行为与生理活动, 通过产生ROS对大型蚤造成氧化损伤, 通过释放毒性更大的金属离子产生毒性效应, 也可能与共存污染物一起对大型蚤产生复合毒性效应. 纳米颗粒性质、大型蚤生长状况、培养基组成、毒性实验方法等众多因素均会影响毒性实验结果. 因此, 对致毒机理的判断必须基于对这些影响因素的充分分析, 否则可能得出不准确的研究结论.

5 小结及展望

纳米颗粒相关的毒理学已经成为研究热点, 其对大型蚤的毒性效应是评价纳米颗粒环境安全性的重要指标. 目前, 在纳米颗粒对大型蚤的毒性效应研究方面已积累了一些重要数据, 为评估纳米颗粒的环境风险提供了参考. 但是, 研究结果存在差异性大、重复性差、甚至互相矛盾等问题, 毒性评价方法缺乏统一性和可比性. 随着对纳米颗粒大型蚤毒性效应研究的深入, 以下几方面值得进一步探究.

(1) 大型蚤作为一种标准的毒性受试生物, 已经被普遍应用于毒性试验, 但是大型蚤对生长环境比较敏感, 不同实验中, 大型蚤生长状况并不相同, 这可能会影响研究结论. 因此, 在比较不同课题组的研究结果时, 应该首先保证实验体系一致. 另外, 真实水体的理化性质与实验室培养基差别巨大, 纳米颗

粒在真实水体中的毒性结果可能与实验室模拟研究结果差异悬殊, 今后需要加强真实水体中纳米颗粒的毒性研究.

(2) 现有文献中慢性毒性实验浓度远高于纳米颗粒的实际环境浓度, 而且实际环境中纳米颗粒对大型蚤作用时间远比实验室内模拟时间长. 因此, 需要加强研究低浓度纳米颗粒对大型蚤的长期影响.

(3) 目前关于大型蚤对纳米颗粒生物累积作用的研究数据还不完善, 一方面实验暴露浓度相差太大, 另一方面实验结果表示方法不统一, 因此难以进行不同研究间生物累积能力的比较分析. 首先, 需要建立大型蚤对纳米颗粒生物累积实验的标准方法, 确定暴露浓度的设立标准以及富集结果的统一计算方式等; 其次, 纳米颗粒往往不能被大型蚤完全排出, 存在一定程度的残留, 这些残留在大型蚤体内的纳米颗粒的形态转化、长期慢性毒性、代际转移及食物链迁移等有待深入研究.

(4) 目前, 关于纳米颗粒对大型蚤的致毒机理在学术界尚未形成共识, 纳米颗粒性质、大型蚤生长状况、培养基组成、毒性实验方法等众多因素均会影响对致毒机理的判断. 因此需要进一步加强毒理研究, 探明这些影响因素对致毒机理的影响规律, 加深对纳米颗粒基因层面影响的认识, 以更好地了解纳米颗粒对水生生物的毒理效应.

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Summary for “纳米颗粒对大型蚤毒性效应的研究进展”

A review of the toxicity of nanoparticles to *Daphnia magna*

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With the wide production and usage of nanoparticles, nanotoxicity has received worldwide researches. As a model organism, *Daphnia magna* has been extensively used in the nanotoxicity studies. In this review, we overviewed research advance in the toxicity of nanoparticles to *Daphnia magna*, including acute toxicity, chronic toxicity, bioaccumulation, and the underlying mechanisms. Nanoparticles have dose-responsive acute toxicity to *Daphnia magna* and their toxicity is related to types of nanoparticles and culture media. Smaller nanoparticles generally have higher toxicity to *Daphnia magna*, presumably due to their easier transport through cell membranes. Due to polar functional groups and organic macromolecules are able to change surface properties of nanoparticles, most studies suggest that the acute toxicity of nanoparticles might be weakened by surface modification. High concentrations of nanoparticles can suppress the growth and reproduction of *Daphnia magna*. Bioaccumulation studies showed that nanoparticles could accumulate in *Daphnia magna* via water, feeding food, and absorbing through the skin. Since the concentration of nanoparticles, exposure time and cultivation media adopted in the studies varied greatly, the body burden and bioconcentration factor of nanoparticles were largely different, which makes it hard to compare accumulation capacity of *Daphnia magna* to different nanoparticles. At high exposure concentrations, accumulation amount of nanoparticles by *Daphnia magna* could reach $\mu\text{g}/\text{mg}$ level. Although the toxicity mechanisms of nanoparticles to *Daphnia magna* have not been fully understood, below points are generally used to explain the toxicity: nanoparticle specific toxic, the release of toxic metal ions, and forming toxic complexes with other compounds. Nanoparticles and the release of metal ions can adhere and aggregate onto surfaces of *Daphnia magna*, causing the physical damage, membrane permeability changes, and cell function loss. They can also promote the production of the reactive oxygen species (ROS) and free radical, leading to lipid peroxidation, protein carbonylation and DNA damage. In addition, some nanoparticles themselves are not toxic, but can form complexes with toxic substance.

At the end of text, we proposed several future research needs. First, compared with the experimental cultivation media, the physical and chemical properties of natural waters are obviously different, likely to cause big difference in the toxicity results. Therefore, realistic toxicity in natural waters needs to be studied. Second, the exposure concentrations of nanoparticles in chronic experiments are much higher than that in the real water environment, and the exposure time is also not long enough compared with practical condition. Lower concentrations and longer exposure time of nanoparticles are of great significance. Third, there is no unified approach in bioaccumulation experiments, making it difficult to compare and analyze the results from different labs. A standard test method established for the bioaccumulation test is thus required. Moreover, nanoparticles can remain in *Daphnia magna* and transfer to their offspring and other organisms though food chains. Hence, it is necessary to study the transformation, chronic toxicity, intergenerational transfer, and migration though food chains of nanoparticles. Lastly, up to date, toxicity mechanisms of nanoparticles to *Daphnia magna* have yet to reach a consensus. Nanoparticle characteristics, the growth status of *Daphnia magna*, culture medium compositions, toxicity experimental method, and many other factors might influence the judgment of the toxicity mechanisms. In order to better understand the toxic effects caused by nanoparticles, more researches are supposed to be done to find the impacts of these factors on the toxicity mechanisms.

nanomaterials, aquatic organism, ecological effect, bioaccumulation, nanotoxicology

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