BOMBYX MORI XITOZANI MATRITSASIDA *IN SITU* SHAROITIDA MARGANES NANOZARRACHALINING SINTEZI VA XOSSALARI

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Annotatsiya. Ushbu tadqiqotda “*in situ*” sharoitida qaytaruvchi agentlar ishtirokida xitozan bilan barqarorlashtirilgan, o’rtacha o‘lchami 100 nm gidrodinamik radiusli hamda plyonkalarida 200-600 nm li kubsimon, tetragonal shaklli Mn nanozarrachalari tutgan nanosistemalar sintez qilingan. Rentgen analizi tahlili Mn^{2+} ionlarining Mn^{0} ga qaytarilganligini, marganesing oksidlari kristallari hosil bo’lmaganligini, Mn nanozarrachalarining xitozani bilan xemosorbsiya usulida barqarorlashishini tasdiqlaydi. Bu kabi marganes nanozarrachalari kelajakda reproduktiv terapiyada qo‘llash uchun qiziqish uyg‘otadi.

Kalit so'zlar: maranes, xitozan Bombyx mori, marganes nanozarrachalari, in situ sintezi, gidrodinamik o'lcham

Abstract. In this study, nanosystems containing cubic and tetragonal Mn nanoparticles with an average hydrodynamic radius of approximately 100 nm, as well as 200–600 nm particles embedded in chitosan-based films, were synthesized *in situ* in the presence of reducing agents. X-ray diffraction analysis confirmed the complete reduction of Mn^{2+} ions to metallic Mn^{0}, with no detectable formation of manganese oxide phases. The resulting Mn nanoparticles were effectively stabilized through chemisorption interactions with the chitosan matrix. These manganese-based nanosystems hold significant potential for future applications in reproductive therap.

Keywords: manganese, chitosan Bombyx mori, manganese nanoparticles, in situ synthesis, hydrodynamic size

Аннотация. В данном исследовании наносистемы, содержащие кубические и тетрагональные наночастицы марганца со средним гидродинамическим радиусом около 100 нм, а также частицы размером 200–600 нм, внедрённые в хитозановые плёнки, были синтезированы *in situ* в присутствии восстановителей. Рентгеноструктурный анализ подтвердил полное восстановление ионов Mn^{2+} до металлического Mn^{0} без образования оксидных фаз марганца. Полученные наночастицы были эффективно стабилизированы за счёт хемосорбционных взаимодействий с хитозановой матрицей. Разработанные марганец-содержащие наносистемы обладают значительным потенциалом для использования в репродуктивной терапии.

Ключевые слова: марганец, хитозан, Bombyx mori, наночастицы марганца, синтез in situ, гидродинамический размер

Kirish

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Ekologik toza, biomoyil va funksional biomateriallar yaratish uchun polimer–metall nanozarrachalarini sintez qilish so‘nggi yillarda dolzarb yo‘nalishlardan biriga aylandi. Tabiiy polisaxarid bo‘lgan xitozan (XZ) amin va gidroksil guruhlari orqali metall ionlari bilan kompleks hosil qilib, nanozarrachalarning (NZ) barqarorligi va dispersligini oshiradi. Biologik tizimlarda muhim rol o‘ynaydigan marganets ionlari oksidlanish–qaytarilish reaksiyalarida ishtirok etib, antioksidant fermentlarning kofaktori sifatida faoliyat ko‘rsatadi, biroq ularning faolligi va potentsial toksikligi doza va nanoo‘lchamdagi holatiga bog‘liq. Shu sababli xitozan matritsasida in situ usulda barqarorlashtirilgan marganes nanozarrachalarini olish hamda ularning fizik-kimyoviy xossalarini tadqiq etish nanotexnologiya va biomateriallar kimyosida yangi avlod samarali va xavfsiz nanokompozitlarini yaratish uchun muhim ilmiy-amaliy asos bo‘lib xizmat qiladi.

ADABIYOTLAR TAHLILI

Marganes (Mn) organizm uchun ferment faoliyati, antioksidant himoya va gormonlar balansini ta’minlovchi muhim mikroelement hisoblanadi. Ushbu elementning reproduktiv tizimdagi o‘rni so‘nggi yillarda diqqat markazida bo‘lib, uning ta’siri dozaga bog‘liq holda ijobiy yoki salbiy bo‘lishi mumkin [1]. So‘nggi tadqiqotlar ushbu ta’sirlarning aniq molekular mexanizmlarini ochishga qaratilgan bo‘lib, bu klinik tadqiqotlar uchun mustahkam asos bo‘la oladi [2]. Shu nuqtai nazardan, marganesning nanozarracha shaklidagi sintezi – uning to‘qimaviy spesifiklik va farmakokinetik xususiyatlarini yaxshilash orqali, terapevtik qo‘llanilishini amalga oshirishda mumkin.

Marganes NZ ni sintez qilishda qo‘llanadigan an’anaviy usullardan biri bo‘lgan co-cho‘ktirish usuli oddiy, arzon va ko‘p miqdorda nano zarrachalar olish imkonini beradi, ammo zarracha o‘lchamini aniq nazorat qilish qiyin, aglomeratsiya ehtimoli yuqori [3]. Gidrotermal va solvotermal usullar yuqori harorat va bosim ostida kristall strukturalar hosil qilish imkonini beradi. Gidrotermal usulda suv, solvotermalda esa organik erituvchilar asosiy muhit bo‘ladi. Bu usulning afzalliklari fazaviy tozalik yuqori, shakl va o‘lcham nazorati oson [4,5]. Zamonaviy usullaridan biri “yashil sintez” o‘simlik ekstraktlari (flavonoidlar, polifenollar kabi fitokimyoviy moddalar) yordamida Mn tuzlarini nano zarrachalarga aylantiradi. Shuningdek mikroorganizmlar (ba’zi bakteriya va zamburug‘lar) yordamida Mn^{2+} ni oksidlab, bio-nano zarrachalar hosil qilish mumkin. Yashil sintez usuli atrof-muhit uchun xavfsiz, qulay, arzon, ammo reaksiya vaqti uzoq, masshtablashtirishda qiyinchiliklar mavjud [6]. Bundan tashqari mikroto‘lqinli va ultratovushli sintez usullari energiya samarador va tezkor reaksiyani ta’minlaydi. Mikroto‘lqinli usulda reaksiya bir xil va tez isitiladi. Ultratovushli sintezda kavitatsiya effekti tufayli zarrachalar maydalanadi [7].

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Marganes havo ta’sirida tezda oksidlanib ketadi va MnO, Mn_3O_4, MnO_2 kabi oksid fazalar hosil qiladi [8]. Hatto inert muhitda sintez qilinganda ham oksidlangan qatlam hosil bo‘lishi ehtimoli yuqori. Shu e’tibordan xam elementar Mn^0 zarrachalariga sinteziga yetarli e’tibor berilmagan. Shundan kelib chiqib, mazkur ishning maqsadi marganes nanozarrachalarining oksidlanishga moyilligi va aglomeratsiyasi bilan bog‘liq muammolarni bartaraf etish uchun stabilizator xususiyatiga ega *Bombyx mori* xitozani ishtirokida barqarorlashtirilgan Mn^0 ni sintez qilishdan iborat.

TADQIQOT METODOLOGIYASI

Reagentlar: Tadqiqot ishi uchun *Bombyx mori* xitozani (MM 41×10^3; deasetillanish darajasi 86%), tozalik darajasi ≥ 99.0% bo‘lgan $MnCl_2\cdot4H_2O$; (Shanghai Aladdin Biochemical Technology Co., Ltd.), qaytaruvchi agent sifatida tozalik darajasi 98% bo‘lgan $NaBH_4$ (Sinopharm Chemical Reagent Co., Ltd.) ishlatilgan. Barcha reagentlar “analytical grade” markali bo‘lib, tozalik darajasi ≥99.0% ni tashkil etgan va qo‘shimcha tozalash amaliyotlarisiz qo‘llanilgan. Barcha eritmalar deionlashtirilgan suvda tayyorlangan.

in situ sharoitlarida Mn^0 nanozarrachalarini sintez qilish (XZ-Mn^0).

Dastlab xitozan eritmasi tayorlab olindi hamda magnitli aralashtirgichda intensiv aralashtirgan holda XZ:Mn^{2+}=2:1 mol’ nisbatini saqlab 0,05 mol/l konsentratsiyali $MnCl_2$ eritmasi qo‘shildi. Reaksion aralashmaga qaytaruvchi modda $NaBH_4$ eritmasi tomchilatib qo‘shildi. Sintez jarayoni tugagandan keyin hosil bo‘lgan Mn^0–xitozan suspenziyalari ortiqcha ionlar va kichik molekulalardan dializ orqali tozalandi va vakum sharoitda muzlatgichli quritgichda quritildi.

Dinamik yorug‘lik tarqalishi (DLS) tahlili. Zarrachalarning gidrodinamik o‘lchamlari va taqsimoti DLS usuli orqali aniqlangan va tahlillar Photocor Compact spektrometrida, 632,8 nm to‘lqin uzunligiga ega He-Ne lazeri manbai bilan amalga oshirilgan. Namunalar suvli muhitda tayyorlanib, harorat 25±0,1°C da termostatlangan holda saqlandi. Zarrachalarning o‘lcham diapazoni 1 nm dan 100 mkm gacha bo‘lgan oraliqda aniqlandi.

Rentgenfazaviy tahlil (XRD). Namunalarning fazaviy tarkibi va kristalllik xususiyatlari DRON–3M rentgen difraktometrida, Co Kα nurlanishi (U=22 kV, I=16 mA) sharoitida o‘rganildi. Kristallit o‘lchami Debay-Sherrer tenglamasi orqali hisoblandi (K = 0,9; β — FWHM; λ — Co Kα). Kristallizatsiya darajasi esa J_k (kristall pik) va J_a (amorf fon) intensivliklariningg nisbatiga ko‘ra aniqlandi [32].

Skanerlovchi elektron mikroskopiya (SEM). Namunalarning yuza morfologiyasi JEOL JSM–IT210 skanerlovchi elektron mikroskopida o‘rganildi. Ta’sir kuchlanishi 5–15 kV diapazonida, ishchi masofa esa ≈ 10,8 mm sharoitida amalga oshirildi. Turli masshtablardagi tasvirlar InTouchScope dasturi yordamida olindi.

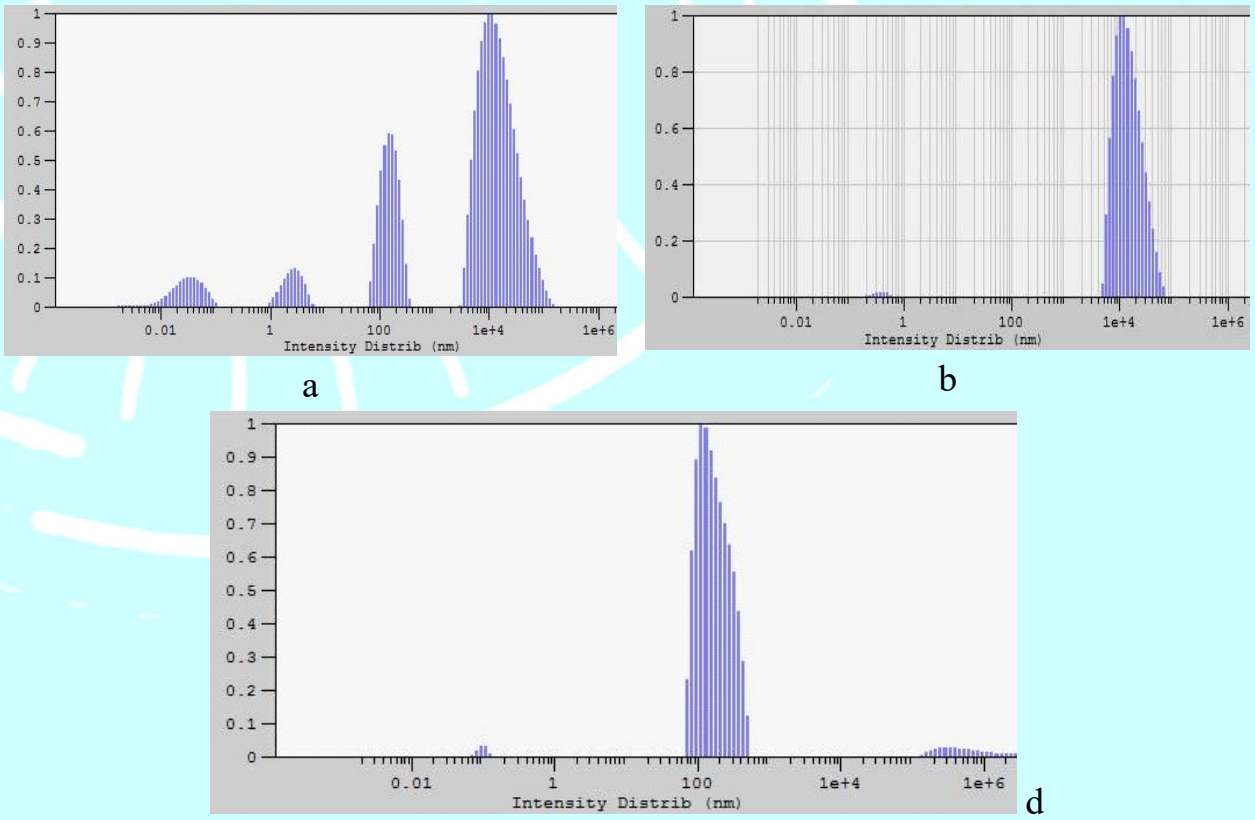
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Statistik tahlil. Barcha eksperimentlar kamida uch marta (n = 3) takrorlandi va natijalar o‘rtacha qiymat±standart og‘ish (mean ± SD) ko‘rinishida taqdim etildi. Barcha hisob-kitoblar va grafiklar OriginPro 2023 (OriginLab, USA) dasturlari yordamida amalga oshirildi. Barcha statistik testlarda ahamiyat darajasi $p < 0.05$ sifatida qabul qilindi.

MUHOKAMA VA NATIJALAR

Gidrodinamik o‘lchamlar (DLS tahlillari)

DLS tahlil natijalari sintez qilingan Mn^0 nanozarrachalarning o‘lcham taqsimoti va suspenziya barqarorligini baholashda asosiy manba bo‘ldi. Xitozan eritmasida sistema polidispers bo‘lib 30% gacha 158 nm gacha, qolgan 70 % 19 mkm gacha bo‘lgan gidrodinamik radiusli zarrachalardan iborat (1-rasm, a). Perekursor $MnCl_2$ ning suvli eritmasi o‘rtacha 17 mkm gidrodinamik radiusli zarrachalardan iboratligi aniqlandi (1-rasm, b).



a b d

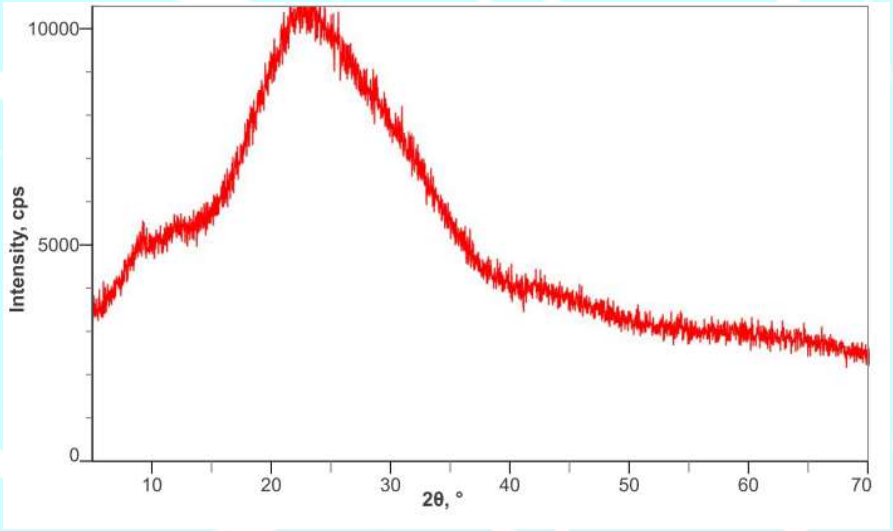
1-rasm. Xitozan (a), perekursor $MnCl_2$ (b) eritmalari va XZ-Mn^0 suspenziyasining (d) gidrodinamik o‘lchamlari

in situ sharoitlarida olingan XZ-Mn^0 suspenziyasining gidrodinamik o‘lchamlari 97% 118 nm ni tashkil etdi (1-rasm, d). Ko‘rish mumkinki xitozanning baqarorlashtiruvchi ta’siri SXZ-Mn^0 suspenziyasida yaqqol sezilgan. Bu xitozanning polikation tabiati tufayli yadro–o‘sish jarayoni nazorat qilinayotgani va suspenziyaning kolloid barqarorligi yuqori darajada ta’minlanganini ko‘rsatdi [9, 10].

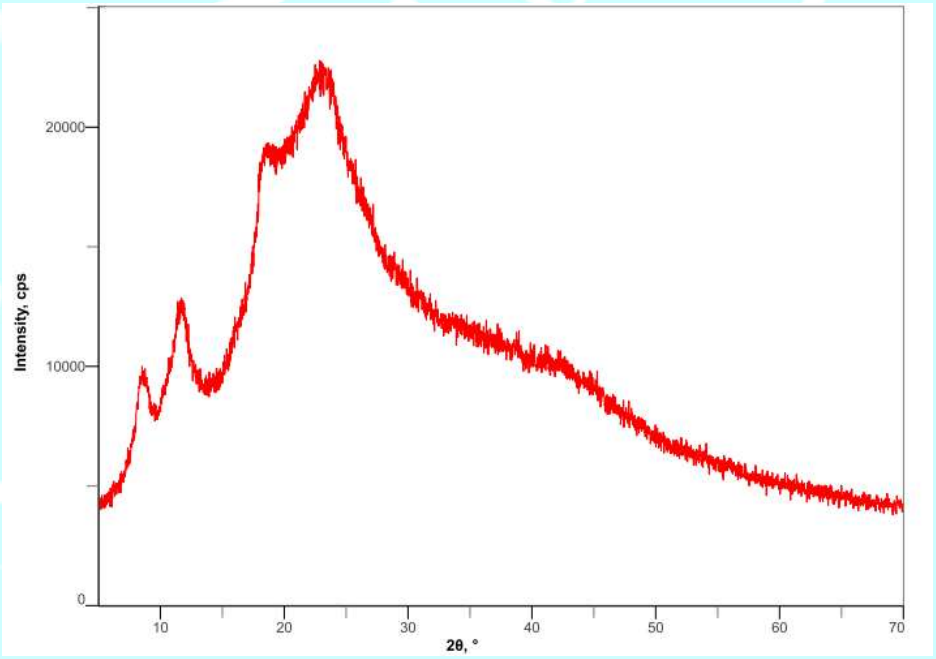
XRD analiz

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Rentgen difraktogrammalari xitozanning kristallik strukturasi yarim amorf holatda bo‘lishini, u ikki asosiy difraksiya piklari ko‘rsatdi: 2θ = 10.49° (020) va 19.95° (110) (2-rasm) [11].



a



b

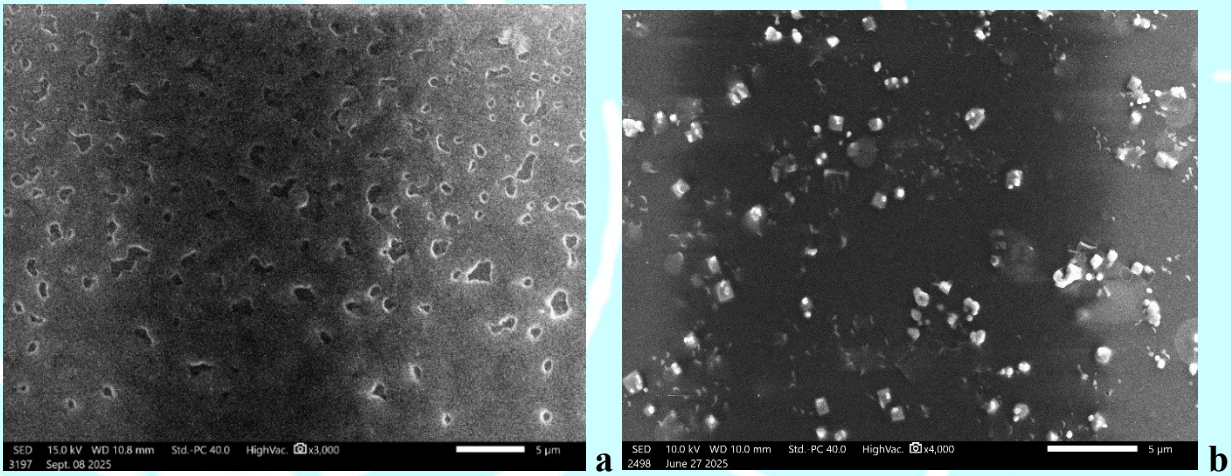
2 rasm. Xitozan (a), va XZ-Mn^0 (b) namunalarining XRD difraktogrammasi

XZ-Mn^0 namunasining XRD grafigida 2θ 8.53°, 11.73°, 18.26°, 21.78° xitozanni Mn^0 nanozarracha bilan o‘zaro ta’sir natijasida ko‘chishga uchragan piklaridir. Bu piklar marganes nanozarrachalarining xitozan zanjirlari bilan o‘zaro ta’siri natijasida strukturaviy qayta shakllanishini ko‘rsatadi. 2θ 43.63° pik nanozarrachalarda Mn^0 metall holat barqaror saqlanganligini ko‘rsatadi, u asosan (111) kristall yuzasida aks etadi [12, 13]. XZ-Mn^0 namuna tarkibi α-Mn kubiksimon (a- 5.218, b-5.218, c-5.218 Å), β-Mn kubiksimon (a-4.433, b-4.433, c-4.433 Å) va tetraganal tuzilishli (a-10.784, b-11.329, c-4.449 Å) kristall tiplari hosil bo‘lishi aniqlandi [14].

Morfologik tahlili

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Dastlab xitozan SEM (Skanerlovchi elektron mikroskop) tasviri o‘rganilganda uning matritsasi ko‘p poralik va notekis yuza bilan xarakterlandi. Tasvirdagi poralar diametri taxminan 0,2–1,0 mkm oralig‘ida bo‘lib, ularning turli tuzilishlari xitozan zanjirlarining amorf qayta shakllanishi va polimerning tabiiy g‘ovakligidan dalolat beradi (3 rasm).



3-rasm. XZ (a) va XZ-Mn^0 (b) namunalarining SEM tasviri

SEM natijalariga ko‘ra, XZ-Mn^0 namunasini tashkil etuvchi xitozan bilan barqarorlashtirilgan Mn nanozarrachalari asosan kubiksimon va tetragonal shaklda hosil bo‘lgani aniqlandi. Namunalar plyonka holatda ko‘rilganligi sababli undagi shakllangan zarrachachalarning malum soxalarda o‘sganligi va aglomeratsiyasini kuzatildi. Umuman olganda nanozarrachalar o‘lchami 100 nm dan 800 nm gachani tashkil etgan (3-rasm). Turli tuzilishga ega nanozarrachalarning hosil bo‘lishi, asosan, qaytaruvchining potensiali va reaksion muhitning kimyoviy tabiatiga bog‘liq bo‘lib, ular sintez jarayonida zarrachalarning nukleatsiya va o‘sish mexanizmlarini muayyan yo‘nalishda boshqaradi [15].

XULOSA VA TAKLIFLAR

Xulosa qilganda, *in situ* sharoitlarida marganes (Mn) nanozarrachalari olindi hamda ularning gidrodinamik o‘lchamlari o‘rtacha 118 nm ni tashkil etdi. Xitozan–marganes nanosistemasidagi XRD tahlili orqali strukturaviy o‘zgarishlar, metall Mn^0 ning ($2\theta=43.40°$) hosil bo‘lishi va xitozanning qayta kristallanishini aniq tasdiqlandi. SEM natijalarida Mn^{2+} ning $NaBH_4$ bilan tetroganal, kubsimon barqaror nanozarrachalar hosil bo‘lishini tasdiqladi. Aytish mumkinki, xitozan matritsasi marganes zarrachalarining barqaror taqsimlanishi va uzoq muddatli kolloid barqarorligini ta’minladi.

Moliyalashtirish

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