

Calcined oyster shell nanoparticles (COS NPs): a new, efficient and reusable catalyst for one-pot rapid preparation of 1,8-dioxo-octahydroxanthenes under solvent-free conditions

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Abstract Calcined oyster shell nanoparticles (COS NPs) as a novel heterogeneous nanocatalyst were prepared and fully characterized by X-ray fluorescence analysis, Fourier transform infrared spectroscopy, X-ray powder diffraction, scanning electron microscopy equipped with an energy dispersive spectrometry (SEM-EDS) and transmission electron microscopy. The composition of this catalyst was determined, and it was clearly found that the particle size of COS NPs was about 100–120 nm. The nano-structured solid catalyst as an efficient and eco-friendly catalyst was used for the synthesis of 1,8-dioxo-octahydroxanthenes via the one-pot condensation reaction of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with various aldehydes under solvent-free conditions. This new methodology is cost-effective and offers several advantages such as high yield, excellent purity, short reaction time, high atom economy, simple operation and a convenient workup procedure without the use of any injurious solvents. Moreover, the catalyst can be readily reusable, and considerable catalytic activity could be achieved after the six runs.

Keywords 1,8-Dioxo-octahydroxanthenes · Calcined oyster shell nanoparticles (COS NPs) · Solvent-free synthesis · Heterogeneous nanocatalyst · Aldehyde · 5,5-Dimethylcyclohexane-1,3-dione (dimedone)

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Introduction

Oxygen-containing heterocyclic compounds such as xanthene and its derivatives are extensively applied in organic synthesis, pharmaceutical chemistry and industry. Xanthene derivatives, especially 1,8-dioxooctahydroxanthenes, as an important class of organic compounds were found in many naturally occurring as well as synthetic derivatives. They have aroused great interest in medicinal chemistry because of their variety of biological and therapeutic properties such as antibacterial, antioxidant, antifungal, antiviral, anti-inflammatory, anti-depressant and anti-malarial and use in photodynamic therapy and as an antagonist for the paralyzing action of zoxazolamine [1, 2]. Furthermore, in addition to their use as valuable synthetic precursors for many organic compounds [3] and dyes [4], they are being utilized in laser technologies [5, 6] and fluorescent materials for visualization of biomolecules [7, 8]. 1,8-Dioxooctahydroxanthenes as a key structural motif in a number of natural products [9–11] have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring [12]. Since these moieties are privileged pharmacophores as well as valuable reactive intermediates, synthesis of 1,8-dioxooctahydroxanthenes is a continuing hot topic in synthetic and medicinal chemistry. The first method involves the condensation reaction of resorcinol and phthalic anhydride in the presence of sulfuric acid, which was reported by Bayer [13]. So far, many efforts have been continued for the development of synthetic methods for 1,8-dioxooctahydroxanthenes, which contain the condensation reactions of aldehydes and 1,3-cyclohexanediones under the influence of several efficient catalysts.

The commonly used homogeneous catalysts such as H_2SO_4 [14], BiCl₃ [15–17], InCl₃ [18], ZrO(OTf)₂ [19], [Et₃N–SO₃H]Cl [20], I₂ [21], L-proline [22] and NaHSO₄ [23] have not been entirely satisfactory, being associated with some disadvantages, such as low yields, long reaction times, usage of volatile and toxic solvents, large amounts of poisonous and corrosive reagents, strongly acidic conditions, tedious workup procedures, high catalyst loading, lack of easy availability of the catalyst, expensive and/or unrecyclable catalysts. To overcome all of the drawbacks to using environmentally harmful homogeneous catalysts, solid heterogeneous catalysts have been tested, such as nano-TiO₂ [24], TiO₂/SO₄²⁻ [25], PPA/SiO₂ [26], PMA/SiO₂ [27], HClO₄-SiO₂ [26], SiO₂ [28], SbCl₃/SiO₂ [29], FeCl₃/SiO₂ [30], silica sulfuric acid [31], NaHSO₄-SiO₂ [29] Fe₃O₄@SiO₂-imid-Dowex-50w [33], Amberlyst-15 [34], $H_3PMo_{12}O_{40}$ nanoparticles [32], [Hmim][TFA] [35], [bmim]HSO₄ [36], nanosized MCM-41-SO₃H [37] and ceric ammonium nitrate-supported HY-zeolite [38].

The recycling of oyster shell waste has become an issue of concern. To date, a portion of oyster shell waste has been recycled for use as spat and as a substitute for limestone in fertilizers and chicken feed. Oyster shell can be utilized as a solid catalyst because the main phase in oyster shells is calcite, which is transformed to quicklime (COS NPs) upon calcination at high temperature. Waste egg [39], oyster [40], shrimp [41], mullusk [42], cockle shells [43], waste mud crab [44] and fish scales [45] have been used as resources for obtaining CaO-based catalysts. Oyster

shell can act as a bifunctional catalyst. Existence of the conjugate anion (oxygen) displays a strong basic property [46], and the metal cation, due to its small electronegativity, exhibited very weak Lewis acidity. In recent years, ground oyster shells have been successfully reused as various construction materials, as promising adsorbents of metal ions in sewage [47–50] and as a catalyst for synthesis of 1,2,3-triazoles. The use of COS NPs as a catalyst is appropriate because of the low cost, low solubility, non-toxicity, high alkalinity, reusability, environmental compatibility, availability and also ease of handling [42, 51].

As a part of our research on the development of environmentally friendly methods for the synthesis of organic compounds using reusable catalysts [52–73] in the present study, preparation of COS NPs has been implemented and reported for the first time as a novel and efficient catalyst for successful synthesis of 1,8-dioxo-octahydroxanthenes (Scheme 1).

Experimental

General

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FTIR spectra were provided on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹. The NMR spectra were obtained in Brucker Avance 300 MHz instruments in DMSO- d_6 . Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70-eV electron impact ionization in m/z (rel %). The chemical compositions of the COS NPs were specified with X-ray fluorescence spectroscopy (XRF) using a BRUKER axs-S4 EXPLORER spectrometer. The crystal structure of the catalyst was analyzed by XRD using a D8 ADVANCE-Bruker diffractometer operated at 40 kV and 30 mA utilizing Cu Ka radiation ($\lambda = 0.154$ Å). SEM images were recorded using a Leo 1450 VP (LEO, Germany) scanning electron microscope operating at an acceleration voltage of 20 kV. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620 energy-dispersive spectrometer (SEM-EDS) presenting a 133-eV resolution at 20 kV. Transmission electron



Scheme 1 Preparation of COS NPs

microscopy (TEM) was performed with a 120-kV Zeiss Leo 912 AB (Germany) with an accelerating voltage of 120-kV imaging with $80-500,000 \times$ magnification and equipped with a high-resolution CCD camera. All yields refer to isolated products after purification by recrystralization.

Preparation of COS NPs

The oyster shells were soaked in distilled water at room temperature for 4 h, washed several times with H₂O/EtOH to remove impurities and then dried for 12 h at 100 °C. The oyster shell samples were later crushed and milled to obtain fine powder. Subsequently, COS NPs were generated from calcination of waste oyster shells at high temperature (900 °C for 6 h).

Typical procedure for synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9hexahydro-1H-xanthene-1,8(2H)-dione in the presence of COS NPs

A mixture of benzaldehyde (1 mmol, 0.106 g) and 5,5-dimethylcyclohexane-1,3dione (dimedone) (2 mmol, 0.289 g) in the presence of 0.025 g of COS NPs was stirred at 90 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. Then, hot EtOH (3 ml) was poured into the reaction flask, and the catalyst was removed by filtration. Finally, the crude 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9hexahydro-1*H*-xanthene-1,8(2*H*)-dione was recrystallized from EtOH obtaining 0.343 g of white color crystals (98% yield).

3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione [24] (Table 3, 3a) White solid; yield (0.343 g, 98%); mp 198–200 °C (Lit., 199–201 °C); FT-IR (KBr): v_{max}/cm^{-1} 3084.20 (alkenyl CH str.), 3026.55 (aromatic CH str.), 2955.61 (aliphatic CH str.), 1662.93 (C=O str.), 1560.19 (alkenyl C=C str.), 1492.54 (aromatic C=C str.), 1271.62–1043.68 (C–O–C str.); ¹H NMR (300 MHz, DMSO- d_6 , ppm) δ : 7.26–6.89 (m, 5 H), 4.93 (s, 1 H, CH-9), 2.42 (s, 4 H, 2 H-2, 2 H-7), 2.03 (s, 4 H, 2 H-4, 2 H-5), 0.92 (s, 6 H, equatorial 2CH₃), 0.89 (s, 6 H, axial 2CH₃); ¹³C NMR (75 MHz, DMSO- d_6 , ppm) δ : C-1, C-8 (C=O); 195.75, C-11, C-13; 163.39, C-1'; 144.99, C-3', C-5'; 127.43, C-2', C-6'; 127.09, C-4'; 126.87, C-10, C-12; 115.30, C-2, C-7; 50.47, C-9; 47.44, C-4, C-5; 32.35, C-3, C-6; 31.65, C-14, C-16 (equatorial); 30.81, C-15, C-17 (axial); 29.63; MS (EI): m/z (%) 350 (10) [M⁺], 347 (100) [M⁺–3H], 270 (100) [M⁺–C₆H₈], 78 (62) [M⁺–C₁₇H₂₀O₃], 29 (100) [M⁺–C₂₁H₂₁O₃].

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione [24] (Table 3, 3b) White solid; yield (0.346 g, 95%); mp 214–216 °C (Lit., 216–218 °C); IR (KBr): v_{max}/cm^{-1} 3051.99 (alkenyl CH str.), 3019.30 (aromatic CH str.), 2954.96 (aliphatic CH str.), 1689.05 (C=O str.), 1563.99 (alkenyl C=C str.), 1507.38 (aromatic C=C str.), 1271.88–1042.50 (C–O–C str.); ¹H NMR (300 MHz, DMSO- d_6 , ppm) δ : 6.94 (d, J = 8.4 Hz, 2 H, H-2', H-6'), 6.90 (d,

 $J = 8.4 \text{ Hz}, 2 \text{ H}, \text{H-3'}, \text{H-5'}, 4.92 (s, 1 \text{ H}, \text{CH-9}), 2.21 (s, 3 \text{ H}, \text{CH}_3), 2.15 (s, 4 \text{ H}, 2 \text{ H-2}, 2 \text{ H-7}), 2.10 (s, 4 \text{ H}, 2 \text{ H-4}, 2 \text{ H-5}), 1.02 (s, 6 \text{ H}, equatorial 2 \text{ CH}_3), 0.96 (s, 6 \text{ H}, axial 2 \text{ CH}_3); {}^{13}\text{C} \text{ NMR} (75 \text{ MHz}, \text{DMSO-}d_6, \text{ppm}) \delta: \text{C-1}, \text{C-8} (\text{C=O}); 195.88, \text{C-11}, \text{C-13}; 165.83, \text{C-1'}; 141.49, \text{C-3'}, \text{C-5'}; 132.96, \text{C-2'}, \text{C-6'}; 128.29, \text{C-4'}; 127.36, \text{C-10}, \text{C-12}; 115.49, \text{C-2}, \text{C-7}; 50.30, \text{C-9}; 47.44, \text{C-4}, \text{C-5}; 31.65, \text{C-3}, \text{C-6}; 30.44, \text{C-14}, \text{C-16} (equatorial); 29.47, \text{C-15}, \text{C-17} (axial); 28.05, \text{CH}_3; 20.98; \text{MS} (\text{EI}): \text{m/z} (\%) 364 (5) [M^+] 362 (20) [M^+ - 2\text{H}], 271 (28) [M^+ - \text{C}_7\text{H}_9], 240 (88) [M^+ - \text{C}_{10}\text{H}_{12}\text{O}], 225 (100) [M^+ - \text{C}_{10}\text{H}_{11}\text{O}_2], 170 (75) [M^+ - \text{C}_{12}\text{H}_{18}\text{O}_2], 91 (65) [M^+ - \text{C}_{17}\text{H}_{21}\text{O}_3], 83 (80) [M^+ - \text{C}_{19}\text{H}_{21}\text{O}_3], 41 (85) [M^+ - \text{C}_{22}\text{H}_{27}\text{O}_2].$

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [24] (Table 3, 3c) White solid; yield (0.353 g, 93%); mp 242–244 °C (Lit., 243–245 °C); MS (EI): m/z (%) 380 (2) [M⁺], 281 (8) [M⁺– C₆H₁₁O], 255 (100) [M⁺–C₇H₁₀O₂], 241 (75) [M⁺–C₈H₁₁O₂], 225 (90) [M⁺–C₈H₁₁O₃], 173 (70) [M⁺–C₁₃H₁₉O₂], 145 (75) [M⁺– C₁₄H₁₉O₃], 83 (80) [M⁺–C₁₉H₂₂O₃], 41 (70) [M⁺– C₂₂H₂₇O₃].

9-(4-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [24] (Table 3, 3d) White solid; yield (0.347 g, 95%); mp 252–254 °C (from EtOH) (Lit., 252–254 °C); MS (EI): m/z (%) 366 (8) [M⁺], 363 (100) [M⁺– 3H], 270 (98) [M⁺–C₆H₈O], 241 (98) [M⁺–C₈H₁₅O], 83 (95) [M⁺– C₁₈H₁₉O₃], 41 (30) [M⁺–C₂₀H₂₁O₄].

9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [25] (Table 3, 3e). White solid; yield (0.311 g, 85%); mp 204–206 °C (Lit., 205–206 °C); MS (EI): m/z (%) 366 (2) [M⁺], 280 (15) [M⁺– C₅H₁₀O], 226 (10) [M⁺–C₈H₁₂O₂], 122 (100) [M⁺–C₁₅H₁₆O₃], 93 (25) [M⁺– C₁₇H₂₁O₃], 76 (30) [M⁺–C₁₇H₂₂O₄], 39 (70) [M⁺– C₂₀H₂₃O₄].

9-(4-(dimethylamino)phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione [26] (Table 3, 3f) White solid; yield (0.377 g, 96%); mp 222–224 °C (Lit., 222–225 °C); MS (EI): m/z (%) 393 (15) [M⁺], 284 (48) [M⁺–C₇H₁₁O], 271 (50) [M⁺–C₈H₁₂N], 224 (55) [M⁺–C₁₁H₂₁O], 133 (75) [M⁺–C₁₆H₂₀O₃], 98 (70) [M⁺–C₁₉H₂₁NO₂], 82 (100) [M⁺–C₂₀H₂₅NO₂], 43 (60) [M⁺–C₂₂H₂₄NO₃].

9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [24] (Table 3, 3g) White solid; yield (0.376 g, 98%); mp 228–230 °C (Lit., 229–231 °C); IR (KBr): v_{max}/cm^{-1} 2956.23 (aliphatic CH str.), 1620.44 (C=O str.), 1580.64 (alkenyl C=C str.), 1517.84 (aromatic C=C str.), 1227.39–1146.56 (C–O–C str.); ¹H NMR (300 MHz, DMSO-d₆, ppm) δ : 7.19 (d, J = 8.4 Hz, 2 H, H-2', H-6'), 6.99 (d, J = 8.1 Hz, 2 H, H-3', H-5'), 4.67 (s, 1 H, CH-9), 2.51 (s, 4 H, 2 H-2, 2 H-7), 1.93 (s, 4 H, 2 H-4, 2 H-5), 1.00 (s, 6 H, equatorial 2 CH₃), 0.98 (s, 6 H, axial 2 CH₃); ¹³C NMR (75 MHz, DMSO-d₆, ppm) δ : C-1, C-8 (C=O); 195.75, C-11, C-13; 167.35, C-1'; 144.10, C-4'; 131.50, C-2', C-6'; 129.26, C-3', C-5'; 128.94, C-10, C-12; 115.07, C-2, C-7; 49.51, C-9; 47.50, C-4, C-5; 32.48, C-3, C-6; 31.65, C-14, C-16 (equatorial); 30.52, C-15, C-17 (axial); 29.16; MS (EI): m/z (%) 385 (5) $[M^++1]$, 384 (18) $[M^+]$, 380 (90) $[M^+-4H]$, 269 (90) $[M^+-C_6H_{11}O_2]$, 258 (45) $[M^+-C_7H_{12}O_2]$, 82 (90) $[M^+-C_{18}H_{19}CIO_2]$, 41 (65) $[M^+-C_{21}H_{24}CIO_2]$, 28 (100) $[M^+-C_{22}H_{25}CIO_2]$.

9-(2-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [24] (Table 3, 3h) White solid; yield (0.364 g, 95%); mp 221–223 °C (Lit., 223–235 °C); IR (KBr): v_{max}/cm^{-1} 3064.25 (alkenyl and aromatic CH str.), 2954.70 (aliphatic CH str.), 1719.86 (C=O str.), 1565.04 (alkenyl C=C str.), 1507.38 (aromatic C=C str.), 1268.87–1038.95 (C–O–C str.); MS (EI): m/z (%) 384 (2) [M⁺], 270 (18) [M⁺– C₆H₁₀O₂], 138 (68) [M⁺– C₁₅H₁₅ClO] 82 (70) [M⁺– C₁₈H₁₉ClO₂], 41 (70) [M⁺– C₂₁H₂₄ClO₂], 30 (100) [M⁺– C₂₂H₂₃ClO₂].

9-(3-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [25] (Table 3, 3i) White solid; yield (0.420 g, 98%); mp 202–204 °C (Lit., 203–204 °C); ¹H NMR (300 MHz, DMSO- d_6 , ppm) δ : 7.59–7.15 (m, 4 H, ArH), 4.51 (s, 1 H, CH-9), 2.11 (s, 4 H, 2 H-2, 2 H-7), 2.03 (s, 4 H, 2 H-4, 2 H-5), 1.04 (s, 6 H, equatorial 2 CH₃), 1.02 (s, 6 H, axial 2 CH₃); ¹³C NMR (75 MHz, DMSO- d_6 , ppm) δ : C-1, C-8 (C=O); 195.65, C-11, C-13; 169.33, C-1'; 148.54, C-2'; 132.47, C-5'; 129.79, C-4'; 129.43, C-6', 128.58, C-3'; 127.23, C-10, C-12; 114.76, C-2, C-7; 50.35, C-9; 47.36, C-4, C-5; 31.68, C-3, C-6; 30.83, C-14, C-16 (equatorial); 29.54, C-15, C-17 (axial); 27.94; MS (EI): m/z (%) 429 (30) [M⁺], 307 (28) [M⁺– C₈H₁₁O], 302 (100) [M⁺–C₇H₁₀O₂], 225 (100) [M⁺–C₇H₁₀BrO₂], 83 (100) [M⁺– C₁₈H₁₈BrO₂], 41 (100) [M⁺– C₂₁H₂₄BrO₂].

9-(4-fluorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [29] (Table 3, 3j) White solid; yield (0.361 g, 98%); mp 224–226 °C (Lit., 226–227 °C); IR (KBr): v_{max}/cm^{-1} 3080.12 (alkenyl and aromatic CH str.), 2956.57 (aliphatic CH str.), 1660.95 (C=O str.), 1623.74 (alkenyl C=C str.), 1509.68 (aromatic C=C str.), 1224.89–1143.95 (C–O–C str.); ¹H NMR (300 MHz, DMSOd₆, ppm) δ : 7.22–7.02 (m, 4 H, ArH), 4.53 (s, 1 H, CH-9), 2.51 (s, 4 H, 2 H-2, 2 H-7), 2.12 (s, 4 H, 2 H-4, 2 H-5), 1.04 (s, 6 H, equatorial 2 CH₃), 0.91 (s, 6 H, axial 2 CH₃); ¹³C NMR (75 MHz, DMSO-d₆, ppm) δ : C-1, C-8 (C=O); 196.55, C-11, C-13; 163.43, C-4'; 159.45, C-1'; 140.92, C-2', C-6'; 130.33, C-3', C-5'; 115.18, C-10, C-12; 114.90, C-2, C-7; 50.44, C-9; 40.81, C-4, C-5; 32.34, C-3, C-6; 31.11, C-14, C-16 (equatorial); 29.09, C-15, C-17 (axial); 26.95; MS (EI): m/z (%) 368 (30) [M⁺], 364 (100) [M⁺–4H], 270 (90) [M⁺–C₁₉H₁₈FO₃].

3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [24] (Table 3, 3k) White solid; yield (0.387 g, 98%); mp 224–226 °C (Lit., 224–226 °C); MS (EI): m/z (%) 395 (5) [M⁺], 254 (50) [M⁺– C₆H₈NO₃], 224 (42) [M⁺–C₈H₁₃NO₃], 160 (32) [M⁺–C₁₄H₁₉O₃], 139 (50) [M⁺–C₁₅H₁₄NO₃], 83 (90) [M⁺–C₁₈H₁₈NO₄], 28 (95) [M⁺– C₂₁H₂₁NO₅]. 4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile [24] (Table 3, 31) White solid; yield (0.367 g, 98%); mp 219–221 °C (Lit., 220–222 °C); IR (KBr): v_{max}/cm^{-1} 2956.68 (aliphatic CH str.), 2226.29 (CN str.), 1695.23 (C=O str.), 1558.74 (alkenyl C=C str.), 1494.45 (aromatic C=C str.), 1271.45–1042.74 (C–O–C str.); ¹H NMR (300 MHz, DMSO-d₆, ppm) δ : 7.62 (d, J = 8.1 Hz, 2 H, H-2′ H-6′), 7.16 (d, J = 7.8 Hz, 2 H, H-3′, H-5′), 5.08 (s, 1 H, CH-9), 2.14 (s, 8 H, 2 H-2, 2 H-7, 2 H-4, 2 H-5), 0.99 (s, 12 H, 4 CH₃); ¹³C NMR (75 MHz, DMSO-d₆, ppm) δ : C-1, C-8 (C=O); 195.52, C-11, C-13; 164.22, C-1′; 152.34, C-3′, C-5′; 131.71, C-2′, C-6′; 128.39, CN; 119.96, C-10, C-12; 114.55, C-4′; 107.15, C-2, C-7; 50.43, C-9; 47.43, C-4, C-5; 31.66, C-3, C-6; 29.12, C-14, C-16, C-15, C-17 (equatorial, axial); 28.45; MS (EI): m/z (%) 375 (5) [M⁺], 372 (35) [M⁺– 3H], 250 (65) [M⁺–C₈H₁₃O], 126 (75) [M⁺–C₁₅H₂₂O₃], 83 (100) [M⁺–C₁₉H₁₈NO₂], 41 (100) [M⁺– C₂₂H₂₄NO₂].

3,3,6,6-tetramethyl-9-(thiophen-2-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [29] (Table 3, 3m) White solid; yield (0.303 g, 85%); mp 163–165 °C (from EtOH) (Lit., 164–165 °C); MS (EI): m/z (%) 356 (2) [M⁺], 353 (100) [M⁺–3H], 270 (90) [M⁺–C₄H₆S], 245 (75) [M⁺–C₅H₄OS], 233 (90) [M⁺–C₆H₄OS], 121 (50) [M⁺–C₁₄H₁₉O₃], 110 (65) [M⁺–C₁₅H₁₉O₃], 82 (90) [M⁺– C₁₇H₂₂O₃], 43 (70) [M⁺–C₁₈H₁₇O₃S].

3,3,6,6-tetramethyl-9-(pyridin-4-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)dione [74] (Table 3, 3n) White solid; yield (0.315 g, 90%); mp 211–213 °C (Lit., 212–214 °C); ¹H NMR (300 MHz, DMSO- d_6 , ppm) δ : 8.30 (d, J = 5.4 Hz, 2 H, H-2', H-6'), 6.96 (d, J = 4.8 Hz, 2 H, H-3', H-5'), 4.43 (s, 1 H, CH-9), 2.16 (s, 4 H, 2 H-2, 2 H-7), 2.10 (s, 4 H, 2 H-4, 2 H-5), 1.07 (s, 6 H, equatorial 2 CH₃), 1.05 (s, 6 H, axial 2 CH₃); ¹³C NMR (75 MHz, DMSO- d_6 , ppm) δ : C-1, C-8 (C=O); 195.61, C-11, C-13; 169.30, C-1'; 154.98, C-3', C-5'; 149.76, C-2', C-6'; 123.13, C-10, C-12; 114.14, C-2, C-7; 50.30, C-9; 47.30, C-4, C-5; 31.66, C-3, C-6; 30.89, C-14, C-16 (equatorial); 29.55, C-15, C-17 (axial); 28.13; MS (EI): m/z (%) 351 (10) [M⁺], 349 (95) [M⁺– 2H], 271 (100) [M⁺–C₄H₆N], 215 (48) [M⁺–C₈H₈O₂], 160 (38) [M⁺–C₁₂H₁₈NO], 83 (50) [M⁺–C₁₇H₁₈NO₂], 55 (35) [M⁺–C₁₈H₁₈NO₃].

Results and discussion

Characterization of the catalyst

The chemical composition of the COS NPs was confirmed by X-ray fluorescence spectroscopy (XRF). Based on the data in Table 1, the principal composition of the COS NPs is CaO.

The oyster shell and COS NPs were characterized using FT-IR spectroscopy, as shown in Fig. 1. The observed absorption bands for aragonite phases (calcium carbonate) in the oyster shell structure are due to the planar CO_3^{2-} ion (Fig. 1a). There are four vibrational modes in the free CO_3^{2-} ion [75]: the symmetric

	1					
Constituent	CaO	SrO	Fe ₂ O ₃	SiO ₂	SO ₃	Moister
Percentage	86.522	0.245	0.204	0.102	0.489	12.439

Table 1 Chemical composition of COS NPs



Fig. 1 FT-IR spectra of (a) oyster shells; (b) COS NPs; (c) sixth reused COS NPs

stretching vibration of the carbonate ion at about 1080 cm⁻¹ (v_1); the out-of-plane bending absorption at about 856 cm⁻¹ (v_2); the asymmetric stretching vibrations at about 1130–1720 cm⁻¹ (v_3); the split in-plane bending vibration at about 717 cm⁻¹ (v_4). The strong band detected at 1760 cm⁻¹ can also be attributed to the C=O group of the carbonated ion. The FT-IR spectrum of COS NPs was shown as Fig. 1b. As can be seen, the absorption bands at 1332–1620 show the existence of CaO phase in the structure.

Also, XRD analysis was applied to detect the crystallinity of the COS NPs and the sixth recovered COS NPs. As presented in Fig. 2, the characteristic peaks at 2θ , 30.5° , 38.1° , 52.6° , 63.2° , 66.9° and 79.1° , corresponded to the $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 2\ 0)$, $(3\ 1\ 1)$, $(2\ 2\ 2)$ and $(4\ 0\ 0)$ crystallographic faces, which are in agreement with the standard data of CaO (JCPDS 04-007-9734) [76]. The XRD results also demonstrate the presence of cubic phase CaO. These indicated diffraction peaks clearly pointed to a cubic structure for the catalyst and the sixth recovered one. The average crystallite size of CaO NPs, calculated using the Debye-Scherrer equation $d = K\lambda/\beta \cos\theta$, is about 100 nm.

To figure out the morphology and nanostructure of COS NPs, scanning electron microscope imaging combined with associated EDS and transmission electron microscope imaging was performed. The SEM images of COS NPs are depicted in



Fig. 2 The XRD patterns of (a) COS NPs; (b) 6th recovered COS NPs

Fig. 3a. As is obvious, the SEM images of COS NPs were illustrated with a spherical morphology. According to the TEM images in Fig. 3b, the average diameters of the COS NPs were estimated to be 120 nm. As seen from the pictures, the morphology of COS NPs is spherical.

The existence of Ca, O and C as the main components of the COS NPs was demonstrated using the energy-dispersive spectrum (EDS), which is in good agreement with the XRF results (Fig. 4).

Catalytic synthesis of 1,8-dioxo-octahydroxanthene derivatives

After successful preparation and full characterization of the nanocatalyst, the catalytic efficiency of COS NPs was evaluated in the synthesis of 1,8-dioxo-octahydroxanthene derivatives via a three-component condensation reaction of aromatic aldehydes and two equivalents of dimedone (Scheme 2).

In a series of experiments, the promotion effect of COS NPs in the preparation of 1,8-dioxo-octahydroxanthene derivatives was studied by the reaction of benzaldehyde with two equivalents of dimedone under different reaction conditions. The effects of the molar ratio of the reaction components, amount of catalyst, solvent and temperature were investigated in a typical experiment (Table 2).

No significant formation of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione was observed when the blank experiment was carried out in the absence of COS NPs and solvent even after a long period of time (Table 2, entry 1). Interestingly, performing the same reaction in the presence of finely powdered oyster shells and bulk CaO as catalysts at 90 °C results in 15% and 25% yields of product, respectively, after 18 h (Table 2, entries 2, 3). Due to the longer reaction time in the presence of oyster shells and bulk CaO (as the main component of COS NPs), the model reaction was conducted in the presence of COS



Fig. 3 a SEM images of COS NPs; b TEM images of COS NPs

NPs (Table 2, entry 4). Surprisingly, a significant improvement was observed in the yield and reaction rate (the yield was dramatically increased to 98% after 30 min). To ascertain the optimum conditions with respect to the reaction temperature, the model reaction was performed at different temperatures. No improvement in the yield and reaction rate was observed by increasing the reaction temperature (Table 2, entries 5, 6). Performing the model reaction at lower temperature (80 °C) increased the duration of the reaction (Table 2, entry 7). To evaluate the most appropriate catalyst loading, the model reaction was carried out using different amounts of COS NPs under solvent-free conditions (Table 2, entries 8, 9). It was found that the best results in terms of yield, as well as reaction time, were obtained using 0.025 g of catalyst. Moreover, the effect of reaction media on the reaction rate as well as on the yield of product was investigated. The results showed that among the tested solvents, such as H₂O, EtOH and the solvent-free conditions (Table 2, entries 10, 11). To improve the yield of the desired product, the reaction is



Fig. 4 EDS spectrum of COS NPs



$$\label{eq:R} \begin{split} R &= C_6H_5, 4\text{-}CH_3C_6H_4, 4\text{-}CH_3OC_6H_4, 4\text{-}HOC_6H_4, 2\text{-}HOC_6H_4, 4\text{-}(CH_3)_2NC_6H_4, 4\text{-}CIC_6H_4, 2\text{-}CIC_6H_4, 3\text{-}BrC_6H_4, 4\text{-}FC_6H_4, 4\text{-}O_2NC_6H_4, 4\text{-}NCC_6H_4, 2\text{-}C_4H_3S, 4\text{-}C_5H_4N \end{split}$$

Scheme 2 Preparational of 1,8-dioxo-octahydroxanthene derivatives in the presence of COS NPs

performed using an additional quantity of dimedone (Table 2, entry 12). According the result obtained in Table 2, increasing the amount of dimedone does not improve the reaction rate or product yield. In continuing of our study, by considering the main component of the COS NPs (see the XRF results in Table 1), we decided to probe the catalytic reactivity of the principal composition of the COS NPs. Toward this point, analytical-pure CaO was also used as catalyst in the model reaction. As is depicted in Table 2, analytical-pure CaO under optimized reaction conditions catalyzed the condensation reaction as well as COS NPs (Table 2, entry 13). The obtained result validated the efficiency of CaO (as the main component of COS NPs) for catalyzing this transformation, and no impurity elements/phase in oyster shells promoted the catalytic activity of COS NPs.

The remarkable results obtained with the above reaction conditions encouraged us to show the generality and scope of this new protocol. A variety of aromatic aldehydes with different substituents were condensed with two equivalents of dimedone in the presence of COS NPs under optimized reaction conditions. The results are shown in Table 3. From the results, we found that both categories of aromatic aldehydes bearing either electron-withdrawing or electron-donating

	-			-			
Entry	Molar ratio 1a:2a	Catalyst	Amount of catalyst (g)	Solvent	Temperature (°C)	Time (min)	Isolated yield (%)
1	1:2	_	-	-	90	18 (h)	Trace
2^{a}	1:2	Oyster shells	0.03	-	90	18 (h)	15
3 ^b	1:2	CaO	0.03	_	90	18 (h)	25
4	1:2	COS NPs	0.03	-	90	30	98
5	1:2	COS NPs	0.03	_	110	30	98
6	1:2	COS NPs	0.03	_	100	30	98
7	1:2	COS NPs	0.03	_	80	50	90
8	1:2	COS NPs	0.025	-	90	30	98
9	1:2	COS NPs	0.02	_	90	35	95
10	1:2	COS NPs	0.025	H_2O	Reflux	10	10
11	1:2	COS NPs	0.025	EtOH	Reflux	1 (h)	90
12	1:2.5	COS NPs	0.025	_	90	30	98
13	1:2	Analytical- pure CaO	0.025	-	90	35	90

 Table 2
 Optimization of various reaction parameters for the synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione in the presence of COS NPs

^aThe reaction was performed in the presence of finely powdered oyster shell

^bThe reaction was performed in the presence of bulk CaO

^cBold values refer to optimized conditions

substituents underwent an electrophilic substitution reaction with dimedone and uniformly afforded good yields of the corresponding products in high yields within 20–35 min under solvent-free conditions. The nature and electronic properties of substituents on the aromatic ring had no obvious effect on the yield or reaction time. The high yield was also obtained in the case of the heterocyclic aldehydes (Table 3, entries 13–14).

In this study, completion of the reaction was established by the disappearance of 5,5-dimethylcyclohexane-1,3-dione (dimedone) and formation of the desired product on TLC, followed by the appearance of C=O and C=C stretching frequencies at 1719–1620 cm⁻¹ and 1623–1558 cm⁻¹, respectively, in the Fourier transform infrared (FT-IR) spectra. Primary elucidation of the structures of all isolated products (after purification by crystallization) was done by comparison of their melting points and mass spectra with the authentic samples. In all of the cases, the molecular ions were evident in the mass spectra as well as some useful fragmentation information for each compound, which can be beneficial for depicting the desired products. The selected products were further characterized by ¹H NMR, ¹³CNMR and FT-IR spectroscopy. In ¹H NMR spectra of 1,8-dioxooctahydroxanthenes, the C-9 proton at the bridge between the two dimedone rings appears in the region 5.08-4.51 ppm. The C-4 and C-5 protons (two methylene groups) and C-2 and C-7 protons give rise to two resonating signals in the region of 2.14–1.93 ppm and 2.51–2.11 ppm, respectively. Two sets of methyl groups (in axial and equatorial positions) appeared as two singlet peaks around 1.02–0.89 ppm

Entry	Aldehydes	Product	Time (min)	Isolated yield (%)
1	PhCHO	o o o o o o o o o a	30	98
2	4-CH ₃ C ₆ H ₄ CHO	CH ₃ o o o 3b	30	95
3	4-CH ₃ OC ₆ H ₄ CHO	H ₃ C ₀ 0 0 3c	30	93
4	4-HOC ₆ H ₄ CHO	OH O O O O O O O O O O O O O O O O O O	35	95
5	2-HOC ₆ H ₄ CHO		35	85
6	4-(CH ₃) ₂ NC ₆ H ₄ CHO	H ₃ C _N CH ₃ O O O O O O O O	30	96
7	4-ClC ₆ H₄CHO	Cl o o o 3g	20	98

Table 3 Synthesis of different structurally 1,8-dioxo-octahydroxanthenes in the presence of COS NPs under solvent-free conditions

Entry	Aldehydes	Product	Time (min)	Isolated yield (%)
8	2-ClC ₆ H ₄ CHO	CI O	25	95
9	3-BrC ₆ H ₄ CHO	Br O O O O O O O O O O O O O O O O O O O	20	98
10	4-FC ₆ HCHO ₄		20	98
11	4-O ₂ NC ₆ H ₄ CHO	NO ₂ o	25	98
12	4-CNC ₆ H ₄ CHO	CN O O O 31	20	98
13	2-Thiophene- carbaldehyde	S S O S O O S O O S O O S O O S O O S O O S O O S O O S O O S O O S O O S O O O S O O S O O S O O S O O S O O S O O S O O S O O S O O S S O S O S S O S O S S O S S O S S O S S O S	25	85
14	4-Pyridine-carbaldehyde	N O O O O O O O O O O O O O O O O O O O	20	90

 Table 3
 continued



Scheme 3 Proposed reaction mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes in the presence of COS NPs

and 1.04–0.92 ppm, respectively. In the ¹³C NMR spectra, signals around 195.8–195.5, 169.3–163.3 and 115.4–114.5 ppm were assigned to the quaternary carbon atoms at the (C-1 and C-8), (C-11 and C-13) and (C-10 and C-12) positions, respectively (the equivalent carbon atoms of two dimedone rings give rise to one signal). The resonating peaks of C-9 (carbon at the bridge between the two dimedone rings), (C-2 and C-7), (C-4 and C-5) and (C-3 and C-6) were observed in the expected region around 47.5–47.3, 50.4–49.5, 32.4–31.6 and 31.6–29.1 ppm. In the experimental section, the characteristic spectral data for the synthesized 1,8-dioxo-octahydroxanthenes have been discussed, which were in good corroboration with the literature [77] and proposed structures.

A possible mechanism for this transformation, which is in accordance with the literature studies [26, 78, 79], is proposed in Scheme 3. After a long reaction time, a

comparatively lower yield of product was observed in the absence of COS NPs, which confirmed the catalytic activity of COS NPs in the preparation of 1,8-dioxooctahydroxanthenes (Table 2, entry 1). Initially, COS NPs as a basic solid catalyst facilitated the formation of an enol form of 5,5-dimethylcyclohexane-1,3-dione (dimedone) (activated 1,3-cyclic diketone I) [78]. In the next step, the nucleophilic attack of I to aldehyde led to the formation of intermediate II, which upon dehydration generated the intermediate III [78]. Subsequently, intermediate III was then attacked by another activated 1,3-cyclic diketone (Michael addition) to give tetraketone IV. Dehydration and aromatization of IV afforded the 1,8-dioxooctahydroxanthenes V [78]. In the following, COS NPs re-entered the catalytic cycle. More investigation of the elucidation of the mechanism and scope of this reaction is presently underway in our laboratory.

Furthermore, the probability of reusing and recycling the COS NPs for several runs on the model reaction was also studied. The results displayed in Fig. 5 showed that COS NPs could be reused and recycled for six runs without any significant decrease in the catalytic activity (yields in the range of 98-88%). After completion of the reaction, COS NPs were separated from the reaction mixture, washed with ethanol and dried at 100 °C for 1 h, and the recycling studies were then performed utilizing the separated catalyst in subsequent reactions (model reaction). As can be seen in Fig. 1c, the shapes and intensities of the characteristic peaks were well preserved, and no significant changes occurred in the structure of the nanocatalyst after repeated cycles of the reaction. Due to catalyst pollution with reagents, a slight reduction in the catalytic activity of recycled COS NPs was observed.



Fig. 5 Synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione in the presence of reused COS NPs

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	Refs.
1	H_2SO_4	H ₂ O	Reflux	2	84	[14]
2	$\text{TiO}_2/\text{SO}_4^{2-}$	-	Room temperature	24	84	[25]
3	PMA/SiO ₂	CH ₃ CN	Reflux	4	95	[27]
4	SbCl ₃ /SiO ₂	-	120	50 min	93	[29]
5	Fe ₃ O ₄ @SiO ₂ -imid-H ₃ PMo ₁₂ O ₄₀ nanoparticles	EtOH	Reflux	1.5	94	[32]
6	Dowex-50w	-	100	3	87	[33]
7	Amberlyst-15	CH ₃ CN	Reflux	5	92	[34]
8	COS NPs	_	90	30 min	98	Present study

 Table 4
 Comparison between the efficiency of COS NPs and some other catalysts for the preparation of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione

To attain deeper insight into the efficiency of COS NPs for the synthesis of 1,8dioxo-octahydroxanthene derivatives, an evaluation was performed by comparing its performance with other reported methods in the literature (Table 4). These comparison experiments were based on the model reaction. As Table 4 displays (the data reported in the literature for the synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione), COS NPs have improved the synthesis of the corresponding products in different terms (not only afforded the products in excellent yield in very short reaction times and mild conditions, but also avoided the problems associated with the catalyst cost, difficult preparation and handling, tedious workup, safety and pollution) surprisingly.

Conclusion

In this research, COS NPs were designed and characterized by using X-ray fluorescence analysis (XRF), Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), scanning electron microscopy equipped with an energy-dispersive spectrometry (SEM-EDS) and transmission electron microscopy (TEM). Catalytic application of the new described catalyst was studied for the first time in the synthesis of 1,8-dioxo-octahydroxanthenes via the one-pot condensation reaction of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with various aldehydes under solvent-free conditions. As solvent-free reactions are an efficient technique instead of using harmful organic solvents, the present method offers simplicity of product isolation, a remarkable decrease in reaction time, increased reaction yield, fitting the green chemistry protocol as well as reusability of the catalyst, which can be reused for six cycles without a significant loss of activity.

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