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METAL-UREA COMPLEXES AS PRIMARY PRECURSORS TO GENERATE VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3 AND TeO_2 OXIDES IN THE NANOSCALE RANGE BY THERMAL DECOMPOSITION ROUTE

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ABSTRACT. Six metal chlorides of vanadium, zirconium, niobium, tantalum, gallium, and tellurium (i.e., VCl_3, $ZrOCl_2{\cdot}8H_2O$, $NbCl_5$, $TaCl_5$, $GaCl_3$, and $TeCl_4$) were reacted with urea (referred to as U) in aqueous media at ~ 50 ºC. The resulting metal-urea complexes were characterized using CHN elemental analyses, infrared (IR) spectroscopy, and thermogravimetry. After the synthesized metal-urea complexes were characterized, their ability to form stable metal oxides was examined. The vanadium(IV) oxide; VO_2, zirconium(IV) oxide; ZrO_2, niobium(IV) oxide, NbO_2, tantalum(IV) oxide; TaO_2, gallium(III) oxide; Ga_2O_3, and tellurium(IV) oxide; TeO_2, were generated by the thermal decomposition route of the synthesized metal-urea complexes at low temperature 600 °C in static air atmosphere. The transmission electron microscopy (TEM) revealed that the oxides contain uniform spherical nanoparticles.

KEY WORDS: Metal chloride, Metal-urea complex, Urea, FTIR, TEM

INTRODUCTION

Metal oxides are an essential class of compounds due to their wide applications in several areas, such as physics, chemistry, biology, and material science. Various metal oxide features enable wide applications in manufacturing precision circuits, sensors, piezoelectric devices, fuel cells, anti-corrosion coatings, and catalysts [1-4]. Most computer chips and active parts in the semiconductor industry contain metal oxides [5]. Furthermore, metal oxides are also used to control environmental pollution. Catalysts comprising metal oxides are used to remove several types of pollutants, such as sulfur oxides, nitrogen oxides, and carbon dioxide generated from the combustion of fossil fuels [6]. Metal oxides with semiconductor behaviors can be used as highly efficient photocatalysts to remove hazardous and toxic materials [7]. The photocatalytic properties of metal oxides in visible light enable these oxides to degrade pharmaceutical drugs, pesticides, and textile dyes [8]. Several metal oxides, such as TiO_2, SnO_2, In_2O_3, and ZnO, exhibit photocatalytic solid properties.

Complexation of metal salts (i.e., chlorides, acetates, nitrates) with the simple organic compound urea (NH_2CONH_2) can generate well-defined morphology and nanostructured metal oxides. This work investigated the ability of several metal-urea complexes of vanadium, zirconium, niobium, tantalum, gallium, and tellurium to produce nanostructured and pure metal oxides.

The work focused on the following objectives: (i) Synthesizing six metal-urea complexes *via* the urea (U) chemical reaction with the corresponding metal chloride with a 6:1 urea to metal chloride in a 1:1 (H_2O to MeOH) solvent. (ii) Characterizing synthesized metal-urea complexes using various spectrophotometers (Infrared; IR), CHN elemental analysis, and thermal measurements. (iii) Thermal decomposing of synthesized metal-urea complexes at 600 °C for 3 hours to obtain the nanostructured metal oxides. (iv) Examining the thermal properties of

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*Corresponding authors. E-mail: anaglah@ksu.edu.sa synthesized metal oxides using thermogravimetry and observing their microstructure using transmission electron microscopy (TEM).

EXPERIMENTAL

Chemicals

All metal chlorides used in this study were analytical-grade and purchased from the Sigma-Aldrich Chemical Company (St Louis, MO, USA) at the highest purity. These chlorides were: i) vanadium(III) chloride (VCl_3; molecular weight 157.30 g/mol; purity 97.0%), ii) zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$; molecular weight 322.25 g/mol; purity 98.0%), iii) niobium(V) chloride ($NbCl_5$; molecular weight 270.17 g/mol; purity 99.0%), iv) tantalum(V) chloride ($TaCl_5$; molecular weight 358.21 g/mol; purity $\geq$ 99.99%), v) tellurium(IV) chloride ($TeCl_4$; molecular weight 269.41 g/mol; purity 99.0%), and vi) gallium(III) chloride ($GaCl_3$; molecular weight 176.08 g/mol; purity $\geq$ 99.99%). Fluka Chemical Company (Seelze, Germany) provided urea (NH_2CONH_2; 60 g/mol) with purity of $\geq$ 99.5%. Solvents used for the preparation were methanol (MeOH), which was acquired from Merck Chemical Company (KGaA, Germany), and water, which is a type of deionized water (DI) generated using a Milli-Q system (Millipore Co., Bedford, MA, USA).

Instrumentation techniques

Spectra of Fourier-Transform Infrared (FT-IR) and the thermogravimetric analysis (TGA) of the synthesized solid metal-urea complexes and the oxides were collected by a Bruker ALPHA compact FT-IR spectrophotometer (Bruker Optic GmbH, Germany), and a Shimadzu TG/DTG-50H thermal analyzer, respectively. All FT-IR data were scanned in the wavenumber range of 4000 to 400 cm^{-1}, whereas the TG thermograms were collected in an air atmosphere from 25 to 1000 °C. Collecting the carbon, nitrogen, and hydrogen contents in (%) was performed using a Perkin-Elmer 2400 series II CHN Microanalyzer (Perkin-Elmer Inc, Waltham, MA, USA), whereas collecting the metal (V, Zr, Nb, Ta, Ga, and Te) and water contents in (%) was performed using gravimetric analysis. The transmission electron microscope (TEM) photos were captured using a JEM-2010 JEOL TEM instrument (Japan) operating with an electron accelerating voltage of 200 kV.

Synthesis

Synthesis of the metal-urea complexes

Metal-urea complexes were synthesized as follows [9-13]: (i) Six beakers containing 1.0 mmol of each metal chloride salt were dissolved in 25 mL of MeOH solvent (VCl_3, $ZrOCl_2 \cdot 8H_2O$, $NbCl_5$, $TaCl_5$, $GaCl_3$, and $TeCl_4$). Gently heat was used to complete the dissolving of the metal salts. (ii) 6.0 mmol of urea dissolved in DI water was added to each beaker. No residues were observed after the addition of urea aqueous solution. (iii) The individual mixture of urea-VCl_3, urea-$ZrOCl_2 \cdot 8H_2O$, urea-$NbCl_5$, urea-$TaCl_5$, urea-$GaCl_3$, and urea-$TeCl_4$ were stirred at 50 °C for 24 hours. By the end of this step, white precipitates were obtained in each beaker. (iv) The obtained precipitates were separated by filtration and washing the collected products thoroughly with hot DI water.

Synthesis of the metal oxides

The VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3, and TeO_2 oxides in the nanoscale range were generated by the thermal decomposition of the corresponding primary precursors at 600 °C for 3 hours in ambient air in an electric furnace. After grinding the resulting oxides into a fine powder with particle sizes of approximately ~ 5-6 mm, they were subjected to FT-IR and TEM analyses [9-13].

RESULTS AND DISCUSSION

Synthesis of the metal-urea complexes

Reaction

The metal-urea complexes of urea-VCl_3, urea-$ZrOCl_2{\cdot}8H_2O$, urea-$NbCl_5$, urea-$TaCl_5$, urea-$GaCl_3$, and urea-$TeCl_4$ were generated by the co-precipitation of urea with the corresponding metal chloride under the following reaction conditions: i) Starting reagent state: liquid-liquid, ii) Temperature: 50 °C, iii) Time: ~24 h, iv) Stoichiometry: 4:1 (urea to $ZrOCl_2{\cdot}8H_2O$), and 6:1 (urea to other metal chlorides), and v) Solvent: (H_2O to MeOH) 1:1. Based on these conditions the metal chlorides VCl_3, $ZrOCl_2{\cdot}8H_2O$, $NbCl_5$, $TaCl_5$, $GaCl_3$, and $TeCl_4$ formed the following metal-urea complexes $[VU_6]Cl_3$, $[ZrOU_4]Cl_2$, $[NbU_6]Cl_5$, $[TaU_6]Cl_5$, $[GaU_6]Cl_3$, and $[TeU_6]Cl_4$, respectively, (where U is urea) by the following chemical reactions:

$$VCl_3 + 6U \rightarrow [VU_6]Cl_3 \quad (1)$$

$$ZrOCl_2{\cdot}8H_2O + 4U \rightarrow [ZrOU_4]Cl_2 + 8H_2O \quad (2)$$

$$NbCl_5 + 6U \rightarrow [NbU_6]Cl_5 \quad (3)$$

$$TaCl_5 + 6U \rightarrow [TaU_6]Cl_5 \quad (4)$$

$$GaCl_3 + 6U \rightarrow [GaU_6]Cl_3 \quad (5)$$

$$TeCl_4 + 6U \rightarrow [TeU_6]Cl_4 \quad (6)$$

The synthesized metal-urea complexes: $[VU_6]Cl_3$, $[ZrOU_4]Cl_2$, $[NbU_6]Cl_5$, $[TaU_6]Cl_5$, $[GaU_6]Cl_3$, and $[TeU_6]Cl_4$ were referred to as A, B, C, D, E, and F, respectively.

Compositions

Microanalysis of the synthesized metal-urea complexes of carbon, nitrogen, and hydrogen percentages was conducted using elemental analysis. The metal contents in (%) were performed using gravimetric analysis. The compositions of the metal-urea complexes are described below:

Complex A. $C_6H_{24}N_{12}O_6VCl_3$ (517.29 g/mol) microanalytical data (%): found (calculated) for C, 13.70 (13.92); H, 4.82 (4.64); N, 32.29 (32.47); V, 10.00 (9.85).

Complex B. $C_4H_{16}N_8O_5ZrCl_2$ (418.12 g/mol) microanalytical data (%): found (calculated) for C, 11.70 (11.48); H, 4.08 (3.83); N, 26.93 (26.79); Zr, 22.07 (21.82).

Complex C. $C_6H_{24}N_{12}O_6NbCl_5$ (630.16 g/mol) microanalytical data (%): found (calculated) for C, 11.58 (11.43); H, 4.00 (3.81); N, 26.79 (26.66); Nb, 14.95 (14.74).

Complex D. $C_6H_{24}N_{12}O_6TaCl_5$ (718.20 g/mol) microanalytical data (%): found (calculated) for C, 10.26 (10.03); H, 3.46 (3.34); N, 23.20 (23.39); Ta, 24.93 (25.19).

Complex E. $C_6H_{24}N_{12}O_6GaCl_3$ (536.07 g/mol) microanalytical data (%): found (calculated) for C, 13.26 (13.43); H, 4.60 (4.48); N, 31.11 (31.34); Ga, 12.88 (13.00).

Complex F. $C_6H_{24}N_{12}O_6TeCl_4$ (629.40 g/mol) microanalytical data (%): found (calculated) for C, 11.26 (11.44); H, 3.65 (3.81); N, 26.50 (26.69); Te, 20.50 (20.27).

These compositions indicate that the reaction stoichiometry is 4:1 (urea to $ZrOCl_2{\cdot}8H_2O$) and 6:1 (urea to other metal chlorides) and complies with the suggested general compositions for the synthesized metal-urea complexes. Figure 1 presents the proposed chemical structure of the manufactured metal-urea complexes.

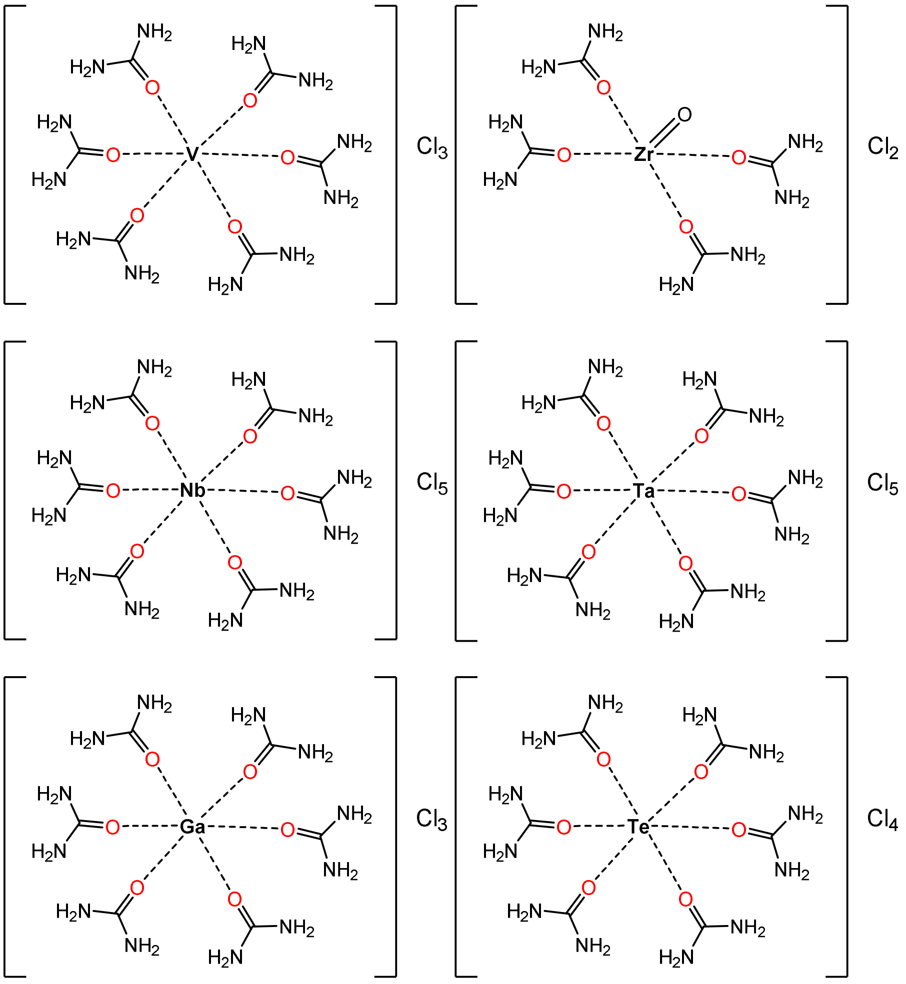

Figure 1. Proposed chemical structure of the manufactured metal-urea complexes.

FT-IR spectra

Figure 2 contains the FT-IR spectra of the manufactured metal-urea complexes (A-F). Free urea molecule (NH_2CONH_2) has two functional groups: $–NH_2$ and $–C=O$. The two $–NH_2$ groups in the urea molecule exhibited four characteristic vibrational modes. These are $\nu(–NH_2)$, $\delta_{def}(–NH_2)$,

$\delta_{twist}(-NH_2)$, and $\delta_{rock}(-NH_2)$. Among these vibrational modes, the band generated from the $\nu(-NH_2)$ vibration is broad with medium-strong intensity. In the FT-IR spectra of manufactured metal-urea complexes, the bands resonated in the region 3320-3310 cm^{-1} referred to as the $\nu(-NH_2)$ vibrations, bands located in the region 1445-1400 cm^{-1} caused by the $\delta_{def}(-NH_2)$ vibrations, bands observed from 960 to 870 cm^{-1} generated from the $\delta_{twist}(-NH_2)$ vibrations, whereas bands observed from 610 to 580 cm^{-1} arose from the $\delta_{rock}(-NH_2)$ vibrations. In the metal-urea complexes, the bands located in the region 1560-1545 cm^{-1} result from the $\nu(-C{=}O)$ vibrations. The bands observed in the region 520-485 cm^{-1} could be attributed to $\nu(M-O)$ vibrations [14].

Thermogravimetry

Figure 3 illustrates the thermograms of the manufactured metal-urea complexes collected over the 25-800 °C temperature range under a nitrogen atmosphere. All the complexes were decomposed in two-step decomposition patterns except Complex A, which disintegrated in three-stage degradation steps. All complexes started decomposing at 40-50 °C and completely decomposed at 450-650 °C. In the first decomposition step, the lost molecules from the degradation of A, B, C, D, E, and F complexes were ($3NH_3 + 3N_2$), ($2H_2O + 2N_2$), ($4CO + 3.5N_2$), ($4CO + 3.5N_2$), ($3N_2 + 0.5H_2O$), and ($4N_2$), respectively. The corresponding molecules released in the second decomposition step were ($3NH_4Cl$), ($2NH_4Cl + N_2O + C_2H_2 + H_2$), ($5NH_4Cl + 2H_2$), ($5NH_4Cl + C_2H_2 + H_2$), ($3NH_4Cl + 4CO + 3NH_3 + H_2$), and ($4NH_4Cl + 4CO + 4H_2$), respectively. The third step in Complex A occurred from 380-650 °C and was associated with losing 4CO and $1.5H_2$ molecules. The decompositions of metal-urea complexes were almost completed, leaving VO_2 for Complex A, ZrO_2 for Complex B, NbO_2 for Complex C, TaO_2 for Complex D, Ga_2O_3 for Complex E, and TeO_2 for Complex F as the final decomposition residues. All these oxides were contaminated with some residual carbons.

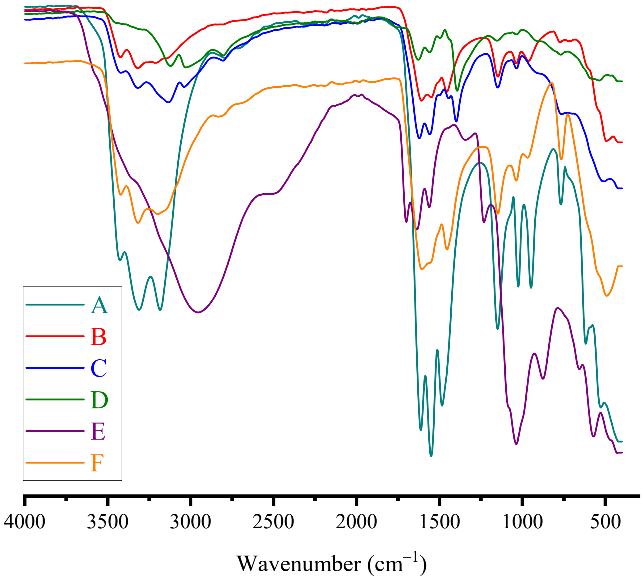

Figure 2. The IR spectra of the manufactured metal-urea complexes (A-F).

Synthesis of the metal oxides

Reaction

The VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3, and TeO_2 oxides were generated by the thermal decomposition of the corresponding metal-urea complexes at 600 °C for 3 hours in ambient air in an electric furnace through the following chemical reactions:

$$[V(NH_2CONH_2)_6]Cl_3 \rightarrow VO_2 + 3NH_4Cl + 4CO + C_2H_2 + 3NH_3 + 3N_2 + 0.5H_2 \quad (7)$$

$$[ZrO(NH_2CONH_2)_4]Cl_2 \rightarrow ZrO_2 + 2NH_4Cl + 2C_2H_2 + 2H_2O + N_2O + 2N_2 \quad (8)$$

$$[Nb(NH_2CONH_2)_6]Cl_5 \rightarrow NbO_2 + 5NH_4Cl + 4CO + C_2H_2 + 3.5N_2 + H_2 \quad (9)$$

$$[Ta(NH_2CONH_2)_6]Cl_5 \rightarrow TaO_2 + 5NH_4Cl + 4CO + C_2H_2 + 3.5N_2 + H_2 \quad (10)$$

$$2[Ga(NH_2CONH_2)_6]Cl_3 \rightarrow Ga_2O_3 + 6NH_4Cl + 8CO + 2C_2H_2 + 6NH_3 + 6N_2 + H_2O \quad (11)$$

$$[Te(NH_2CONH_2)_6]Cl_4 \rightarrow TeO_2 + 4NH_4Cl + 4CO + C_2H_2 + 4N_2 + 3H_2 \quad (12)$$

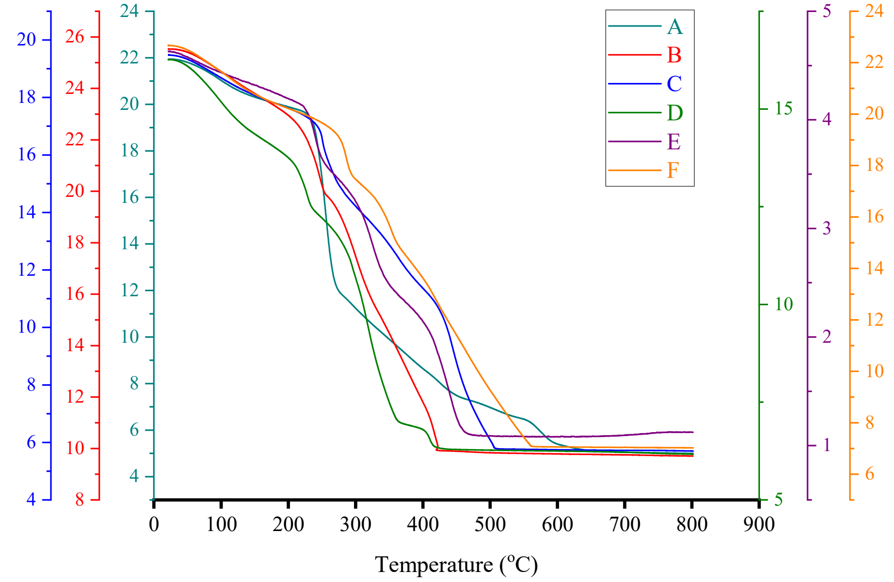

Figure 3. Thermograms of the manufactured metal-urea complexes (A-F).

FT-IR spectra

Figure 4 presents the FT-IR spectra of the manufactured metal oxides: VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3 and TeO_2. In the FT-IR spectra of NbO_2, TaO_2, Ga_2O_3, and TeO_2 oxides, the characteristic absorption bands resulted from the vibrations of –C=O and $–NH_2$ bonds: ν(C=O), $\delta_{twist}(NH_2)$, $\nu(NH_2)$, $\delta_{rock}(NH_2)$, and $\delta_{def}(NH_2)$, were no longer observed. A clear band was observed in the IR spectra of NbO_2, TaO_2, Ga_2O_3, and TeO_2 oxides at 533, 525, 460, and 442 cm^{-1}, respectively, which was likely due to the stretching vibration of the M–O (M: Nb, Ta, Ga, or Te). The IR profiles of VO_2 and ZrO_2 oxides contain a group of bands at 3340-3350, 1634-1638, and 1400-1427 cm^{-1}; these bands can be assigned to the vibrations of ν(O–H) of physically molecular water adsorbed on the oxide's surface [15]. The IR spectra of VO_2 and ZrO_2 also displayed absorption bands located at 580 and 593 cm^{-1}, which could be revered to the ν(V–O) and ν(Zr–O) vibrations, respectively [16, 17].

TEM photos

Four of the manufactured metal oxides (VO_2, ZrO_2, Ga_2O_3, and TaO_2) were scanned by a JEM-2010 JEOL TEM instrument to capture their TEM photos, and the obtained photos were presented in Figure 5. The TEM photos of VO_2, Ga_2O_3, and TaO_2 oxides revealed that most of their particles were spherical-shaped, whereas most of TaO_2 oxide's particles were mixed elliptical and spherical-shaped. The TaO_2 oxide's particles tended to aggregate into small clusters. The captured TEM photos indicated that most of the particles of the VO_2, ZrO_2, Ga_2O_3, and TaO_2 oxides exhibited diameters of 6-10 nm, 50-100 nm, 7-10 nm, and 40-90 nm, respectively. The TEM analysis generally revealed that the manufactured metal oxides contain uniform spherical nanoparticles.

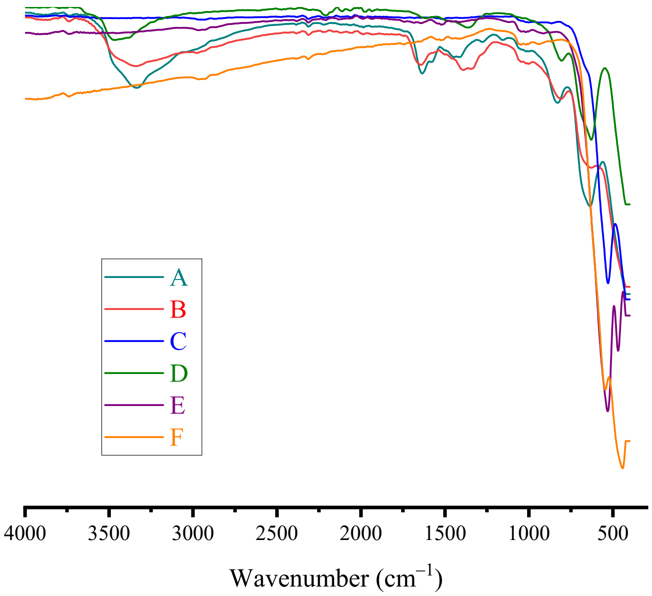

Figure 4. The IR spectra of the manufactured metal oxides: A) VO_2, B) ZrO_2, C) NbO_2, D) TaO_2, E) Ga_2O_3, and F) TeO_2.

TEM analysis

The TEM analysis revealed that the VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3, and TeO_2 oxides are nanostructures and contain uniform spherical nanoparticles (Figure 5).

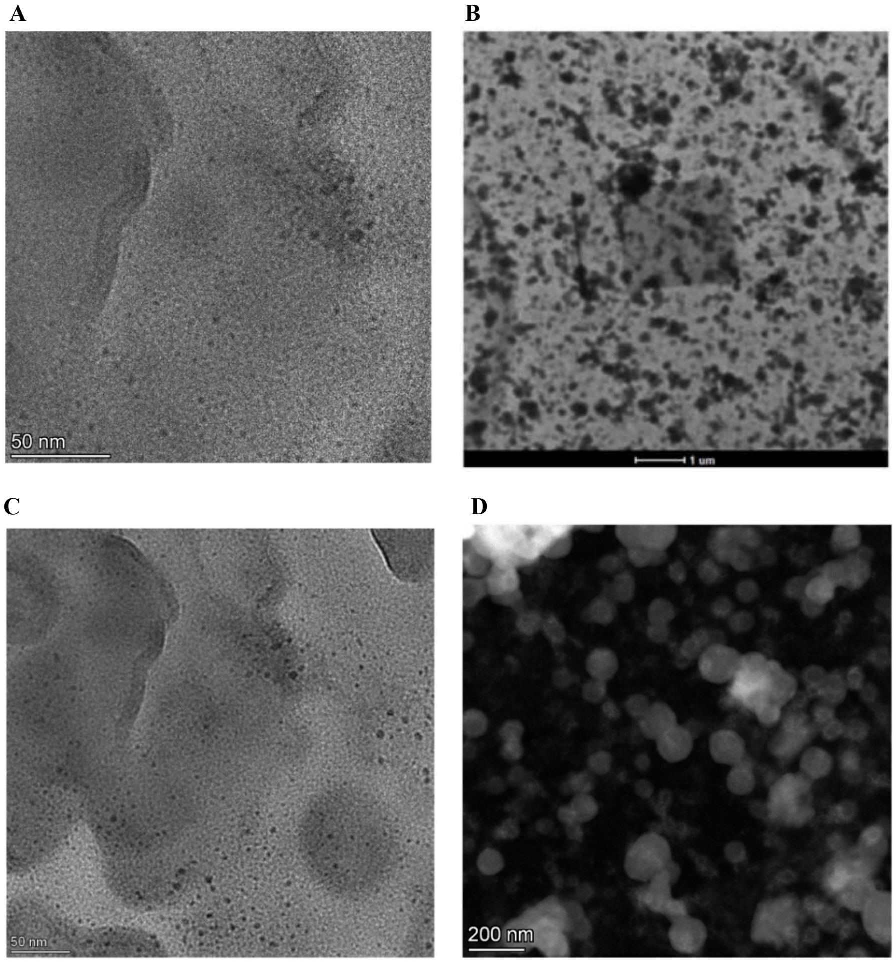

Figure 5. The TEM photos of the manufactured metal oxides: **A**) VO_2, **B**) ZrO_2, **C**) Ga_2O_3, and **D**) TaO_2.

CONCLUSIONS

The rapid increase of the global population, the fast growth of human society, and the rapid progress and development of economic and industrial technology are the three major factors that led to much environmental pollution. One of the important methods for removing the most important environmental contaminants is adsorption over porous materials, such as metal oxides. In this work, a simple and environment-friendly method was proposed for the manufacturing of six metal oxides (VO_2, ZrO_2, NbO_2, TaO_2, Ga_2O_3, and TeO_2) based on the chemical reaction between metal chlorides and urea in aqueous media at ~ 50 ºC. This reaction generated metal-urea complexes ($[VU_6]Cl_3$, $[ZrOU_4]Cl_2$, $[NbU_6]Cl_5$, $[TaU_6]Cl_5$, $[GaU_6]Cl_3$, and $[TeU_6]Cl_4$). After the manufactured metal-urea complexes were characterized, these complexes were calcined in an electrical furnace for three hours at 600°C under ambient air conditions. In future research, we will assess the ability of the manufactured metal oxides to be catalysts for the degradation of several types of pollutants.

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