NOVEL COBALT(II) AND TITANIUM(IV) CONTAINING PHOTOCATALYST DERIVED FROM PHLOROGLUCINOL CARBOXYLIC ACID

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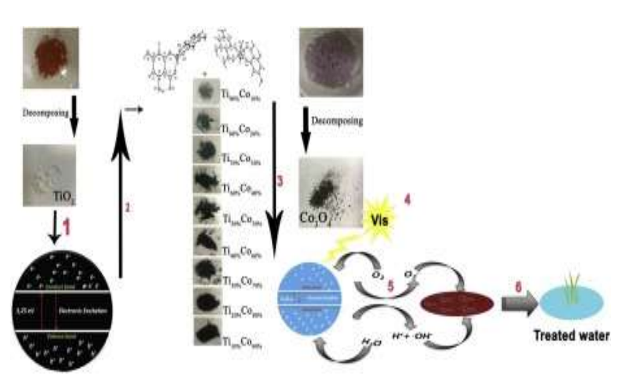
Introduction

Titanium dioxide (TiO2) as a well-known compound is used in different various application such as solar cells (Ashikawa et al., 2018), environmental remediation (Rathi et al., 2018), sensing (Two-dimensional transition metal dichalcogenides and metal oxide hybrids for gas sensing, 2018; Ghoneim et al., 2018), coating, pigment, addition to cement and tiles(Ghoneim et al., 2018). Furthermore, the photocatalytic application of titanium oxide nanoparticles made it more applicable due to being inexpensive, non-toxic, and easy to handle (Chen et al., 2012). The active surface of this compound can make a proper situation to simplify interfacial photochemical reaction. Indeed, the particular energy bandgap of titanium oxide nanoparticles (3.5 eV) makes it powerful to work under UV light, which creates electrons and holes and consequently reduces the concentration of harmful organic substances(Gandolfo et al., 2018; Huang et al., 2018; Li et al., 2019). Rutile and anatase illustrate more valuable phases for photocatalytic reaction due to having reactive crystallographic planes (Allard et al., 2018; Shahiduzzaman et al., 2018; Ceballos-Chuc et al., 2018). However, it is difficult to say which parameters can affect more due to lacking enough knowledge about various parameters such as morphology, surface structure, surface chemistry, and the properties of the target molecules. So as a powerful factor, the energy band gap of photocatalysts can be count as a suitable criterion, which illustrates how the result is different by increasing and decreasing of this parameter (Barawi et al., 2019; Wu et al., 2019; Ruf et al., 2018; Mascaretti et al., 2019).



Key Findings

Titanium oxide nanoparticlesCobalt nanoporous nanoparticlesPhloroglucinol carboxylic acidPhotocatalystWater treatment

materials and Methods

hemicals

Liquid Titanium (IV) butoxide (TBT, 97 %, Sigma-Aldrich), phloroglucinol carboxylic acid (97 %, Sigma-Aldrich), n-butanol (997%, Ekos.1), Cobalt (II) chloride hexahydrate (CoCl2.6H2O, 98 %, Sigma-Aldrich), Bromophenol blue (99 %, Sigma-Aldrich).

2- ynthesis of titanium (IV) and cobalt (II) complexes with 2,4,6- trihydroxybenzoic acid

The complex compound of titanium with phloroglucinol carboxylic acid was isolated at a room temperature. Titanium (IV) butoxide (0.5 mol) was dissolved in n-butanol, and then the solution was added to 1 mol of phloroglucinol carboxylic acid solution in the same solvent. Immediately after addition of metal salt solution, the colour changed from colourless to dark orange. The solvent was slowly evaporated under room temperature. No recrystallization was carried out due to obtaining a pure complex.

The procedure for the isolation of the complex compound of cobalt was the same as for the titanium complex. The colour was changed to very dark blue from colourless.

3- Isolation of titanium oxide (Anatase, Rutile, and Anatase-Rutile mixture (AR)) and cobalt oxide nanoparticles

materials and Methods

Organometallic complex compounds were used as precursors for isolation of titanium and cobalt oxide nanoparticles. The pure and dried complexes were thermally decomposed. The sample (complex compound) was placed into a closed aluminum crucible and heated with the measurement program in the temperature range of 28–900 °C. Different phases of anatase and rutile were obtained at less than 400 °C and 600 °C respectively. Anatase-Rutile mixture (AR) phase was obtained at 500 °C after three and a half hours. The cobalt oxide nanoparticles were obtained through the same process at around 550 °C. (To have a unique nanoparticle, the muffle was set to increase 10 every 5 min).

4- Characterizations

X-ray diffraction (XRD) studies of the samples (both complexes and nanoparticles) were performed by a DRON-7 instrument using Cu Kα irradiation (λ =1.5406 Å). The average crystallite sizes of the nanoparticles and the lattice strain, which characterizes the relative change in the inter-planar distance, were estimated. The phase composition was determined from diffraction patterns recorded in a range of 2θ angles between 10 and 80 deg. with a scanning speed of 20/min. The average size of nanocrystalites for TiO2 and Co3O4 was calculated based on the Scherer equation with respect to reflexes at 2θ = 25,320 (Anatase), 2θ = 275 (Rutile). Analysis of the crystal structure of titanium was carried out using a JCPDS database. Spectroscopy analysis (UV–vis) of nanoparticles was carried out using Varian UV–vis scanning UV–vis diffuse reflectance spectrometer.

The FT-IR spectra from 400 to 4000 cm−1 of the prepared samples were recorded at room temperature by an FT 801 spectrophotometer. The metal analysis of the complexes was carried out by the method of atomic emission spectroscopy with inductively coupled plasma on the Varian 735-OES tool. The CHN analysis was performed by micro-methods.

The 1H NMR spectra were obtained by Jeol JNM ECA 600 (Japan) at room temperature using DMSO as a reference. Excitation and emission spectra of the nanoparticles were recorded by Shimadzu spectrofluoremeter with the use of optical filter 370 nm. Quantum-chemical modeling of the electronic structure of molecules and complexes was carried out within the framework of the density functional theory (DFT) approximation using the hybrid three-parameter Beke function(Becke (1993)) with the correlation functional Li-Yang-Parra (Lee et al., 1988)(B3LYP) (Stephens et al., 1994) and the basic set def2-SV (P) (Schaefer and Huber, 1994). Complete optimization of the geometry was carried out without restrictions on the type of symmetry. To analyze the electronic structure of the ground state of ligand molecules and complexes, the natural binding orbitals (NBO) approach used. The calculations were carried out with complete optimization of geometric parameters. The optimized configurations found were tested for compliance with critical conditions. All calculations were performed using the Firefly 7.1.G software.

The morphology and composition of synthesized oxides was investigated by scanning electron microscopy (SEM) and electron microprobe analysis (EMPA) (EDX detector Oxford INCA350) on Zeiss-EVO-40EP microscope. Synchronous thermal analysis (simultaneous recording of TG and DSC curves) was performed on a Netzsch STA 449 F3 Jupiter installation in air. The irradiation was carried out by halogen lamp as the visible light source and it was set at 410 W.

Results

Complex compounds of titanium (IV) and cobalt (II)

1.IR and elemental analysis

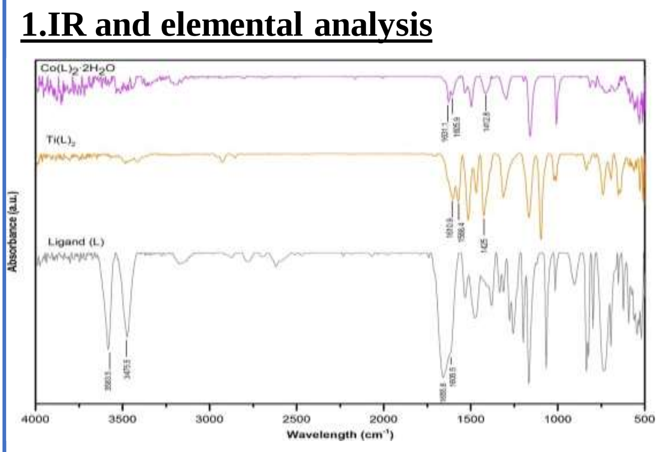


Fig. 1. FT IR of the ligand and complex compounds.

2.XRD pattern

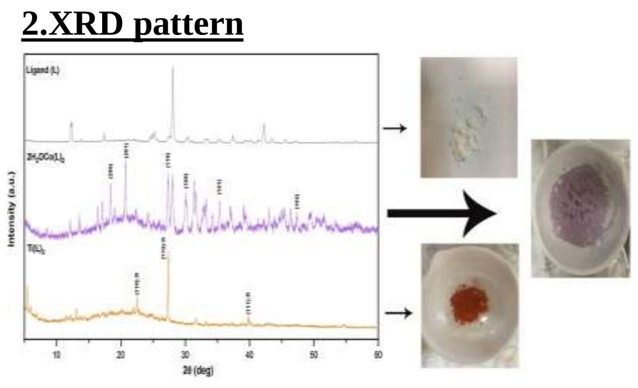


Fig. 2. XRD spectra of phloroglucinol carboxylic acid as the ligand (L) and its Ti(IV) and Co(II) complexes.

3. H NMR analysis

1H NMR spectra of phloroglucinol carboxylic acid as a ligand and its complexes

with titanium (IV) and cobalt (II) are presented on the Fig. 3.

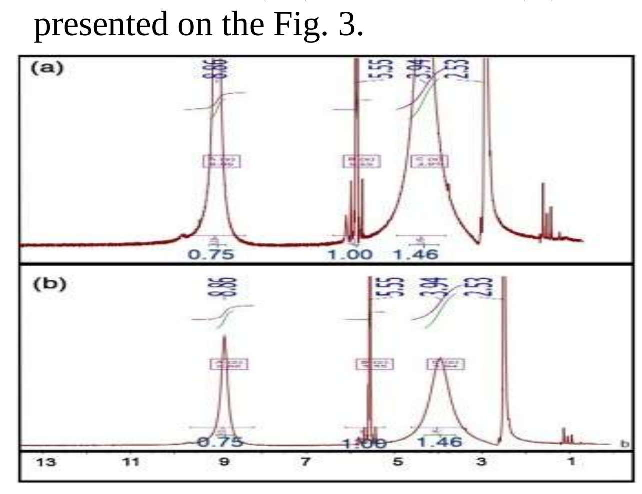


Fig. 3. ^{1}H NMR spectra of phloroglucinol carboxylic acid as (a) the ligand (L) and (b) its Co (II)

4. Thermal decomposition analysis

The thermal decomposition was used to investigate the procedure of converting complex compounds to model oxide nanoparticles. The thermal decomposition of TiL_2 complex is presented in Fig. 4a.

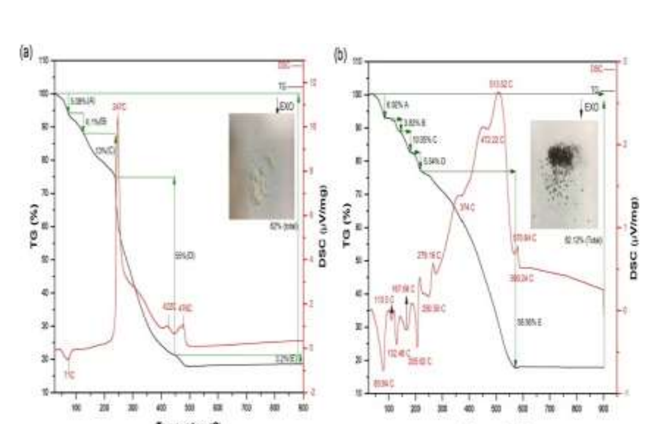


Fig. 4. Thermal decomposition of (a) TiL_2 and Fig. 4. Thermal decomposition of (a) TiL_2 and (b) CoL_2 $2H_2O$.

5. Theoretical modeling

The molecule of phloroglucinol carboxylic acid can exist both in gaseous and

condensed forms or solutions in the form of a tautomer with the maximal numbers of intermolecular H bonds (Fig. 5).

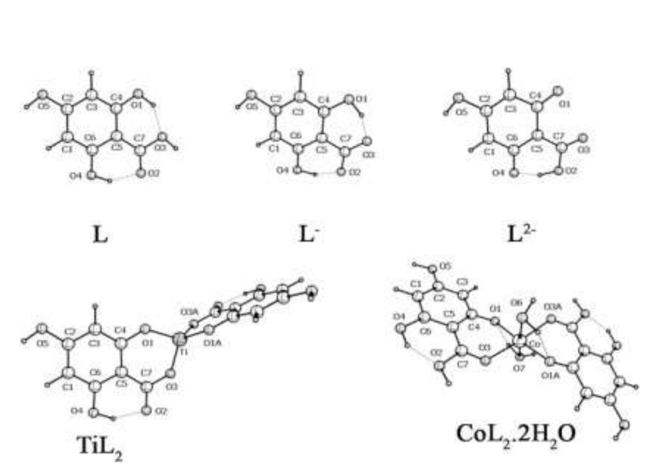


Fig. 5. The optimized structures of phloroglucinol carboxylic acid (L), its mono and dianionic forms and metal complexes.

Results

6. Nano particles isolation and characterization

The thermal analysis of Ti and Co complexes provides information about the optimum temperature to isolate the oxide nanoparticles by the thermal decomposition of the complex compounds. According to the low temperatures of decomposition of TiL_2 and CoL_2 $2H_2O$ Fig. 4,5)

7. XRD pattern

According to the result, the XRD pattern of the cobalt oxide nanoparticle was matched with JCPDS card No.43–1003 of Co3O4 of the cubic symmetry. The outstanding diffraction peak at 36.8 (311) determined excellent crystalline quality of cobalt oxide nanostructures and the obtained results are fully supporting to FESEM study.

Based on the result of Scherrer particle size calculations, the size of titanium oxide nanoparticles grow by increasing temperature. The size of anatase phase was around 9 nm (9.1), AR composition was around 13 nm (13.16), and finally, the size of rutile phase found around 32 nm (32.12). Furthermore, cobalt oxide nanoparticle had a size was around 5 nm (4.65).

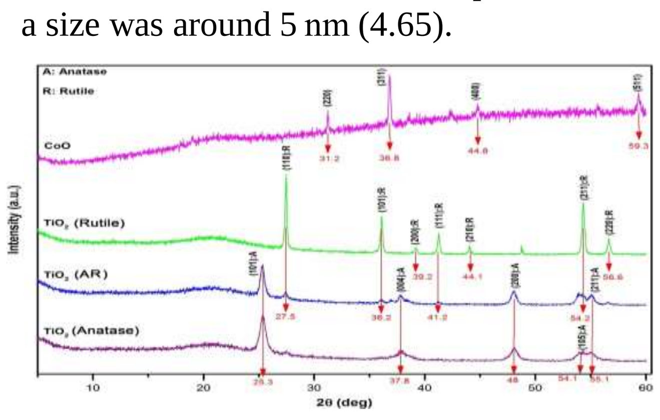


Fig. 6. XRD analysis of the products of thermal decomposition of TiL_2 and CoL_2 $2H_2O$.

8.IR spectroscopy

IR spectra of the isolated nanoparticles are shown on the Fig. 7. Titanium oxide nanoparticles in different phases showed different types of the spectra. Due to the same compounds and method used for the synthesis, the only parameter, which could affect on the result is temperature. As it is observed, at increasing the temperature, the signals related to the organic substance and stretching of water molecules adsorbed on the surface of titanium oxide between 800−3500 cm−1 and smoother and tend to disappear.

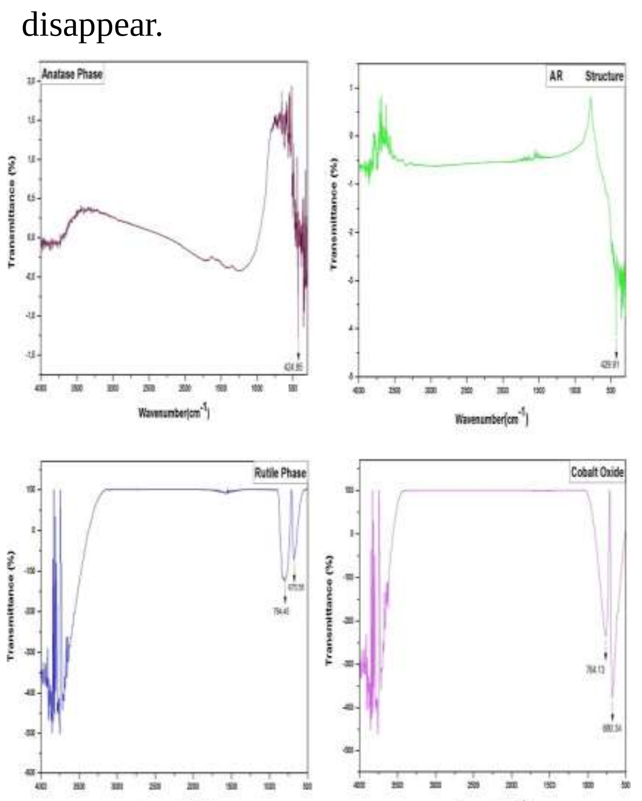


Fig. 7. FT IR spectra of the oxide phases after thermal decomposition of TiL_2 and CoL_2 $2H_2O$.

9.Photoluminescence characterization

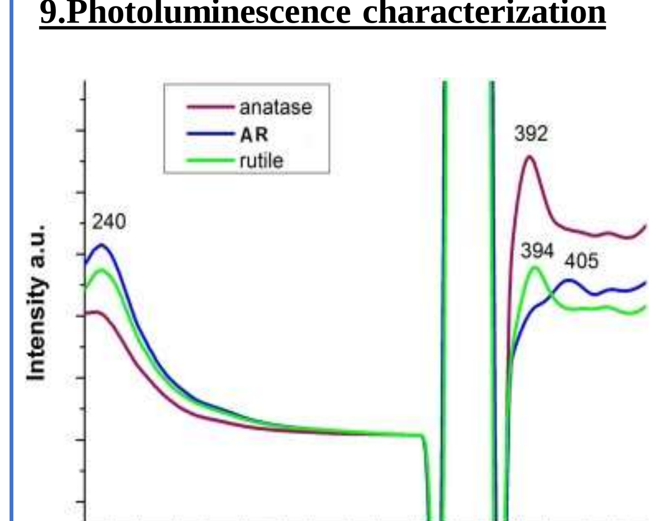


Fig. 8. Excitation spectra TiO2 nanoparticles obtained at 370 nm with the use of Xe lamp.

Conclusions

tanium oxide in three different phases/structures (Anatase, Rutile, and AR), nanoporous cobalt oxide, and nine titanium-cobalt mixtures in different ratios were synthesized through the complex compounds of phloroglucinol carboxylic acid.Titanium oxide in three different phases/structures (Anatase, Rutile, and AR), nanoporous cobalt oxide, and nine titanium-cobalt mixtures in different ratios were synthesized through the complex compounds of phloroglucinol carboxylic acid. The obtained complexes illustrated proper purity and stability. In addition, nanoparticles obtained through thermal decomposition of the complexes were highly crystallite and mono-dispersed in size, which obtained at low temperature. Based on the XRD analysis of the bimetallic nanoparticles, anatase and rutile peaks are observable in all the XRD patterns, the same as CoTiO3. Peaks related to Co3O4 also could be seen at thermal decomposition of the mixtures with the Ti(L)2 ratio from 10 to 50 %.

Respect to the UV–vis light, the energy bandgap of the pure samples was as the following; anatase > cobalt oxide > AR > rutile. This indicated that although all of them are able to absorb UV light, rutile is more benefit. After modifying titanium oxide by cobalt, the obtained nanoparticles illustrated an ability to absorb visible light, especially the sample with the initial composition TiL2 to CoL2.2H2O as 80 to 20 %. So the ratio of 8 to 2 for titanium and cobalt, respectively, is recommended for absorption visible light, and Co(20 %)Ti(80 %) showed the ability to degrade bromophenol blue to 82 % after 120 min.

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