CUORE (the artificial leaf): Cu_2O nanoparticles for energy recovery

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Abstract

Giacomo Ciamician announced the dream of artificial photosynthesis during the International Congress of Applied Chemistry (New York, 1912). The chemical process consists of the direct conversion of solar energy into chemical energy through the photoinduced synthesis of low-energy chemical species (water and carbon dioxide) in high-energy chemical species (hydrogen and other fuels). Ciamician, fascinated by the ability of plants to use sunlight, imagined the day when humanity would steal the secret of photosynthesis and exploit it to produce fuels. Recent studies have shown that the energy crisis and global warming can be solved using the photocatalysis process. Catalytic photoreduction of CO_2 is a sustainable process that allows the control of emissions and the removal of excess CO_2 in the atmosphere. In addition, photocatalysts convert carbon dioxide and water into chemical compounds in different states:

- Solid, such as coal.
- Liquids, e.g., methanol (CH_3OH), ethanol (C_2H_5OH) and formic acid (HCOOH).
- Gas, like methane (CH_4), carbon monoxide (CO) and formaldehyde (HCHO).

We produced Cu_2O nanoparticles to develop an artificial photosynthesis process to convert CO_2 and water into methanol. Our artificial leaf uses the same portion of green light as the visible spectrum used by plants during natural photosynthesis.

1. Introduction

Global warming has become the 'hot topic' of recent decades: since 1980, high CO_2 emissions have led to a rise in world temperature, thus causing a negative consequence of the greenhouse effect. The greenhouse effect is an essential natural phenomenon to balance and retain the heat needed to enable life on our planet. Its increase causes an increase in greenhouse gases: among the best known are CO_2. Throughout history, there have been several interventions by world powers to improve the climate crisis. There was the publication of the Kyoto Protocol in 1997-1998: an international treaty in which UNFCC's objective is to reduce greenhouse gasses (carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6)) concentrations in the atmosphere. In 2014, UNFCC (United Nations Framework Convention on Climate Change) announced the Paris Agreement, an international agreement whose long-term temperature goal is to keep the rise in global average temperature below 2°C. Starting in 2018 and reaching a peak in 2019, thousands of people participated in Climate Weeks, peaceful marches to demand action from political leaders to take action to prevent climate change.

In fact, the CO_2 concentration is increasing year per year: in 2014, it surpassed the threshold of 400 ppm and, in May 2020, the concentration increased by a further 18 ppm. Very often, the media blames the chemical industry to be the principal cause of global warming. However, most emissions come from electricity and transport (67%), followed by industry (15%), the commercial sector (10%) and finally non-fossil fuel combustion (8%). Globally, the countries with the highest % of emissions are China (30%) and the USA (15%), followed by India (7%) and Japan (3%). In Italy in particular, however, the quantities are not small. The Peninsula pollutes 1%, with no less than 337.09 tons of CO_2, resulting from the combustion of coal (31.7 t), natural gas (146,07) and oil (146.1 t), and other materials (13.22 t).

2. Application of Cu_2O nanoparticles

Nanometric copper oxide Cu_2O has possible applications for solar cells, sensors, superconductors, and photocatalysts Copper oxide is a p-type semiconductor material with a 2,17 eV bandwidth (ΔE). Generally, Cu_2O is a p-type semiconductor due to Cu vacancies in the lattice. However, it can be n-type semiconductor due to O_2 vacancies in the lattice (Fig. 1).

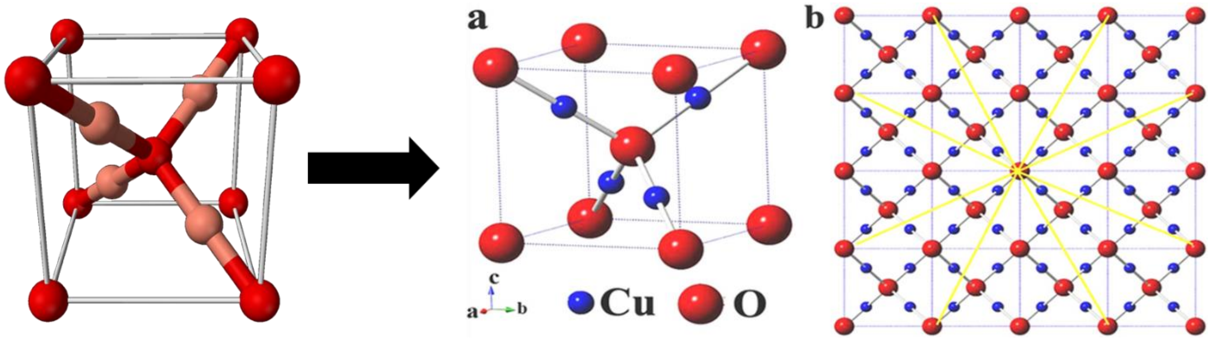


Fig. 1

3. Our project (artificial photosynthesis)

Recent studies have shown that environmental problems can be solved using photocatalysis. Catalytic photoreduction of CO_2 is a sustainable process that allows its emissions control, excess removal from the atmosphere and converts it into chemical compounds in different matter states.

As can be seen, Cu_2O is the semiconductor material with the lowest energy difference between the valence and conduction levels (Fig. 2).

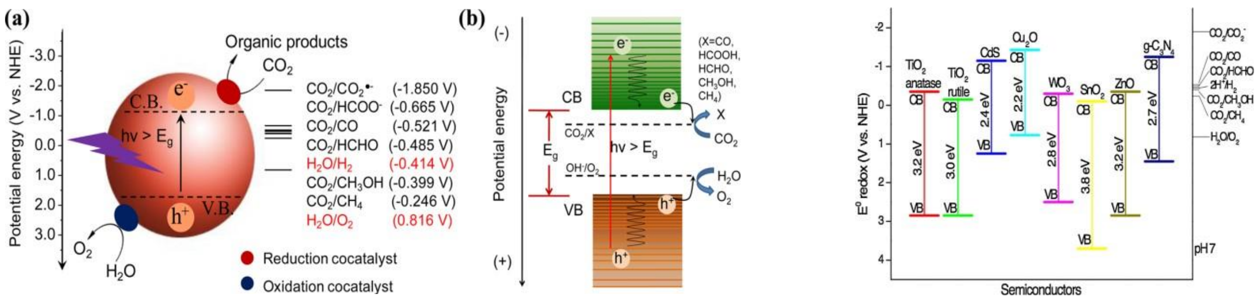


Fig. 2

4. Methanol (CH_3OH)

We aim is to produce methanol from a green synthesis (use of Cu_2O catalysts). Methanol, an organic chemical, is considered as the <<building block>> of chemistry. In fact, other molecules can be synthesised from this molecule, such as:

- Methanal (formaldehyde), CH_2O.
- Acetic acid (ethanoic acid), CH_3COOH.
- Ethers (R-O-R').
- Biofuels.
- Solvents.

Also, methanol has a high capacity and efficiency in transporting energy compared to other gases (H_2 and CH_4) and leads to a net reduction in pollutants such as NO_X and SO_X.

Currently, its production demand is 100 million t per year. However, methanol is generally produced using large amounts of heat and electricity, leading to an increase in pollution. Therefore, it is essential to replace its synthesis with a green one.

5. Synthesis of Cu_2O (Copper Oxide) nanoparticles

We synthesized two types of Cu_2O samples (colloidal syntheses): one containing a mix of cubic and octahedral nanocrystals and the other primarily composed of cubic nanocrystals.

Both the procedures were under constant vigorous magnetic stirring and heated at least at 55°C. At the end of the syntheses methods, it’s important to separate the precipitate from the solution by centrifugation at 5,000 r.p.m. for 5 minutes and wash the glassware with aqueous ethanol solution multiple times until there’s no residue. The final products were dried and stored inside a N_2 gas-flow glove box under room temperature for 48 h to avoid any contaminations.

5.1 *Cubic-Octahedral Cu_2O NPs*: in a three-neck flask, add deionized water (88.2 ml), $Cu(CH_3COO)_2$ aqueous solution (5 ml, 0.1 M) and sodium dodecyl sulphate (0.87 g). After complete dissolution of the sodium dodecyl sulphate powder in 1 h, quickly inject NaOH solution (1.8 ml, 1.0 M) and d-(+)-glucose aqueous solution (5 ml, 0.1 M) and stir again for 1 hour. After that all the compounds have been added, the final volume must be 100 ml. The colour of the solution gradually changes from light blue, dark blue, yellow-orange and finally brick red (Fig. 3).

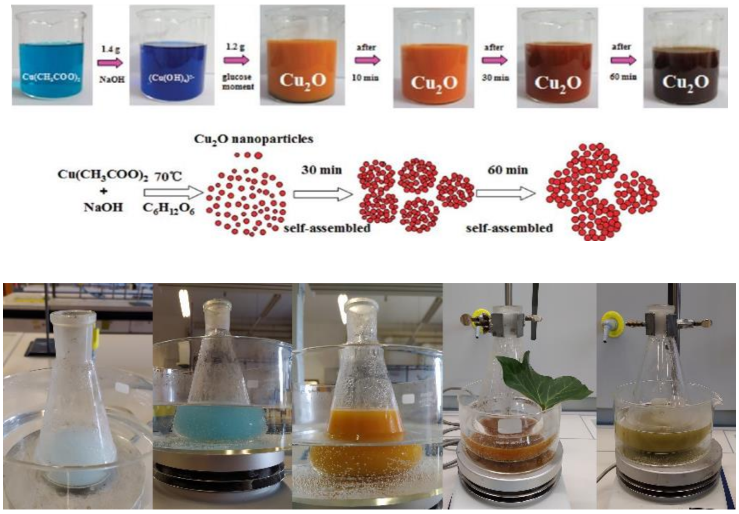


Fig. 3

5.2 *Cubic Cu_2O NPs*: in a three-neck flask, dissolve $CuCl_2 \cdot 2\,H_2O$ (0.171 g) in 100 mL of deionized water. Then, drop by drop, add NaOH aqueous solution (10 ml, 2.0 M) and stir vigorously with a magnetic stir bar for 0.5 h. After, insert Ascorbic acid solution (10 ml, 0.6 M) and wait for the solution to change colour from black to turbid red. The mixture was aged for 3 h (Fig. 4).

Fig. 4

All chemicals were purchased from Sigma Aldrich.

6. Solar simulators

Solar simulators are systems designed to simulate solar radiation with a collimated and uniform light spot. They provide an irradiance as similar as possible to the solar spectrum (from UV to IR). The fundamental part of the solar simulator is the Xenon arc lamp (Fig 5).

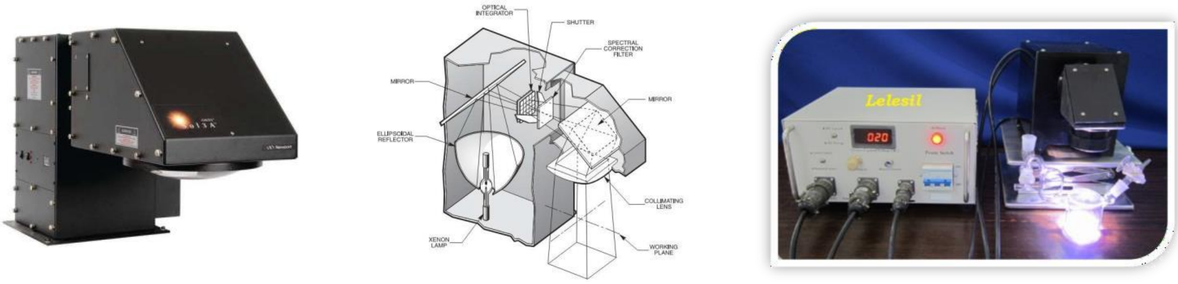


Fig. 5

7. Quantum yield determination (Actinometers)

Actinometry was used to determine the photon flux emitted by the Xe lamp. Since Cu_2O nanoparticles have a bandgap of 2.1 eV corresponding to 590 nm, we chose iron(III) oxalate $Fe_2(C_2O_4)_3 \cdot 6\ H_2O$ as the standard for actinometry. The transformation from Fe^{3+} to Fe^{2+} by photons can be written as follows:

$$2\ [Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow 2\ [Fe(C_2O_4)_2]^{2-} + 2\ CO_2 + C_2O_4^{2-}$$

For the photometric determination of Fe^{2+}, we used 1,10-phenatroline to form the complex $[Fe(phen)_3]^{2+}$ which shows an absorption at 510 nm:

$$[Fe(C2O_4)_2]2- + 3\ phen \rightarrow [Fe(phen)_3]^{2+}$$

8. Artificial photosynthesis test (with Cu_2O catalyst)

In the produced Cu_2O nanoparticles, the face (110) is photocatalytically active for the reduction of CO_2 to methanol, while the surface (100) is inactive. The oxidation state of the active sites changes from Cu (I) to Cu (II) due to the co-adsorption of CO_2 and H_2O. This causes a rapid return to Cu (I) after conversion of CO_2 to methanol by illumination with visible light at λ = 532 nm (Fig. 6).

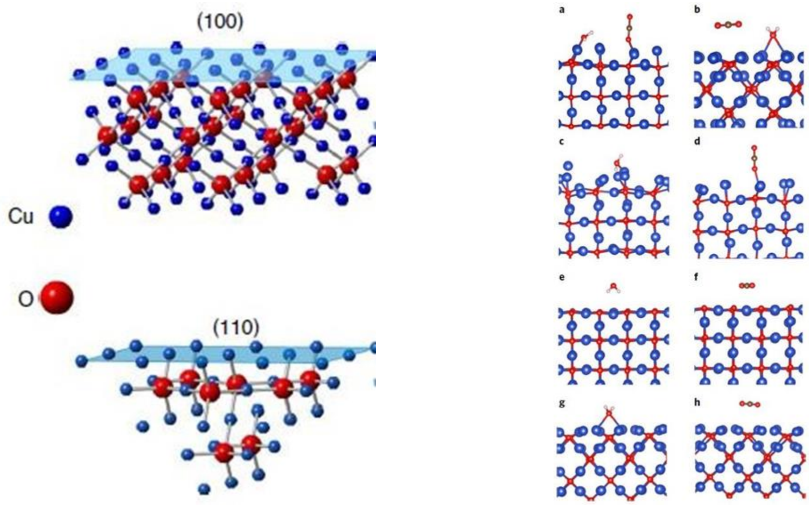


Fig. 6

We characterized the photocatalytic activity of Cu_2O nanoparticles – obtained by two different methods – by measuring their CH_3OH production.

The illumination of the NPs in presence of CO_2 and H_2O showed the main formation of methanol and oxygen (Fig. 7).

__Artificial photosynthesis test__: in a 20 ml Agilent Headspace sealed vial, 0.01 g of purified particles were dispersed in 5 ml of ultrapure deionized H_2O. The suspension was thoroughly degassed to remove air with CO_2 gas for 10 min. CO_2 gas (Airgas, Inc.) was bubbled through a deionized H_2O bubbler glassware for the CO_2/H_2O gas mixture. The suspension was continuously flushed with the CO_2/H_2O gas mixture for another 30 min to saturate the suspension with CO_2. Then the suspension was illuminated using a 300 W Xe lamp (Perkin-Elmer Optoelectronics) at a power of 204 W with continuous CO_2/H_2O gas flow for 0–60 min. The sealed suspension was removed from the gas line after illumination. The methanol in both the gaseous product and the liquid in aqueous solution was extracted out at a temperature above the boiling point of methanol and then injected for quantification using an Agilent Headspace sampler (model 7697 A) connected to an Agilent GC–MS analyser (model 5975C GC–MS, with quadrupole detector, thermal conductivity detector (TCD) detector, DB-5ms column and He carrier gas).

Fig. 7

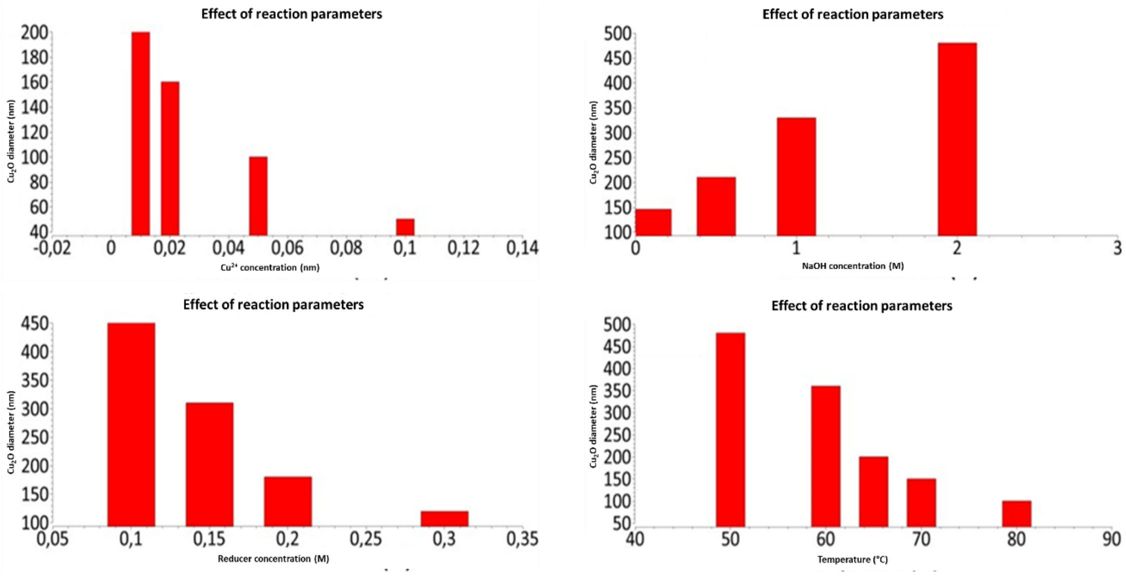
The amount of produced methanol (< 5%) was determined by comparing the obtained area of the gas-chromatographic peaks with that of a standard (pure methanol was used) (Chart 9).

9. Effect of reaction parameters

The variables studied were:

- Cu^{2+} concentration.
- NaOH concentration.
- reducing agent concentration
- temperature.

As the NaOH concentration increased, the diameter of the Cu_2O nanoparticles increased as well: in the first procedure, from 100 to 500nm, meanwhile in the second procedure from 50 to 200nm. In the case of Cu_2O nanoparticles obtained using citric acid (coated with a negative surface charge), the citrate ion also acted as a stabilising agent (via electrostatic stabilisation). The smaller the amount of citrate in the solution, the larger the diameter of the particles obtained. In the case of the procedure with D + Glucose, we used sodium dodecyl sulphate as the stabilising agent. The smaller the amount of D + Glucose in solution, the larger the diameter of the particles obtained (Charts 1-4).



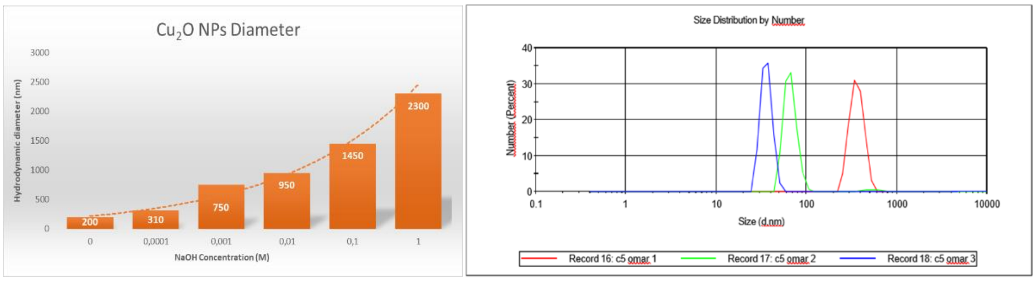
Charts 1-4

10. Analytical characterization: DLS, GS/MS and HSGC

The obtained nanoparticles of Cu_2O and methanol (CH_3OH) were compared and characterized through the following analyses:

10.1 DLS analyses: Dimensional Analysis

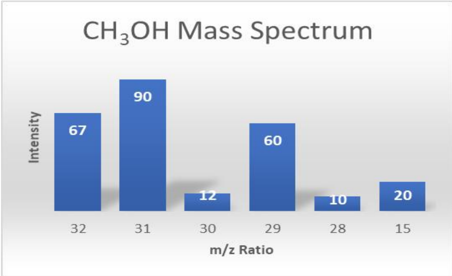
The DLS characterization of Cu_2O gave the following results (Charts 5-6):

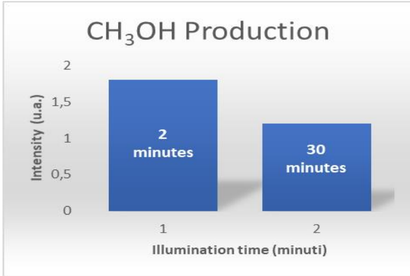


Charts 5-6

10.2 Analysis characterization: Gas chromatography–mass spectrometry

The control of the Cu_2O photo-catalyst was carried out by evaluating the production of CH_3OH by gas-chromatography analysis after an irradiation time of 2 minutes, resulting in a retention time of 1.74 minutes. We also performed a GC/MS analysis of the produced methanol: the obtained ratio (mass/charge) = 44, and it corresponds to the unreacted CO_2. The production of O_2 was observed but not measured quantitatively (Charts 7-8).





Charts 7-8

10.3 HSGC

The HSGC characterization of CH_3OH gave the following result (Chart 9):

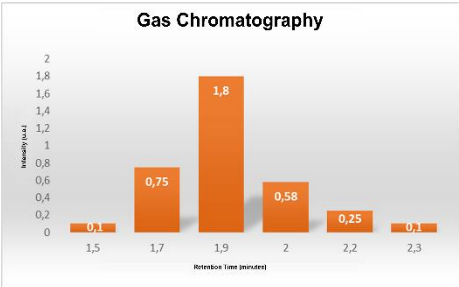
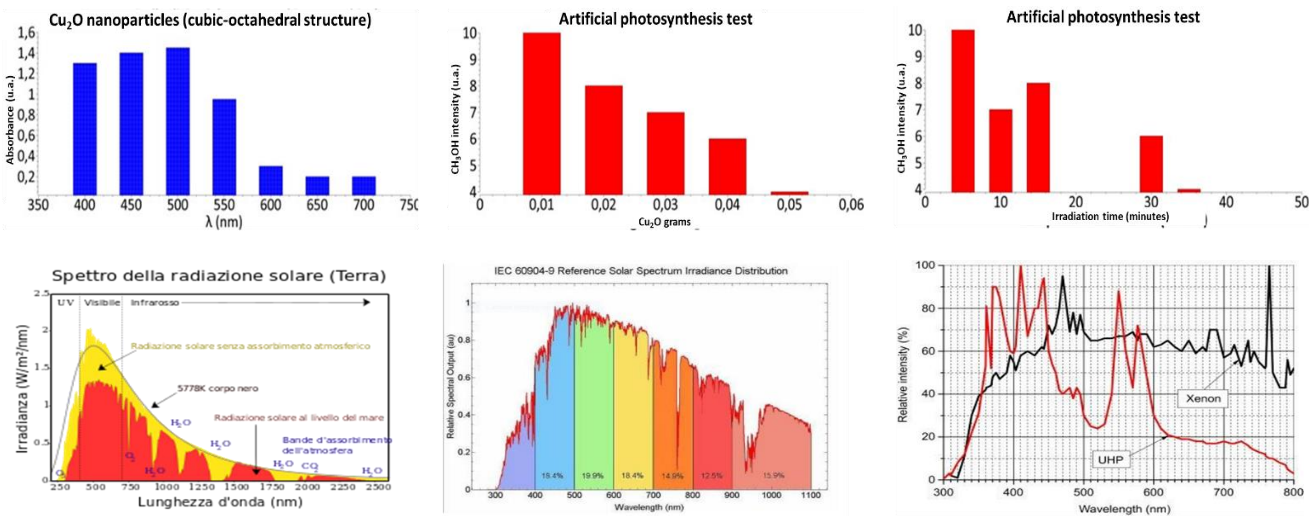


Chart 9

11. Conclusions

From the results obtained and shown in the various charts, we conclude that the production of Cu_2O by the two different methods is promising. The high interaction of the nanoparticles with the visible radiation, and their high sensitivity to changes in shape, made it possible to exploit sets of Cu_2O nanoparticles as photocatalysts for the synthesis of methanol. However, we encountered problems with the reproducibility of the experimental procedure: all the experiments were carried out using the xenon lamps and pressurised mercury lamps present in the projectors, except one test performed with a professional solar simulator (Charts 10-15).

After concluding the artificial photosynthesis test, we obtained the final reaction yield of $CH_3OH < 5\%$. Although this result is relatively low, it confirms the presence of methanol, which was produced by a green synthesis.



Charts 10-15

12. Final considerations and possible future Applications

The idea to be developed further concerns the possibility of doping Cu_2O with other semiconducting metal oxides (e.g., TiO_2). Cu_2O acts as a co-catalyst, making it possible to reduce the bandgap value of TiO_2 by using its conduction and valence bands, which have a lower bang gap value than TiO_2. There could be additional developments, such as more analysis, sonicate the nanoparticles and large-scale extension in a photochemical reactor (*Lelesil*).

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