

Synthesis and characterisation of Nano- $\text{La}_2\text{NiO}_{4+\delta}$ with potential applications as antimicrobial coatings.

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Abstract

In this paper, the K_2NiF_4 system, $\text{La}_2\text{NiO}_{4+\delta}$, has been analysed for potential photocatalytic activity for destruction of organic pollutants under low intensity UV light, with methyl orange used as model pollutants. The $\text{La}_2\text{NiO}_{4+\delta}$, was shown to have promising photocatalytic activity. In addition, there was also evidence for catalytic decomposition of methyl orange in the dark, most likely due to a redox process, although further work is required to confirm this. The results show that the nano La_2NiO_4 samples prepared by sol-gel method have better photocatalytic activity than La_2NiO_4 prepared by solid state method since the sol-gel method produces a smaller particles sizes comparing to the solid state method. X-ray diffraction (XRD), thermogravimetric analyses (TGA), and The Brunauer–Emmett–Teller (BET) were used for surface characterizations.

تحضير وتشخيص مركبات نانوية $\text{La}_2\text{NiO}_{4+\delta}$ مع امكانية استعمالها كطبقات مضادة للبكتريا

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مفتاح البحث: مضادات البكتريا, عوامل مساعدة الضوئية

الخلاصة :

في هذا البحث K_2NiF_4 system, $\text{La}_2\text{NiO}_{4+\delta}$ قد تم اختبارها كعوامل مساعدة ضوئية مع امكانية استعمالها كمواد ذات فعالية لتحطيم الملوثات العضوية تحت اشعة فوق البنفسجية واطئة الشدة مع استعمال المثيل البرتقالي كمثال عن هذه الملوثات. المواد المحضرة في هذا البحث اظهرت فعالية ضوئية جيدة. بالاضافة الى ذلك هنالك دليل على تحطيم المثيل البرتقالي في الظلام وبدون الضوء والذي يمكن ان يعزى الى تفاعلات الاكسدة والاختزال للنكل الثنائي والثلاثي. هذه الفعالية تحتاج الى

Introduction

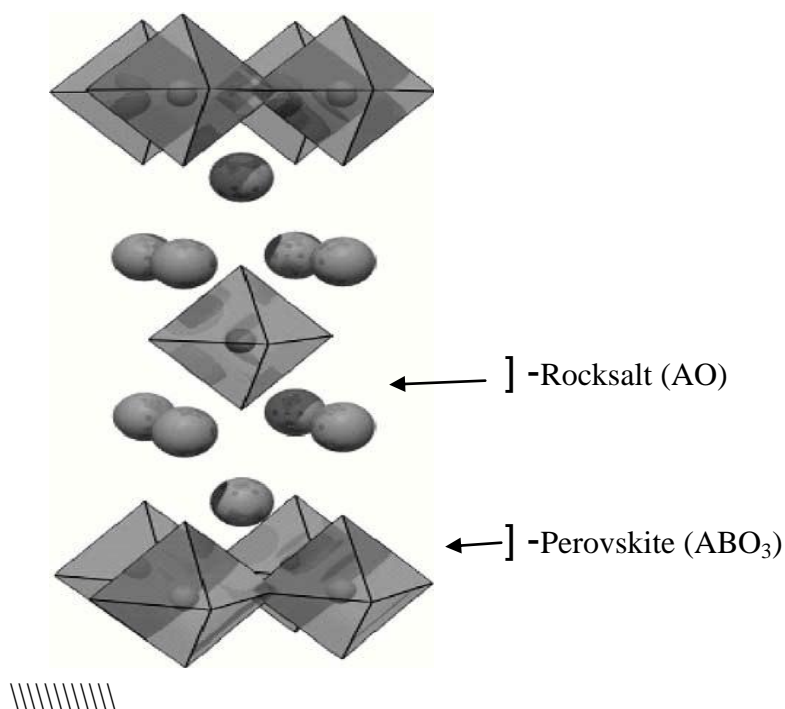
The rapid spread of resistant bacteria, the bursting *Clostridium difficile* hospital-acquired infection, the occurrence of severe acute respiratory syndrome (SARS) and the return of avian influenza has draw attention to the development and application of antiviral materials for preventive measures either in addition to, or as an alternative to the conventional concept of disinfection [1-3].

An Antimicrobial material is a substance which can kill or inhibit the growth of microbes such as bacteria, fungi, or viruses, while antimicrobial drugs (antibiotics) ether kill microbes or prevent the growth of microbes. However, the spread of antibiotic resistant pathogens is still a growing concern globally [3]. Moreover, some infectious bacteria can survive for more than 90 days on various surfaces such as polymeric and textile materials [3]. Approximately 2 million persons annually in USA are affected by the infections acquired in hospitals alone, and between 44,000 and 98,000 people die every year from these infections according to the estimation made by the US centres for disease control and prevention (CDC) [1]. Moreover, in the UK, there has been huge concern recently regarding virus infection in UK hospitals. Therefore, antimicrobial surfaces are needed to reduce infections in such public areas. Photocatalysts have been used as a main substance in these applications. Photocatalysts have a wide range of applications, such as water treatment and environment remediation, generation of hydrogen from water, self-cleaning windows and odour control. Antimicrobial function can be represented by essential materials or through the use of coating materials [2]. Antimicrobial surfaces not only provide protection against infectious diseases but also against odour, staining, deterioration and allergies [3].

Antimicrobial surfaces should therefore be necessary features of daily used materials. As a result new strategies are required for conferring common materials, such as glass, plastics and textiles with bactericidal properties. Moreover, low temperature strategies are essential due to the poor heat resistance of plastics, wood and textiles [3].

K_2NiF_4 -type oxides have attracted considerable interest in a range of areas, including superconductivity, electrode materials in solid oxide fuel cells (SOFCs), oxygen separation membranes and catalysts. In terms of the latter, the K_2NiF_4 -type materials, $Ln_2NiO_{4+\delta}$ ($Ln=La,Pr,Nd$), are attracting significant attention as promising materials for ceramic membranes for oxygen separation and partial oxidation of light hydrocarbons, and for solid oxide fuel cell cathodes [4]. La_2NiO_4 -based materials have important properties such as high oxygen permeability and ionic conductivity and high electrocatalytic activity [4]. The crystal

structure of K_2NiF_4 oxides involve a stacking of perovskite layers ABO_3 alternating with AO (rock salt) layer along the c -direction (as shown in figure 1) [5].



0063ig. 1: K_2NiF_4 structure type adopted by the $La_2NiO_{4+\delta}$ type oxides showing alternating AO and ABO_3 layers [5].

The catalytic activity of Mn-containing K_2NiF_4 type oxides, $La_xSr_{2-x}MnO_{4+\delta}$ ($0 \leq x \leq 0.8$), and $Pd/La_xSr_{2-x}MnO_4$ ($x=0.2$) have been investigated by Karta *et al.* [6]. This group controlled and improved the redox property through controlling the oxidation state of the B-site ion by substitution at A-site ion with ions of different valence. The best K_2NiF_4 in terms of both ionic conductivity and electrocatalytic properties is the undoped $La_2NiO_{4+\delta}$, which has the possibility to accommodate a significant oxygen excess [7-9]

The strong redox catalytic activity of these materials therefore also offers potential as antimicrobial coatings.

Experimental

High photocatalytic activities for ceramic materials have generally been correlated with smaller particles sizes and with good crystallinity. Therefore, in this work we used standard solid state, and sol-gel methods for preparation of the samples to compare the effect of synthesis route on particle size, structure formed, and photocatalytic performance. Phase purity was established through X-ray powder diffraction (Panalytical X'Pert Pro diffractometer, $Cu K\alpha_1$ radiation). The Brunauer–Emmett–Teller (BET) model was used to determine the specific surface area of solid using an automated Micromeritics® Gemini III 2375 surface area and porosimetry analyser.

The main benefits of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures [10]. Lanthanum nitrate hexahydrate [La(NO₃)₃.6H₂O, Acros, 98%], Nickel nitrate [Ni(NO₃)₂.6H₂O, Sigma-Aldrich, 98%] were used to prepare the K₂NiF₄-type oxide La₂NiO₄ and the related Ruddlesden Popper system La₃Ni₂O₇ by the Pechinimethod. La(NO₃)₃.6H₂O and Ni(NO₃)₂.6H₂O were dissolved in water with appropriate stoichiometry. After stirring at ambient temperature, citric acid [C₆H₈O₇, Acros, 99.6%] and ethylene glycol [C₂H₆O₂, Acros] were added (1 mole of each per mole of metal). The resulting solution was slowly evaporated on a hotplate till the formation of gel. The obtained gel was heated at 400 and 600°C for 600 minutes to burn off the organic component and form the final compound. After cooling down, the powder was analysed by XRD.

Solid state synthesis

A sample of La₂NiO₄ was prepared from intimately ground mixtures of high purity La₂O₃ and NiO. The mixture was heated in air at 950, 1100, 1200, and 1250°C for 12 hours at each temperature with intermediate regrinding. The powder was analysed by XRD.

Photocatalytic testing

In this study, we have chosen methyl orange dye (MO) as model pollutant. The photocatalytic degradation was performed in 25 mL plastic reactor, being filled with 20 mL of aqueous suspension containing 0.1g catalyst and 10 mgL⁻¹ methyl orange (MO). The mixture suspension was stirred continuously for 3 min before being illuminated, to allow the organic adsorption onto the catalyst surface. As mentioned above, a 250 nm (6 W) mineral light lamp (UVP) was employed as a UV light source. 4 mL aliquots were sampled, immediately centrifuged at 3200 rpm for 10 min to remove the catalyst nanoparticles, and then analysed at given time intervals on a Lambda 750 UV/VIS spectrometer/Perkin Elmer by measuring the absorbance of the solution at 464 nm which corresponds to the maximum absorption of MO.

Results and discussion

The XRD pattern for La₂NiO₄ prepared by sol-gel showed the successful formation of La₂NiO₄ with La₂O₃ and La₃Ni₂O₇ impurities. Figure 2 shows the XRD patterns of this sample with the La₂O₃ and La₃Ni₂O₇ impurities marked. The behavior of La₂NiO₄ as a catalyst in the presence and absence of UV irradiation ($\lambda = 250$ nm, 6 W) is shown in figure 3. Due to the very good catalytic activity, the time duration left between points was too short. A greater loss of MO in the presence of UV light is clearly seen, indicating that the La₂NiO₄ material has a photocatalytic activity under UV light. However, there is also significant MO concentration reduction in the dark, which is either due to absorption on the surface or general catalytic activity (perhaps

In order to gain further information regarding any changes in the sample after photocatalytic testing, TG studies were performed. Figure 4 shows the TG curves for La₂NiO₄ prepared by sol-gel and UV-treated La₂NiO₄ samples. The curve for UV-treated La₂NiO₄ sample shows a gradual weight loss up 250 °C, which becomes much more pronounced, finally levelling off around 750°C at 91.02 wt% (i.e. 8.98 wt % mass loss). The mass losses for the as-prepared sample can be attributed to water (lower temperature), and oxygen loss (higher temperature). The additional mass in the UV-treated sample can be attributed to either absorbed MO or its' decomposition products. These results imply that absorption process was involved (either of MO or its' decomposition products) in addition to the photodegradation process by these materials.

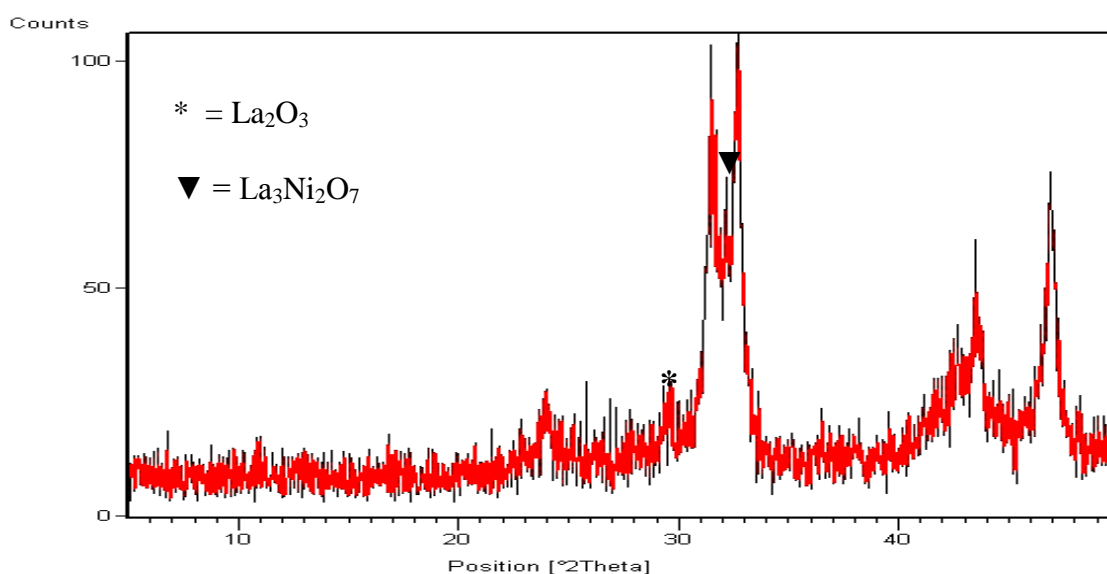


Fig. 2: the XRD pattern of sol gel synthesised La₂NiO₄ heated at 600°C. Impurities marked.

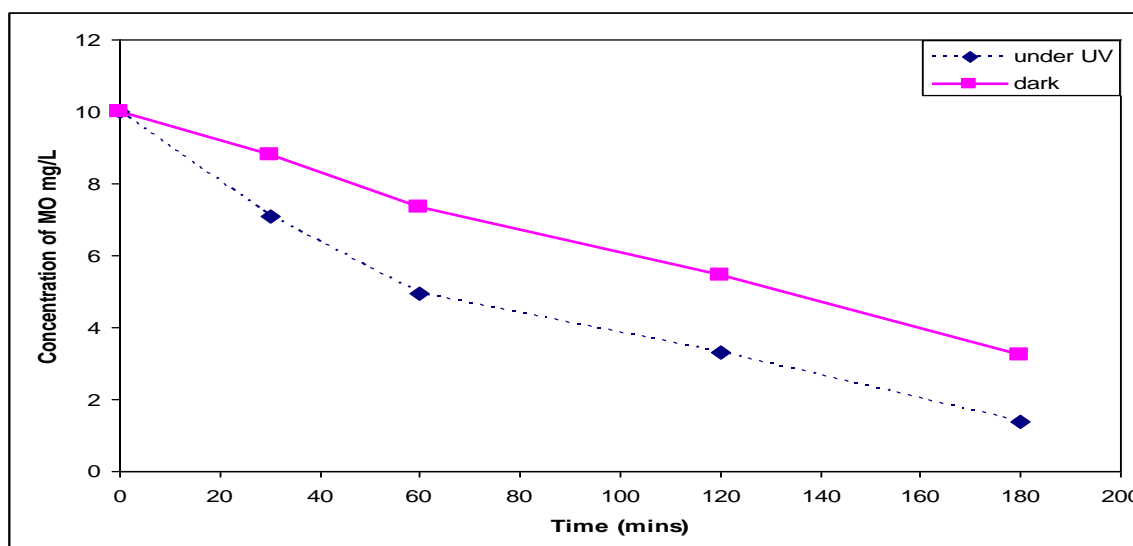


Fig. 3: the change in MO concentration during illumination time for La_2NiO_4 under UV and in the dark.

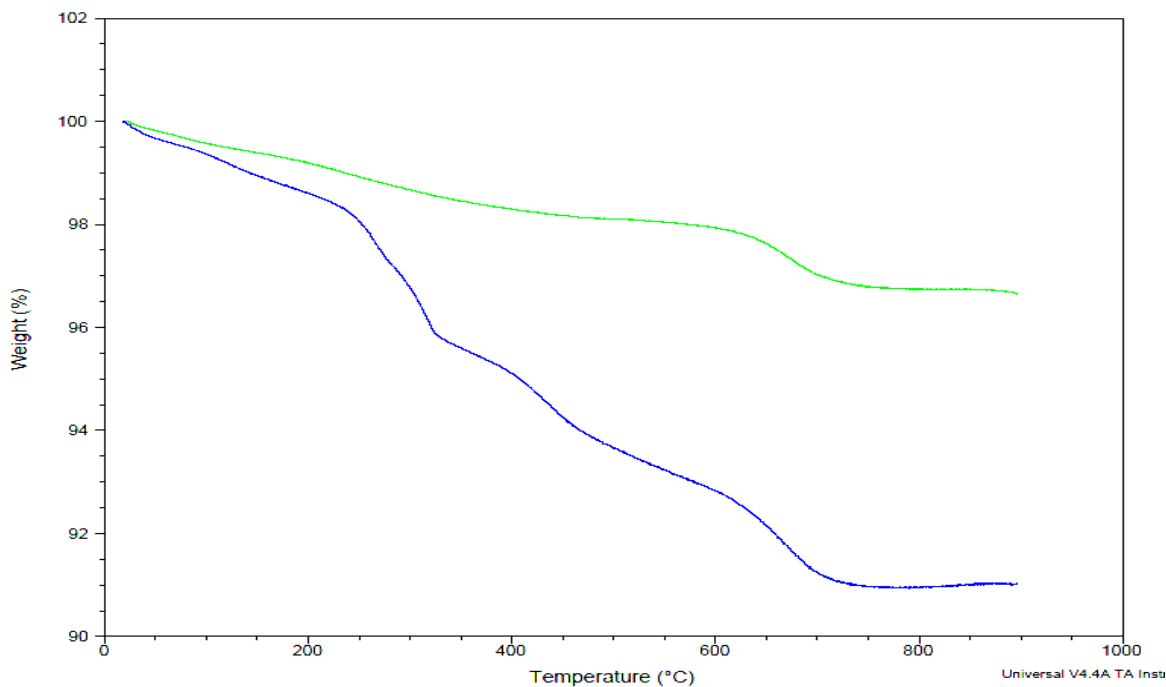


Fig. 4: TG curves for the La_2NiO_4 prepared by sol-gel (curve 1) and UV-treated La_2NiO_4 (curve 2).

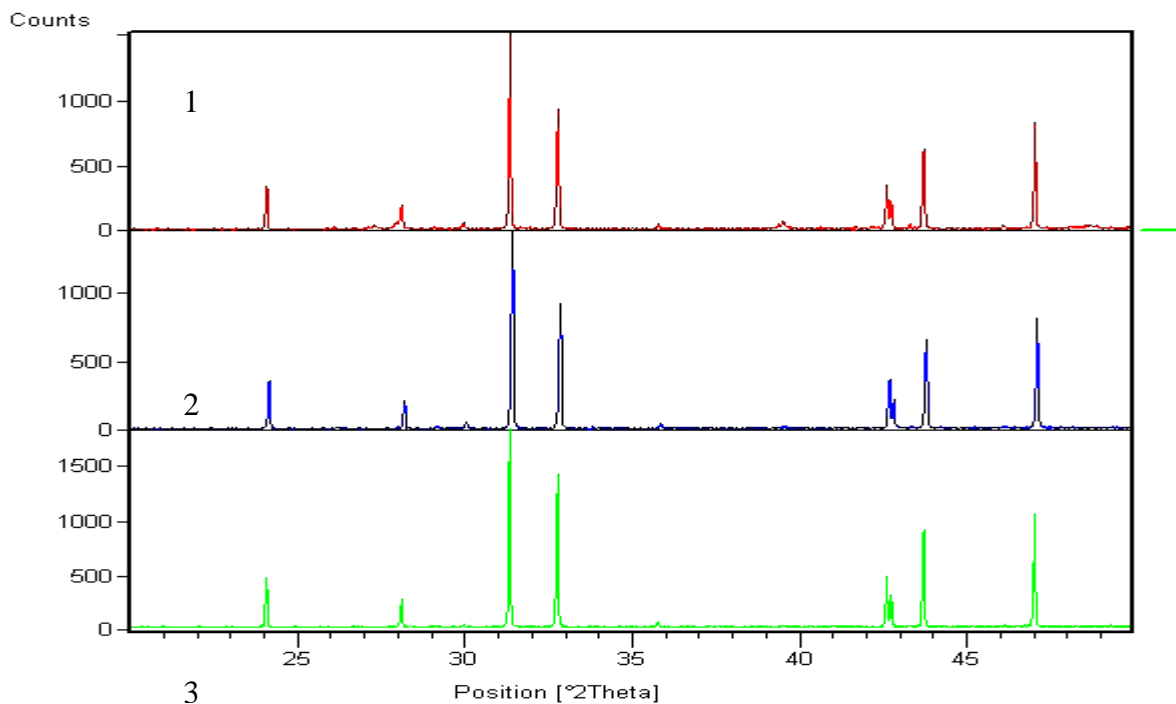


Figure 5: the XRD patterns of La_2NiO_4 (1) after heating at 1100°C , (2) after heating

at 1200°C , and (3) after heating at 1250°C .

Figure 5 shows the change of the XRD patterns of La_2NiO_4 prepared by solid state methods (1) after heating at 1100°C , (2) after heating at 1200°C , and (3) after heating at 1250°C . The XRD patterns revealed that the sample heated at 1250°C was pure K_2NiF_4 type. Figure 6 shows the change of MO during illumination time for (1) La_2NiO_4 prepared by sol-gel, and (2) La_2NiO_4 prepared by solid state. The performance of La_2NiO_4 prepared by the solid state route was compared with that La_2NiO_4 prepared by sol-gel method. The MO photodegradation over La_2NiO_4 prepared by the solid state route is very slow (curve 2) comparing with La_2NiO_4 prepared by sol-gel (curve 1). Therefore, it is easily recognized from figure 6 that the sol-gel prepared sample La_2NiO_4 shows higher photocatalytic activity. The better activity of La_2NiO_4 prepared by sol-gel is most likely attributed to the presence of smaller particle size since the sol-gel method produces a smaller particles sizes comparing to the solid state method. In order to confirm this, surface area analysis was performed.

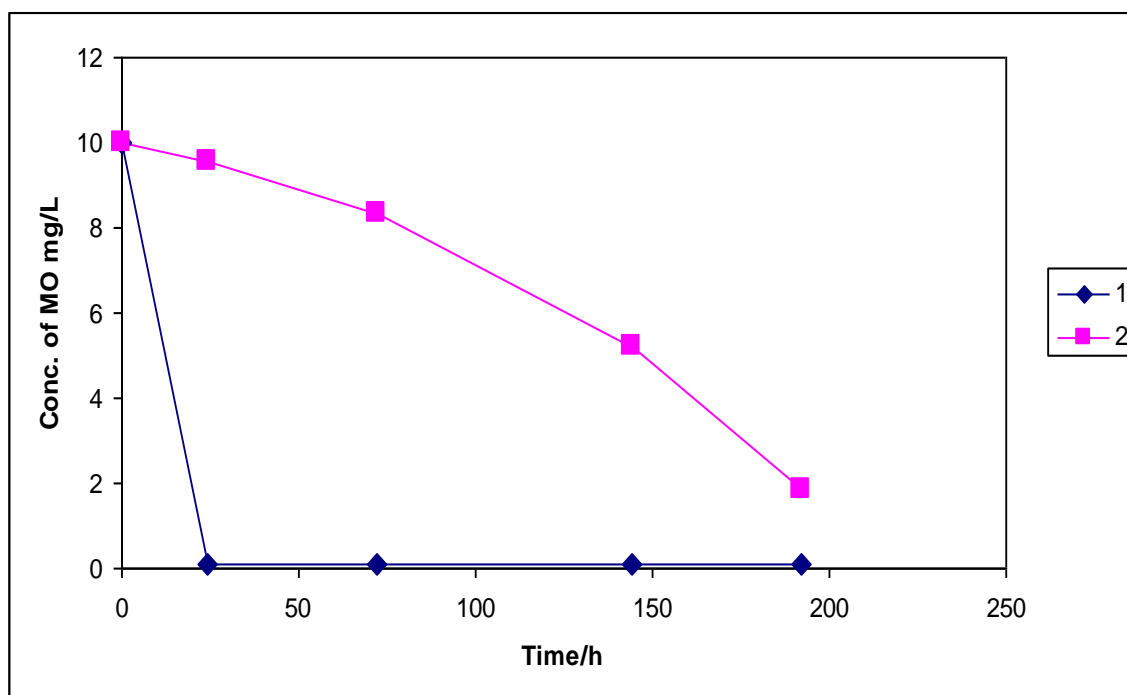


Fig. 6: the change in MO concentration during illumination time for (1) La_2NiO_4 prepared by sol-gel, and (2) La_2NiO_4 prepared by solid state.

Stability of La_2NiO_4 catalytic performance under longer term testing and re-use.

As shown in the previous section, La_2NiO_4 showed promising potential for both photocatalytic activity and general catalytic activity (in the absence of UV-light) for the destruction of

pollutants. The aim here was to investigate any degradation in performance over time, or with re-use (e.g. do decomposition products adsorb on surface and reduce activity).

In this work, the photocatalytic degradation of 10 mg/L MO was carried out in successive batches. After the first run in which the added MO was almost completely degraded, 10 mg/L of MO was freshly added and then the second photocatalytic cycle started. This process was repeated for three cycles of the photocatalytic degradation. Figure 7 illustrates the kinetics of MO degradation over La_2NiO_4 in successive degradation cycles. Each five points corresponding to a degradation cycle is very close to La_2NiO_4 under UV curve in figure 3. The degradation process in the cycles demonstrates that the La_2NiO_4 material has good photocatalytic stability.

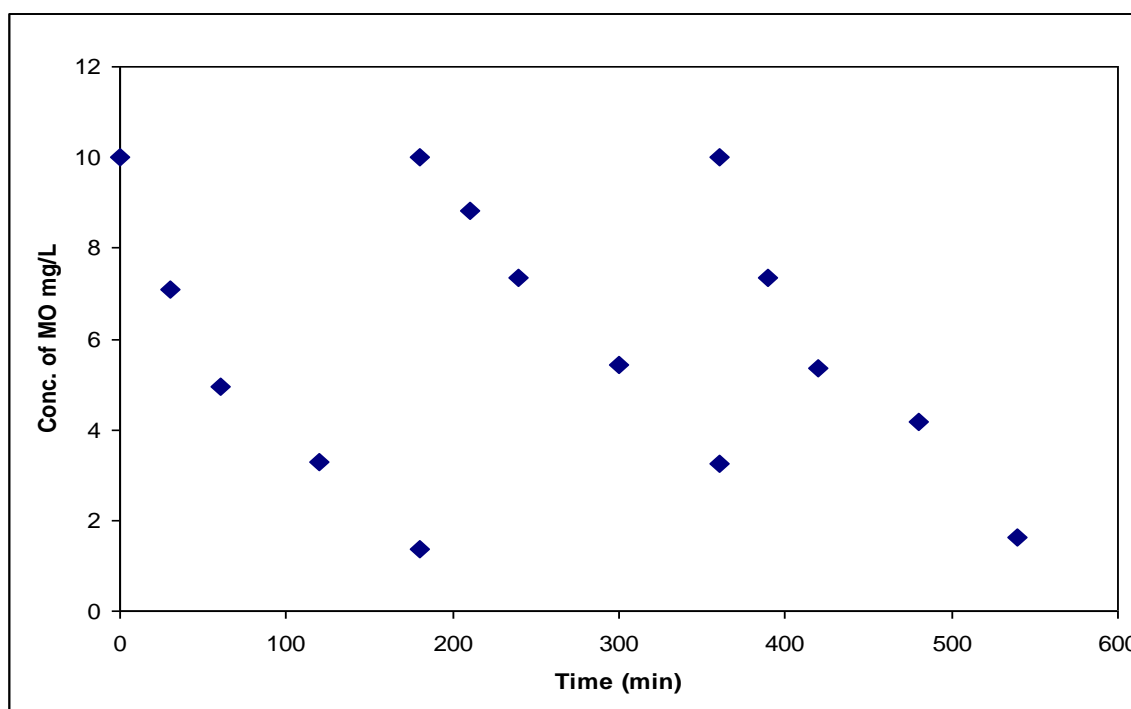


Fig. 7: kinetics of MO degradation over La_2NiO_4 in successive degradation cycles.

BET

The Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) of the sol gel and solid state prepared La_2NiO_4 samples were determined through nitrogen adsorption at 77 K. All samples were shown to have low surface area ($5.38 \text{ m}^2\text{g}^{-1}$ for La_2NiO_4 prepared by sol-gel and $0.07 \text{ m}^2\text{g}^{-1}$ for La_2NiO_4 prepared by solid state). La_2NiO_4 prepared by solid state sample yielded much lower S_{BET} values. This result clearly indicates that the synthesis route has influence on the surface area as become in nano thereby on the photocatalytic activity.

Conclusion

In this work, the K_2NiF_4 system, $La_2NiO_{4+\delta}$, was examined for potential photocatalytic activity for destruction of organic pollutants under low intensity UV light and shown to have promising photocatalytic activity. In addition, there was also evidence for catalytic decomposition of methyl orange in the dark, most likely due to a redox process. Moreover, synthesis route has an effect on the catalytic activity.

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