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SYNTHESIS AND CHARACTERISATION OF AMBIENT PRESSURE DRIED COMPOSITES OF SILICA AEROGEL MATRIX AND EMBEDDED NICKEL NANOPARTICLES

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ABSTRACT

A method for the synthesis of silica aerogel composites with embedded nickel nanoparticles employing ambient pressure drying is successfully developed. Nickel nanoparticles (NiNPs) are introduced into the sol-gel processing of a tetraethoxysilane precursor to produce the immobilised nickel nanoparticles. The microstructures of the aerogel products are studied using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). Specific surface area of the aerogels was characterised with nitrogen gas adsorption and analysed by Brunauer-Emmett-Teller (BET) method. X-ray diffraction and STEM-based energy-dispersive X-ray mapping determined chemical composition. The catalytic activity of the NiNPs-silica aerogel composites for hydration reaction of carbon dioxide in water is verified.

1) BACKGROUND

One of the main applications of porous materials is their use as supports for catalyst materials [1]. Aerogels are the most porous known materials and, therefore, they have been applied as catalyst supports [2, 3]. Supercritical drying (SCD) is a common method to fabricate aerogels due to the very low surface-tension of supercritical fluids (SCF) used in the drying step [4]. However, in order for solvent reaching to supercritical point [5], the energy consumption and the specific design of autoclave for the aerogels manufacturing restrict the reduction of the cost, especially for the demanded low-cost mass production. Ambient pressure drying (APD) was developed to address the shortcomings of SCD [6]. In APD there is no requirement for high pressure due to the use of organic solvents with low surface tension instead of supercritical fluids during the drying process. Therefore, APD is at ambient pressure without any autoclave or supercritical CO₂ extractor. However, the time cost of solvent exchange is the disadvantage of the most of APD methods [7-11].

Nickel catalysts on SiO₂ supports are used for carbon dioxide reforming and methane autothermal reforming in fluidized-bed reactor [12, 13] for production of synthesis gas (CO and H₂), a key step in the conversion of natural gas to liquid fuels and chemicals. The catalytic activity of nickel, in the form of nanoparticles (NiNPs), for the reversible hydration

reaction of carbon dioxide at room temperature and atmospheric pressure has been recently reported [14]. The confirmation that NiNPs are capable of accelerating the mineral carbonation process [15, 16] is potentially important for CO₂ capture technologies and CO₂ mineralisation [14, 15]. It has been suggested that NiNPs based carbon capture technology could be applied primarily to point sources, [14] such as power plants, air-conditioning outlets etc.,. Recovery of NiNPs is limited by technologically challenging use magnetic fields and magnetic separators in fluidized bed reactors to separate the nanoparticles from the reaction mixtures. Therefore, in order for this proposed technology to become viable the immobilisation of NiNPs on porous catalytic supports is an attractive way to overcome the magnetic separation limitation. NiNPs/SiO₂ catalysts were previously prepared with nickel citrate precursors using an incipient-wetness impregnation method [12, 17] and by the sol-gel method using a Ni(NO₃)₂ · 6H₂O precursor and TEOS, the resulting alkogels were then submitted to high temperature supercritical drying [18]. These processes are highly energy intensive.

Here we report the APD synthesis of NiNPs-embedded silica aerogel composites for use as a supported catalyst for hydration of CO₂. The aerogel materials have been characterised by scanning transmission electron microscopy (STEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). Specific surface area of the aerogels was characterised with nitrogen gas adsorption and analysed by Brunauer-Emmett-Teller (BET) method. The catalytic activity of the NiNPs-embedded silica aerogel towards the hydration reaction of carbon dioxide was tested. Prefabricated NiNPs are used in our study to eliminate any variation of catalytic activity, which may arise through changes in particle size resulting from different loading. The catalytic activity of these preformed standalone NiNPs has already been previously confirmed by Bhaduri and Šiller [14, 15].

2) EXPERIMENTAL

Nickel nanoparticles are from Nano Technologies (Korea). Ethanol is from Fisher Scientific UK Ltd. Other materials and solvents are from Sigma-Aldrich (UK) and used without any further purification. Nickel nanoparticles were dispersed in deionised water by ultrasonication (Sonopuls, Bandelin) for 2 minutes in order to obtain nickel nanoparticle suspensions (500/700/900 ppm). Silica gels were prepared by the hydrolysis of the precursor tetraethoxysilane (TEOS) (98%), ethanol (≥ 99.8%) and de-ionised water with a 2:38:33 molar ratio of TEOS:ethanol:water. We used 2 ml of nickel nanoparticle suspension and 33 ml precursor with 1 ml of catalyst (a mixture of ammonium hydroxide (28-30%), ammonium fluoride (≥ 98%) and de-ionised water with a 1:8:111 molar ratio of NH₄F:NH₄OH:H₂O which is utilised to accelerate the process of gelation). After gelation was completed, the gel was removed from the casting mould into 500 ml of ethanol for washing and aging for 24 hours. The washing/aging solvent was replaced by 250 ml of ethanol. After 24 hours, the solvent was replaced by 250 ml of hexane and this process was repeated three times. The gel was subsequently dried at 60°C for 48 hours. Finally, the aerogels were placed in an oven under ambient atmosphere at 100°C for 3 hours. For preparing another silica-only aerogel, the same amount of de-ionised water was added instead of nickel nanoparticle suspensions. Then the other procedures were the same with the preparation of Ni/SiO₂ aerogels.

To analyse the catalytic activity of the nickel-silica aerogel composites for hydration reaction the experiments were carried out in a fluidized-bed bubble column reactor. The bubble column reactor consisted of a cylindrical flask of 150 ml with a perforated glass base (grade 0 Pyrex©). 50 ml of deionized (DI) water (18MΩ/cm resistivity) was introduced in the bubble

column (or 100 mg of NiNPs- silica composite sample (or pure SiO₂ aerogel) was placed in 50 ml of DI water). The pH was recorded on a computer using HI 2550 pH meter (Hanna Instruments, UK). 100 % CO₂ (BOC, UK) was bubbled through the bubble column at a flowrate of 50 ml/min and the pH change was recorded with time interval of 10 sec between reading, respectively. The samples were filtered by draining the water from the bubble column and the aerogel was collected and air-dried at 60 °C.

A FEI XL30 ESEM-FEG was used to image the samples in high vacuum mode at a 10 keV accelerating voltage. Before SEM imaging, the samples are coated with gold. Coulter SA 3100 Surface Area and Pore Size Analyzer is used to determine the nitrogen adsorption isotherms and the specific surface area of the aerogels was determined by Brunauer-Emmet-Teller (BET) method. A PANalytical X'Pert Pro Multipurpose Diffractometer (MPD) is used for X-ray powder diffraction (XRD) employing Cu K α X-rays. All samples are mounted on a silicon low background substrate and diffraction scans were carried out over a 2θ range of 5-130 degrees. Scanning transmission electron microscopy (STEM) experiments are performed by using a Tecnai F30 300 keV microscope at the Materials Science Centre, University of Manchester. Samples examined with HRTEM and STEM were prepared by extended ultrasonication in de-ionised water until there were no pieces of aerogel visible to the naked eye. The procedure described above for the preparation of nickel-silica aerogel composites was used with four different concentrations of nickel nanoparticles and the resulting samples are labelled as SiO₂ aerogel (0 ppm), NS1 (500 ppm), NS2 (700 ppm), and NS3 (900 ppm).

3) RESULTS AND DISCUSSION

Figure 1(a) shows a typical TEM image of the nickel nanoparticles. The nanoparticle size distribution, Figure 1(b), was determined by statistical analysis of the TEM images, with an average diameter of 44 nm found. When incorporated into the aerogels, the high degree of dispersion of the NiNPs result in the aerogel composites appearing to be black, as shown in Figure 2. Also from Figure 2, macroscopic morphology of the synthesised Ni/SiO₂ aerogel is monolith. SEM images of samples NS1, NS2 and NS3 are presented in Figure 3 (a), (b) and (c), respectively and reveals clearly the common nanoporous structure. The densities of nickel-silica aerogel composites, which were calculated from ratio of weight to volume, were found to be 0.23 g/cm³ (NS1), 0.13 g/cm³ (NS2) and 0.21 g/cm³ (NS3). Their respective BET surface areas were 537.09 m²/g, 679.74 m²/g, and 590.78 m²/g using the nitrogen gas adsorption at 77K. We have also characterised the surface area of NiNPs on its own and it is 10.25 m²/g, this is much smaller than measured composite NiNPs-silica aerogel material synthesised in this work. To compare the properties of the NiNPs/SiO₂ aerogels made by supercritical drying method in the past, we note that the reported surface area was in the range of 439-940 m²/g [18, 19] which is similar to our aerogels.

The STEM image of NS1 shown in Figure 4(a) further highlights the nanoporous nature of the aerogel composite. Elemental mapping, using EDX presented in Figures 4(b)-(d) demonstrates that the nickel nanoparticles are well dispersed within a uniform silica aerogel, which can be clearly observed by comparing the Figures 4 (a) and (d). Powder XRD from the NiNPs silica aerogel-composites shows a strong hump at 2θ values of around 20-25 degrees (Figure 5) which is amorphous silica [20]. Two sharp diffraction lines, with positions corresponding to the (111) and (200) crystal planes of nickel are present on the amorphous background demonstrating the presence of well-defined, crystalline NiNPs [21]. Figure 5 also shows the XRD pattern of the crystalline NiNPs used. It is evident from the XRD results that no oxidation of the NiNPs is observed during gelation process. It is known that a passive layer of Ni(OH)_x is formed at nickel particles surface in water which limits their oxidation

and leaching in alkaline, neutral and acidic environments [22]. The low dissolution of solid nickel in solutions is also because nickel has an electrochemical potential of -0.227V with reference to Standard Hydrogen Electrode (SHE), suggesting that the Ni leaching rate is slow in acidic solutions in absence of an oxidizing agent stronger than H⁺ [23]. The samples have been also analysed with XRD by using the Rietveld method to quantify the weight ratio of Ni and SiO₂ in the prepared aerogel samples. The nickel proportions by weight in the Ni/SiO₂ aerogels respectively are 3 wt%, 4.9 wt%, and 2.9 wt%. From the trend of weight ratio, it shows that sample NS3 does not match the trend of the NiNPs concentration from the gel preparation. We suggest that this is because at higher concentrations, some NiNPs might start to agglomerate and precipitate to the bottom of the wet gel during gelation period and therefore can't be embedded, because it will be washed out during solvent exchange.

To examine the catalytic activity of the nickel-silica aerogel composites for hydration reaction, a similar study of dispersed nickel nanoparticles alone in water was performed [14, 24]. It has been explained [14] that the route of hydration reaction of carbon dioxide is as follows:



When CO₂ dissolves in water, the resulting solution has a lower pH, because CO₂ reacts with water and produces carbonic acid. Figure 6 shows the pH change with time when CO₂ is bubbled in DI water alone, DI water containing SiO₂ aerogel or DI water containing NiNPs-SiO₂ aerogel composite. The rate of drop of pH in DI water alone (filled squares) is slower than that in the presence of the SiO₂ aerogel or the NiNPs-SiO₂ aerogel composite. The sudden decrease in pH after 40 sec is due to autocatalytic hydration of CO₂ [14]. In the presence of the SiO₂ aerogel (filled circles), there is a rapid decrease in the pH drop (as compared to DI water alone), indicating that the SiO₂ aerogel support also contributes to the catalytic hydration of CO₂. However, in the presence of the NiNPs-SiO₂ composite (filled triangles) there is still a further considerable increase in the rate of pH drop (as compared to DI water and pure SiO₂ aerogel), confirming a high rate of CO₂ hydration. These results with NiNPs-SiO₂ aerogel composite are similar to the results observed by Bhaduri and Šiller [14] for freely suspended NiNPs in DI water. The NiNPs-SiO₂ aerogel composite separated from solution were air dried at 60 °C for 60 min and then reused. Figure 6 shows the rate of pH change of reused NiNPs-SiO₂ aerogel composite (unfilled triangles). There is no considerable change observed in the catalytic activity of these NiNPs-SiO₂ aerogel composite suggesting they can be reused after drying.

During the catalytic experiments, pure SiO₂ aerogel in DI water disintegrates into smaller particles, however the NiNPs-SiO₂ aerogel composite do not. The structure of the NiNPs-SiO₂ aerogel composite remains intact even after separation under hydrated condition. However, after the drying process (for reuse) the NiNPs-SiO₂ aerogel composite disintegrate into smaller particles. This could be due to liquid water in the aerogel composite pore converting to vapour, which exerts the pressure on the porous structure and creates the cracks that lead to degradation of the porous structure of NiNPs-SiO₂ aerogel composite.

A key advantage of introducing the nanoparticle catalysts directly in the sol-gel process (Figure 7) is that the high degree of uniformity in distribution of NiNPs in silica matrix can be achieved. The NiNPs particles are introduced before gelation when they are effectively mixed with precursor, and upon silica gelation, the NiNPs become immobilised. After replacing the ageing solvent by hexane (low surface tension solvent), the drying capillarity of the nickel-embedded silica gel is reduced and the APD can proceed. Due to their high degree of dispersion (as evident in Figure 3) the NiNPs present a large surface area and thus serve as an effective catalyst for the hydration of CO₂.

5) CONCLUSIONS

Silica aerogels composites containing embedded NiNPs were successfully fabricated via ambient pressure drying method. The density of nickel-silica aerogel composites is in the range of 0.13-0.23 g/cm³ and BET surface area in the range of 537.09-679.74 m²/g. Our synthesis provides an approach to apply directly nickel nanoparticles in the sol-gel process of silica aerogel. The immobilised nickel nanoparticles in the aerogel matrix show catalytic activity for the hydration of carbon dioxide. These findings are significant for incorporation of NiNPs in carbon capture storage and utilization applications, without the need for external magnetic fields or magnetic separators [14, 24].

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REFERENCES

- [1] G. Hasegawa, *Studies on Porous Monolithic Materials Prepared via Sol–Gel Processes*, Springer, 2012.
- [2] E.F. Murphy, L. Schmid, T. Burgi, M. Maciejewski, A. Baiker, D. Gunther, M. Schneider, Nondestructive sol-gel immobilization of metal(salen) catalysts in silica aerogels and xerogels, *Chem Mater*, 13 (2001) 1296-1304.
- [3] Y. Wang, R. Wu, Y. Zhao, Effect of ZrO₂ promoter on structure and catalytic activity of the Ni/SiO₂ catalyst for CO methanation in hydrogen-rich gases, *Catalysis Today*, 158 (2010) 470-474.
- [4] J.L. Gurav, I.K. Jung, H.H. Park, E.S. Kang, D.Y. Nadargi, *Silica Aerogel: Synthesis and Applications*, *J Nanomater*, (2010).
- [5] L. Ji, H. Hayashi, H. Tomita, H. Okuchi, Y. Sato, T. Toshima, M. Iwashita, K. Mitsuoka, G. You, H. Ohno, Supercritical drying method for semiconductor substrate and supercritical drying apparatus, in, 2013.
- [6] S.S. Prakash, C.J. Brinker, A.J. Hurd, S.M. Rao, Silica Aerogel Films Prepared at Ambient-Pressure by Using Surface Derivatization to Induce Reversible Drying Shrinkage, *Nature*, 374 (1995) 439-443.
- [7] T.Y. Wei, T.F. Chang, S.Y. Lu, Y.C. Chang, Preparation of monolithic silica aerogel of low thermal conductivity by ambient pressure drying, *J Am Ceram Soc*, 90 (2007) 2003-2007.
- [8] A.P. Rao, A.V. Rao, J.L. Gurav, Effect of protic solvents on the physical properties of the ambient pressure dried hydrophobic silica aerogels using sodium silicate precursor, *J Porous Mat*, 15 (2008) 507-512.

- [9] A. Shlyakhtina, Y.J. Oh, Transparent SiO₂ aerogels prepared by ambient pressure drying with ternary azeotropes as components of pore fluid, *J Non-Cryst Solids*, 354 (2008) 1633-1642.
- [10] S.K. Hong, M.Y. Yoon, H.J. Hwang, Fabrication of Spherical Silica Aerogel Granules from Water Glass by Ambient Pressure Drying, *J Am Ceram Soc*, 94 (2011) 3198-3201.
- [11] Z.T. Mazraeh-shahi, A.M. Shoushtari, M. Abdouss, A.R. Bahramian, Relationship analysis of processing parameters with micro and macro structure of silica aerogel dried at ambient pressure, *J Non-Cryst Solids*, 376 (2013) 30-37.
- [12] S. He, Q. Jing, W. Yu, L. Mo, H. Lou, X. Zheng, Combination of CO₂ reforming and partial oxidation of methane to produce syngas over Ni/SiO₂ prepared with nickel citrate precursor, *Catalysis Today*, 148 (2009) 130-133.
- [13] J. Guo, J. Gao, B. Chen, Z. Hou, J. Fei, H. Lou, X. Zheng, Catalytic conversion of CH₄ and CO₂ to synthesis gas on Ni/SiO₂ catalysts containing Gd₂O₃ promoter, *International Journal of Hydrogen Energy*, 34 (2009) 8905-8911.
- [14] G.A. Bhaduri, L. Šiller, Nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage, *Catal Sci Technol*, 3 (2013) 1234-1239.
- [15] G.A. Bhaduri, R.A. Henderson, L. Šiller, Reply to the 'Comment on "Nickel nanoparticles catalyse reversible hydration of carbon dioxide for mineralization carbon capture and storage"' by D. Britt, *Catal. Sci. Technol.*, 2013, 3, DOI: 10.1039/C3CY00142C, *Catal Sci Technol*, 3 (2013) 2197-2198.
- [16] M. Bodor, R.M. Santos, Y.W. Chiang, M. Vlad, T. Van Gerven, Impacts of Nickel Nanoparticles on Mineral Carbonation, *The Scientific World Journal*, 2014 (2014) 10.
- [17] S. He, X. Zheng, L. Mo, W. Yu, H. Wang, Y. Luo, Characterization and catalytic properties of Ni/SiO₂ catalysts prepared with nickel citrate as precursor, *Materials Research Bulletin*, 49 (2014) 108-113.
- [18] M.F. Casula, A. Corrias, G. Paschina, Nickel oxide-silica and nickel-silica aerogel and xerogel nanocomposite materials, *Journal of Materials Research*, 15 (2000) 2187-2194.
- [19] S. Martinez, M. Moreno-Manas, A. Vallribera, U. Schubert, A. Roig, E. Molins, Highly dispersed nickel and palladium nanoparticle silica aerogels: sol-gel processing of tethered metal complexes and application as catalysts in the Mizoroki-Heck reaction, *New Journal of Chemistry*, 30 (2006) 1093-1097.
- [20] X. Chen, J. Jiang, F. Yan, S. Tian, K. Li, A novel low temperature vapor phase hydrolysis method for the production of nano-structured silica materials using silicon tetrachloride, *RSC Advances*, 4 (2014) 8703-8710.
- [21] H.-J. Song, X.-H. Jia, X.-F. Yang, H. Tang, Y. Li, Y.-T. Su, Controllable synthesis of monodisperse polyhedral nickel nanocrystals, *CrystEngComm*, 14 (2012) 405-410.
- [22] N. Hernández, R. Moreno, A.J. Sánchez-Herencia, J.L.G. Fierro, Surface Behavior of Nickel Powders in Aqueous Suspensions, *The Journal of Physical Chemistry B*, 109 (2005) 4470-4474.
- [23] L.L. Shreir, R.A. Jarman, G.T. Burstein, Corrosion Volume 1 Metal/Environment Reactions, in, Butterworth Heinemann, London, 1994, pp. 4:122-124:123.
- [24] L. Šiller, G.A. Bhaduri, Carbon capture, PCT/GB2013/051243, World Patent WO2013/171480 (A2).

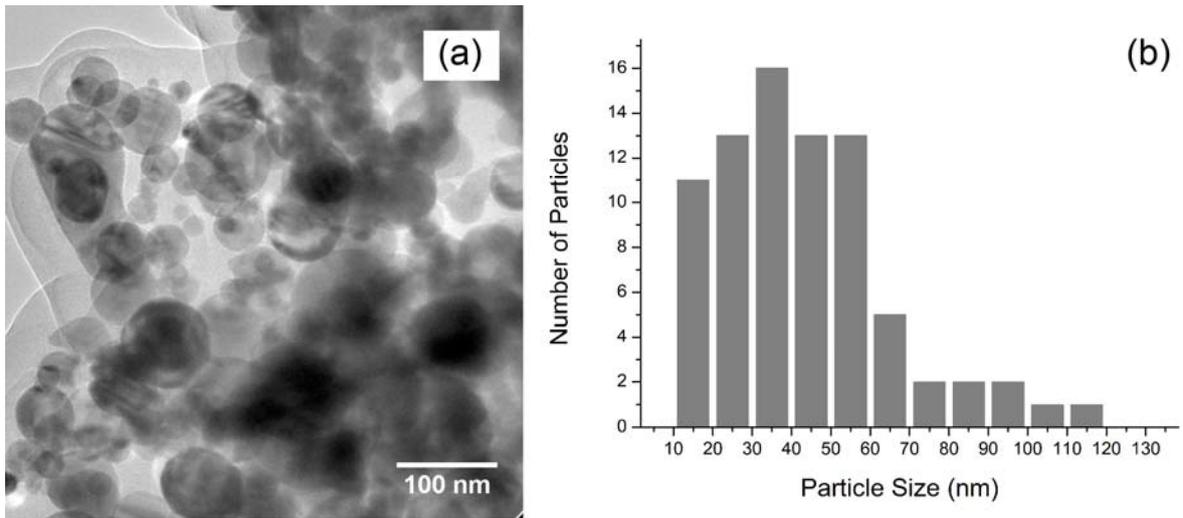


Figure 1: (a) TEM image of nickel nanoparticles; (b) Nanoparticle size distribution determined by TEM.

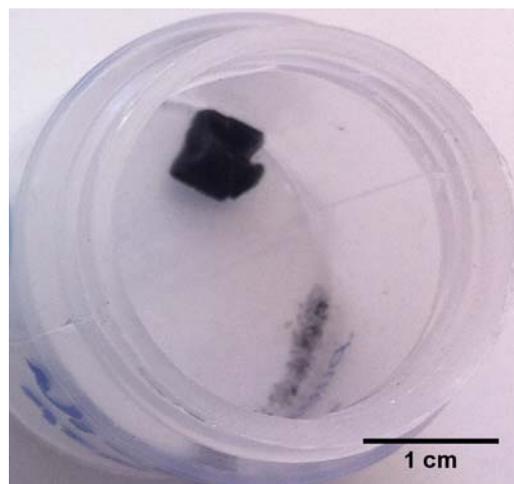


Figure 2: Photo of the nickel-silica aerogel composite.

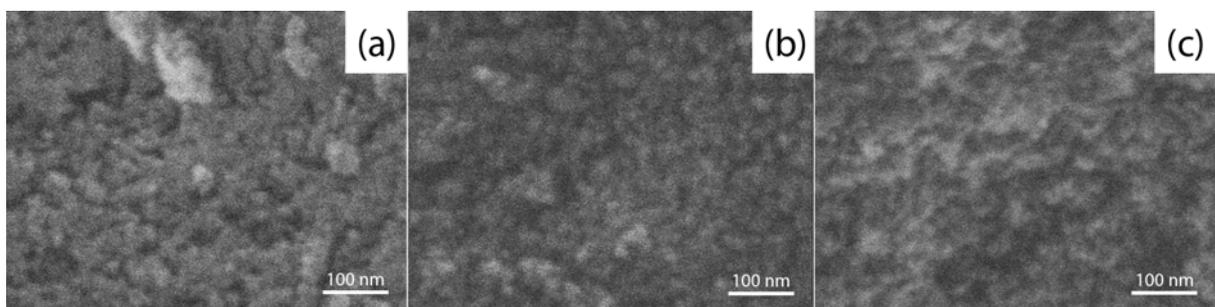


Figure 3: SEM image of the nickel-silica aerogel composites containing different concentrations of nickel: (a) NS1; (b) NS2; (c) NS3.

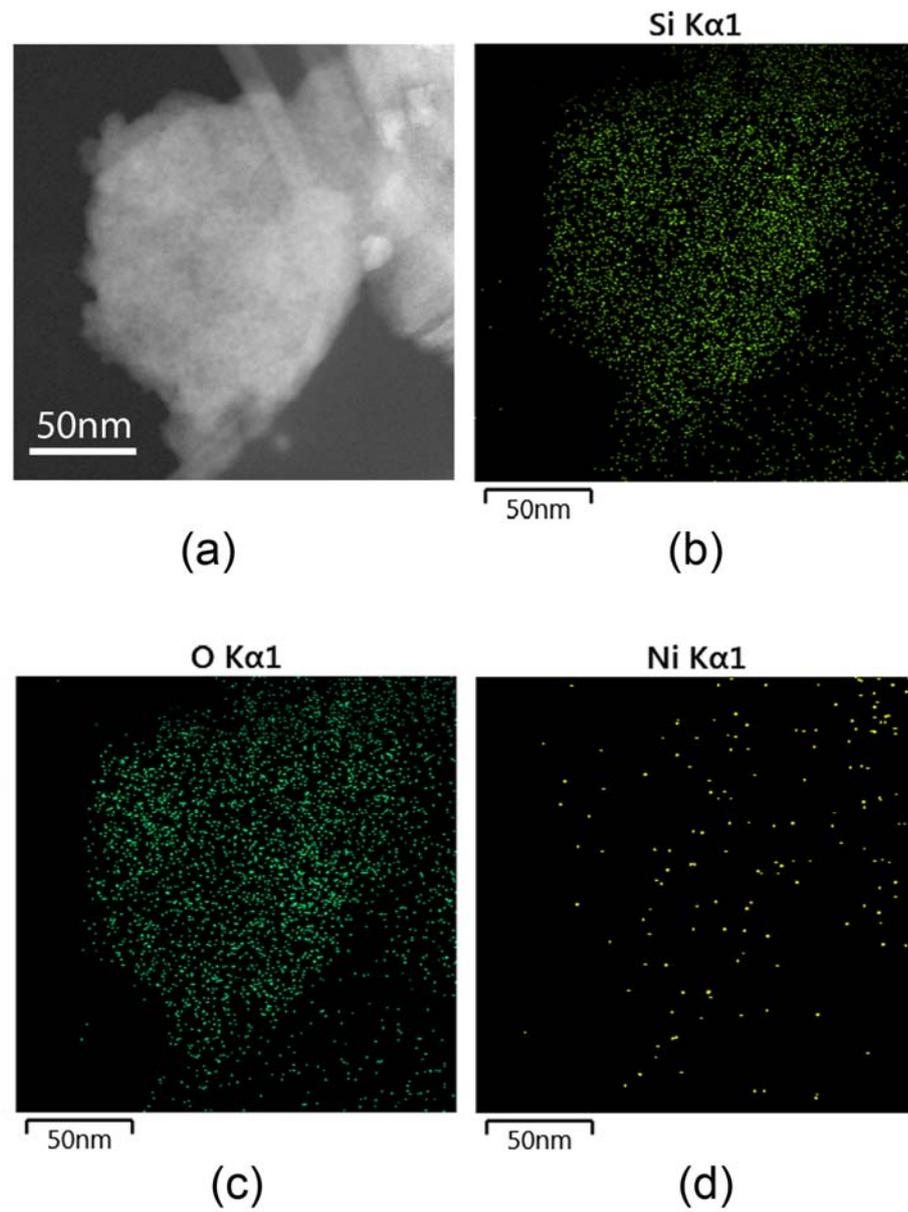


Figure 4: (a) STEM image of ambient pressure dried nickel-silica aerogel composite NS1 and corresponding EDX mapping for (b) Si; (c) O; (d) Ni.

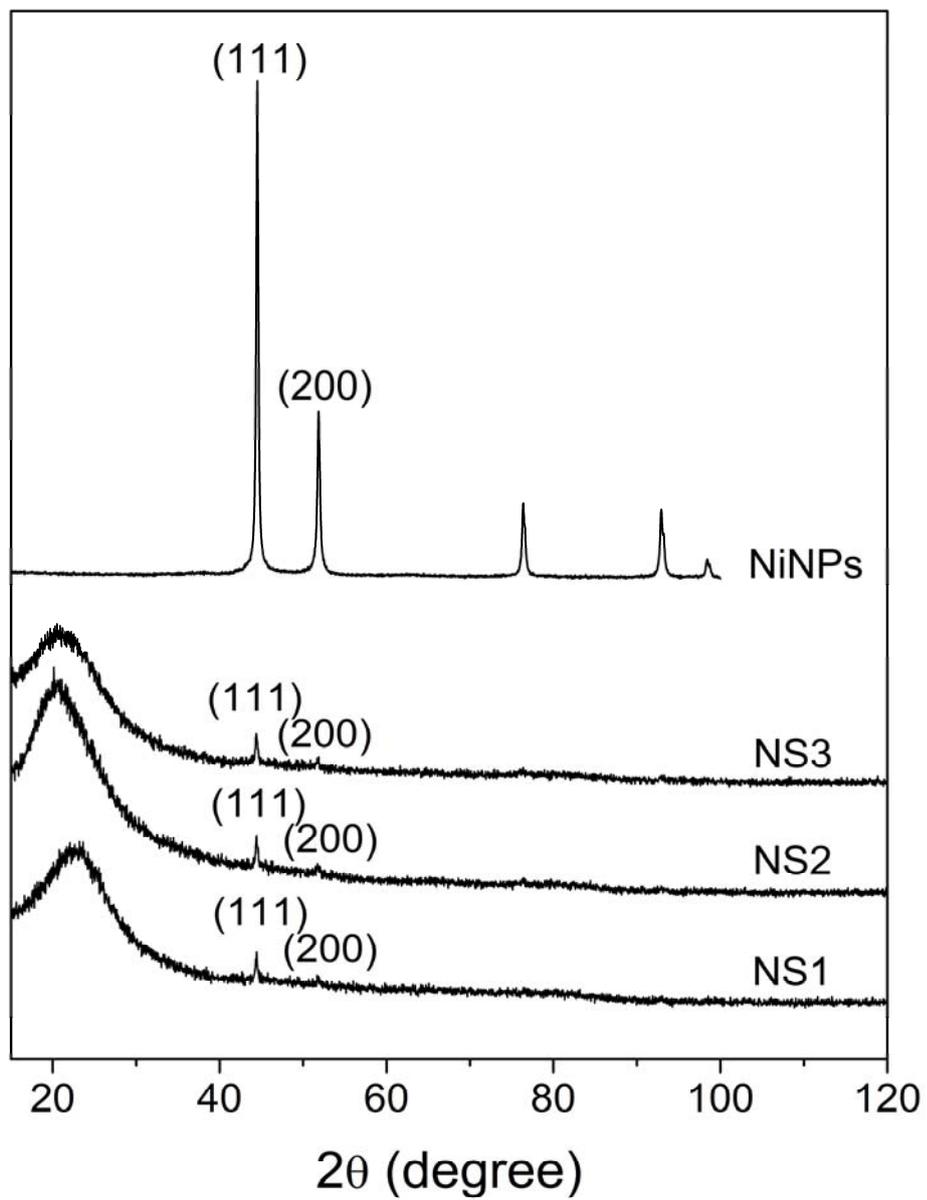


Figure 5: Powder XRD scans from nickel nanoparticles (NiNPs) and nickel-embedded silica aerogel composites NS1, NS2 and NS3.

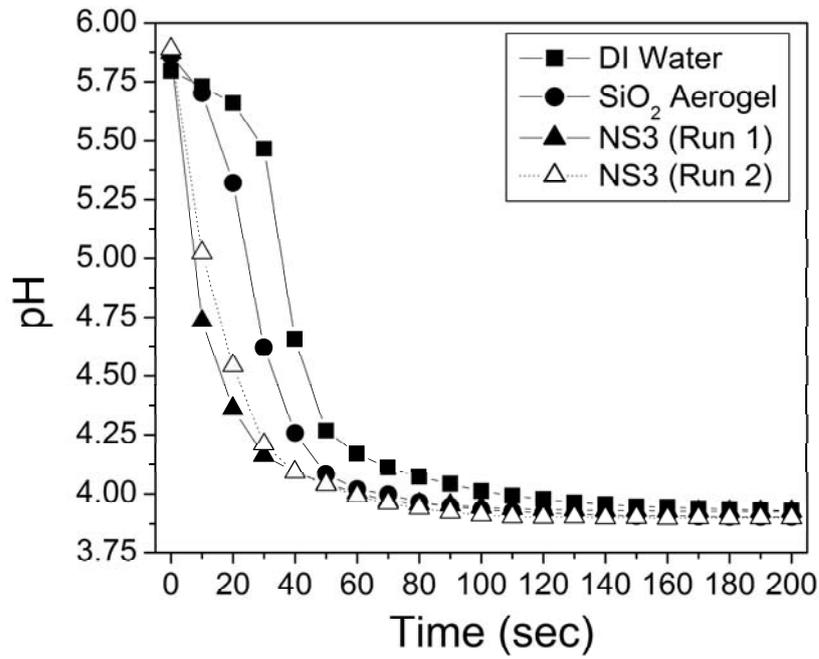


Figure 6: pH change as a function of time upon bubbling 100% CO₂ through de-ionised water with without aerogel (filled squares), with SiO₂ aerogel without NiNPs (filled circles), with NiNPs-SiO₂ aerogel composite (filled triangles) and with NiNPs-SiO₂ aerogel composite reused after drying at 60 °C for 60 minutes (unfilled triangles).

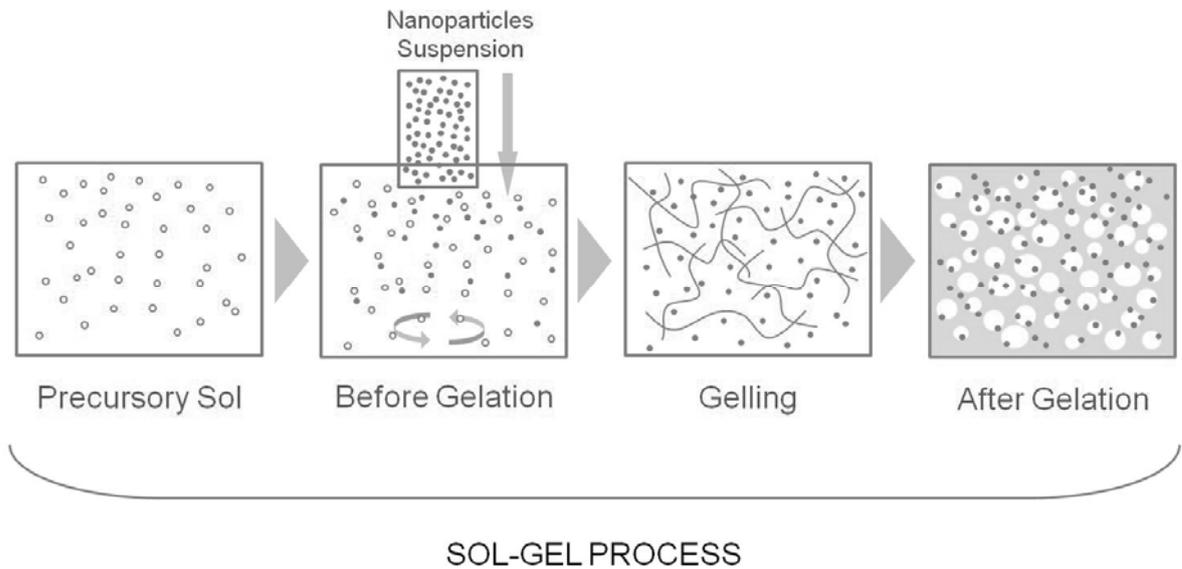


Figure 7: Schematic diagram of the sol-gel process for the production of the aerogel composite.