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# Synthesis and formation mechanism of flowerlike architectures assembled from ultrathin NiO nanoflakes and their adsorption to malachite green and acid red in water

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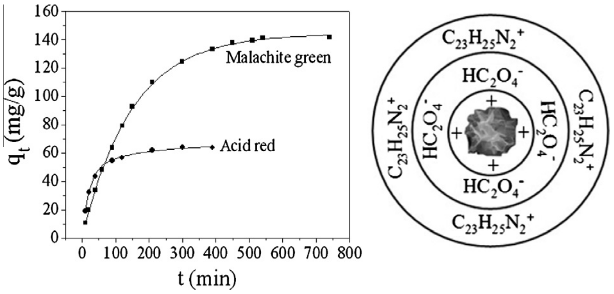
## HIGHLIGHTS

- $Ni(OH)_2 \cdot 0.75H_2O$ flowerlike architectures are synthesized by a hydrothermal process.
- NiO flowerlike architectures are obtained by annealing $Ni(OH)_2 \cdot 0.75H_2O$ precursors.
- NiO flowerlike architectures are constructed with ultrathin nanoflakes.
- NiO flowerlike architectures show excellent adsorbent ability to Malachite green.
- The adsorption capacity depends on structures of adsorbent and dye molecule.

## GRAPHICAL ABSTRACT

The as-obtained NiO flowerlike nanoarchitectures exhibit excellent adsorption capability for Malachite green with a maximum capacity of 142.08 mg/g, and the excellent performance is attributed to their unique hierarchical structure and high surface area as well as molecule structure of Malachite green.



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## ABSTRACT

The flowerlike architectures assembled from ultrathin NiO nanoflakes have been synthesized by a hydrothermal reaction of $Ni(NO_3)_2$ with $H_2O$ in the presence of glycerin and subsequent annealing at 400 °C 2 h in air. The NiO flowerlike architectures with diameters of 7–10 μm are assembled from the nanoflakes with thicknesses of 20–30 nm. The formation of ultrathin $Ni(OH)_2 \cdot 0.75H_2O$ nanoflakes results from the selective adsorption of glycerin on the (100) prismatic faces. The secondary nucleation and growth of $Ni(OH)_2 \cdot 0.75H_2O$ nanoflakes result in the formation of flowerlike architectures. When the NiO flowerlike nanoarchitectures are served as the adsorbent for malachite green (MG) and acid red (AR) in water, the adsorption capacity for MG and AR are 142.08 and 64.23 mg/g, respectively. The high adsorption capacity of the as-prepared NiO flowerlike architectures for the MG removal could be attributed to the unique hierarchical structure and high surface area of the adsorbents as well as molecule structure of MG.

## 1. Introduction

In recent years, the design and fabrication of transition metal hydroxide or oxide self-assembled 3-dimensional nanostructures have attracted a lot of attention because of their higher specific surface area and lower density as well as wide potential applications in catalysis, drug delivery, separation, chemical reaction, and adsorbents [1–8]. Nickel oxide (NiO), an important transition metal oxide can be employed in various fields, such as catalysis [9], gas sensors [10], lithium-ion batteries [11] and supercapacitors [12,13] due to its high chemical and thermal stability,

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and environmental benignity. The NiO nanoflake networks [14], solid and hollow microspheres assembled from nanoflakes [15–17], urchin-like architectures assembled from nanorods [18] have been synthesized by various chemical methods. The hollow microspheres constructed with NiO nanoflakes were found to exhibit ferromagnetic behaviors [19]. The hierarchical NiO nanorod modified biosensor exhibits excellent sensing performance for determination of l-ascorbic acid [20]. The flower-like structures assembled with NiO nanoflakes have been used to fabricate a hybrid capacitor cell giving higher discharge capacitance and cycle stability for 2000 cycles [13]. However, synthesis of superstructure assembled from ultrathin NiO nanoflakes is still a challenge, and the mechanism of self-organization remains far from clear.

Very recently, NiO nanoflake networks [21], solid and hollow microspheres assembled from nanoflakes [15,17] as well as hierarchical porous architectures [22] have been employed in water treatment. These self-assembled NiO 3-dimensional nanostructures were found to be effective adsorbents for the removal of Congo red pollutant from wastewater. However, NiO nanomaterials have never been used to remove malachite green (MG) and acid red (AR) pollutants from waste water.

MG and AR are used regularly in textile, pulp and paper, leather, and paint manufacture and are discharged with effluents. These colors are generally nonbiodegradable and pose serious environmental problems. MG has been known to cause diseases like eye burns, fast breathing, profuse sweating, and cancer at different parts of humanbody [23]. AR is a synthetic azo dye with potential carcinogenicity [24]. The activated carbon derived from rice husk has been used to remove MG, but it offers a poor efficiency ($q_t$ = 11.39 mg/g) [23].

Herein, we report the synthesis of flowerlike $Ni(OH)_2 \cdot 0.75H_2O$ nanoarchitectures by a hydrothermal reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with $H_2O$ in the presence of glycerin. By calcination at an elevated temperature, the as synthesized $Ni(OH)_2 \cdot 0.75H_2O$ precursors were transformed into NiO, and the products maintained their original flowerlike morphology. The reaction mechanism leading to the $Ni(OH)_2 \cdot 0.75H_2O$ precursor and the self-assembly process are discussed. The as-obtained NiO nanomaterials were used as adsorbent in waste-water treatment, and showed an excellent ability to remove MG and AR pollutants from waste water.

## 2. Experimental section

### 2.1. Sample preparation

All reagents used were of analytical purity and were directly used without special purification. Flower-like structure assembled from NiO nanoflakes: In a typical procedure, 0.290 g (1.0 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$, 20.0 mL of $H_2O$ and 4.0 mL of glycerin were put into a 50 mL beaker. The mixture was then stirred for 10 min to form a clear solution. The clear solution was transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity. The autoclave was sealed and heated at 200 °C for 12 h. After the heat treatment, the autoclave was cooled to room temperature naturally. The product was collected by centrifugation, washed three times with deionized water and ethanol, respectively, and then dried naturally in air, the resultant product is light green in color. Finally, the as-prepared light green products were heated to 400 °C at a rate of 1.0 °C/min in a muffle furnace, and then maintained at 400 °C for 2 h. The resultant samples were collected for characterization.

### 2.2. Characterization

The as-prepared products were characterized and analyzed by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared (IR) spectroscopy. SEM images were obtained using a FEI Quanta 200 scanning electron microscope at an accelerating voltage of 20 kV. The XRD analysis was performed using a Rigaku D/MAX-IIIC X-ray diffractometer with Cu Kα1 radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA. The scanning speed was 8°/min. TEM and electron diffraction images were obtained using a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Samples for HRTEM were prepared by dispersing NiO powders on a carbon-coated copper grid. The IR spectrum was recorded using a Nicolet Avatar 360E.S.P Fourier transform IR spectrophotometer at room temperature. The Brunauer–Emmett–Teller (BET) specific surface area measurement was performed by $N_2$ gas adsorption using an America Micromeritics ASAP 2020 surface analytical instrument.

### 2.3. Adsorption kinetic and equilibrium experiments

The adsorption kinetic experiments were carried out by adding 10 mg of as-prepared flower-like NiO powder (adsorbent) to a 100 mL beakers filled with 30 mL of 50 mg/L of aqueous MG or AR solution at room temperature. The aqueous samples were taken at pre-set time intervals. The NiO adsorbent is collected by centrifugation, and the concentrations of MG or AR were measured using UV/vis spectrophotometer (HITACHI U-2910). The amount of adsorption at time $t$, $q_t$ (mg/g), was calculated by equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where $C_0$ and $C_t$ (mg/L) are the liquid phase concentrations of MG or AR at initial and any time $t$, respectively, $V$(L) is the volume of the solution and $W$(g) is the mass of adsorbent used.

Adsorption equilibrium experiments were carried out by adding 10 mg of the as-prepared flower-like NiO powder (adsorbent) to a 100 mL beakers filled with 30 mL of 50 mg/L of aqueous MG or AR solution at room temperature. After 740 min for MG or 390 min for AR, the final concentration of MG or AR in the solution was measured. The amount of MG or AR at equilibrium $q_e$ (mg/g) on the adsorbent samples was calculated from the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where $C_0$ and $C_e$ (mg/L) are the liquid phase concentrations of dyestuff at the initial and equilibrium states, respectively, $V$ (L) is the volume of the solution and $W$ (g) is the mass of adsorbent used.

## 3. Results and discussion

### 3.1. SEM, XRD and TEM analysis

The $Ni(OH)_2 \cdot 0.75H_2O$ precursors obtained via the hydrothermal reaction at 200 °C for 12 h were characterized with XRD and SEM, and the results are shown in Fig. 1. The SEM observations indicate that the products consist of flowerlike architectures with the diameters of 7–10 μm. The flowerlike architectures are assembled from nanoflakes with the thickness of about 20–30 nm (Fig. 1a and b). The corresponding XRD patterns are displayed in Fig. 1c. The diffraction peaks were in good agreement with those for $Ni(OH)_2 \cdot 0.75H_2O$ powder obtained from the International Center of Diffraction Data Card (Hematite, Joint Committee on Powder Diffraction Standards (JCPDS card no. 38-0715). The peaks at $2\theta = 11.3°$, 33.5°, 34.4° and 60.0° can be assigned to (003), (101), (012) and (110) diffraction lines of $Ni(OH)_2 \cdot 0.75H_2O$ with the rhombohedral structure, respectively.

After the synthesis of the precursors, we investigated the effect of calcination on the crystallization and morphology of the products. Fig. 2a and b shows the SEM images of the products obtained