Due to their special role in surface atoms, charge transfer channels and catalytic active sites, morphologies of electrocatalysts produce morphology–property effects in electrocatalysis. To study this effect, a series of stoichiometric ratios of nickel and selenium, $\text{Ni}_{1-x}\text{Se}$, with different surface atom concentrations and morphologies, were synthesized on graphene via several thermal-reduction methods. In addition, we systematically investigated the morphology–property effect of a $\text{Ni}_{1-x}\text{Se}$ series based on electrochemical impedance spectra (EIS), cyclic voltammetry (CV), and Tafel polarization experiments. The $\text{Ni}$_{1.2}$\text{Se}$ nanoparticles demonstrated superior performance in electrocatalysis than that of $\text{Ni}_{0.85}\text{Se}$ nanoflakes. After nanoflakes were assembled to form nanospheres, $\text{Ni}_{0.85}\text{Se}$ nanospheres exhibited higher catalytic activity in terms of reducing $\text{I}_3^-$ and multiple times faster charge-transfer velocities than those of $\text{Ni}_{0.85}\text{Se}$ nanoflakes. Synthetically electrocatalytic properties of $\text{Ni}_{1-x}\text{Se}$ series were also measured as counter cells (CEs) of dye-sensitized solar cells (DSSCs). $\text{Ni}_{1.2}$\text{Se}$ nanoparticles showed a higher power conversion efficiency ($\text{PCE}$) (7.33%) in a DSSC than when using a Pt CE (7.02%). The performance of $\text{Ni}_{0.85}\text{Se}$ nanoparticles (6.57%) was worse than that of $\text{Ni}_{0.85}\text{Se}$ nanoflakes and Pt CEs. Simultaneously the self-assembled $\text{Ni}_{1.2}$\text{Se}$ nanospheres (7.37%) exhibited similar to that found with $\text{Ni}_{0.85}\text{Se}$ nanospheres.

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Fabrication and characterization of Ni$_1$$_3$Se@graphene series thin films.— A Ni$_1$$_3$Se@graphene series materials slurry was made in ethanol by mixing 0.1 g Ni$_1$$_3$Se@graphene powder with 0.025 g PEG20000 which was used as a dispersant as well as a binder and stirred continuously. Then, a thin film was made using a doctor-blade to wipe slurry on FTO conductive glass (LOF, TEC-15, 15 W per square). After the film was steady, the conductive glass with the thin film was heated at 400°C for 1 h under the protection of argon, and the Ni$_1$$_3$Se@graphene thin film was achieved.

All of the electrochemical measurements were measured with the Zahner IM6 exelectrochemical workstation. Photocurrent—voltage curves were conducted in simulated AM 1.5 illumination (100 mW cm$^{-2}$, Trustech CHF-XM-500W) with a Keithley digital source meter (Keithley 2410, USA). Cyclic voltammetry (CV) was recorded with a three electrode system on the ex-electrochemical workstation. Pt was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The solution of 10.0 mM LiI, 1.0 mM I$_2$ and 0.1 M LiClO$_4$ in acetonitrile served as the electrolyte. Electrochemical impedance spectra (EIS) analysis was conducted at zero bias potential and the impedance data covered a frequency range of 0.1 Hz to 1 MHz. The amplitude of the sinusoidal AC voltage signal was 5 mV. The analyses of the resulting impedance spectra were conducted using Zview 2.0. Tafel polarization measurement was employed in a symmetrical three electrode system on the Zahner IM6 ex-electrochemical workstation. Pt was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The solution of 0.05 M I$_2$, 0.1 M LiI, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butyl pyridine with acetonitrile as the solvent. The scan rate was 20 mV s$^{-1}$, and the voltage range was −1.0 to 1.0 V.

**Results and Discussion**

Characterization of Ni$_1$$_3$Se@graphene series— X-ray diffraction (XRD) was performed to verify the phase structures of Ni$_1$$_3$Se nanosheets. Figure 1 shows the XRD patterns of Ni$_1$$_3$Se nanoparticles, Ni$_1$$_3$Se nanosheets and Ni$_1$$_3$Se nanofibers. All of the diffraction peaks in three patterns can be readily indexed as pure-phase compounds of hexagonal Ni$_1$$_3$Se (JCPDS no. 18-0888, vertical line in Fig. 1). The diffraction peak at about 16.84° also belongs to hexagonal Ni$_1$$_3$Se; however, the data derived from XRD analysis software (Jade) does not provide the relevant information. No impurities, such as selenium, nickel oxide or other phases of nickel selenides, were observed, indicating that the products were pure phase.

The morphologies and structures of the as-prepared Ni$_1$$_3$Se samples were studied by SEM and TEM. The TEM images of Ni$_1$$_3$Se nanoparticles in Figs. 2a and 2b revealed that the nanoparticles with diameters of ~20 nm dispersed in situ on graphene uniformly. Careful observation also finds that the shadows in Figs. 2a and 2b were graphene. The well-dispersed nanoparticles on the graphene increased the number of catalytic active sites. As the SEM image (Fig. 2d) shows, each Ni$_1$$_3$Se nanosheet, with the size of 400~500 nm, is composed of numerous primary nanoparticles. In the TEM image of Fig. 2e, Ni$_1$$_3$Se nanosheets can be observed to be porous among nanoparticles. The porous structure is beneficial to accommodating I$_3^−$ molecules between nanosheets through the intercalation process, as well as the collision among I$_3^−$ and catalytic active sites. The morphology and structure of Ni$_1$$_3$Se nanosheets are shown in Figs. 2g and 2h, and Ni$_1$$_3$Se nanoparticles show irregular plate-like morphology with a side length of 30~60 nm. Furthermore, it can be clearly observed that nanosheets grow on graphene nanosheets. TEM and SEM images demonstrate that Ni$_1$$_3$Se nanoparticles, Ni$_1$$_3$Se nanosheets, and Ni$_1$$_3$Se nanofibers have been successfully synthesized in situ on graphene. More detailed information about morphologies of three Ni$_1$$_3$Se samples are shown in supporting information, Se Figure S1 through S3.

The chemical composition of these samples was further investigated by energy dispersive spectrometer (EDS) (Figs. 3a–3c). EDS profiles indicate the existence of Cu, Ni, Se (Fig. 3f). The Cu peak is from the copper wire mesh, while the Ni and Se peaks are from Ni$_1$$_3$Se products. The peaks of the elements Ni and Se were detected in the EDS pattern and the molar ratio was calculated as 0.90:1, 0.89:1, and 0.86:1 for Ni$_1$$_3$Se nanoparticles, Ni$_1$$_3$Se nanosheets, and Ni$_1$$_3$Se nanofibers, respectively.

**Electrocatalytic property of the Ni$_1$$_3$Se@graphene series.—** EIS experiments were carried out on two symmetric thin films of Ni$_1$$_3$Se@graphene samples to confirm the charge transfer and electrolyte molecules diffusion between CEs materials and electrolytes. As is shown in Fig. 4, two features are observable in the recorded spectra: a low-frequency feature due to the electrolyte diffusion and a high-frequency arc due to the charge transfer in the interface. The Nyquist plots obtained with EIS measurements can be simulated by the equivalent circuit (inset in Fig. 4) and the relevant values are summarized in Table 1. In an equivalent circuit, series resistance ($R_s$) is deduced by high-frequency cut on the real axis ($Z'$ axis), and charge-transfer resistance ($R_{ct}$) is derived from the radius of high-frequency
Figure 3. EDS profiles of Ni$_{1-x}$Se nanoparticles (a), Ni$_{1-x}$Se nanospheres (b), and Ni$_{1-x}$Se nanoplates (c). Elements analysis and molar ratio of Ni/Se are given.

The impedance spectra indicates that the $R_{ct}$ value of Ni$_{1-x}$Se nanospheres (0.50 Ω) is smaller than Ni$_{1-x}$Se nanoparticles (0.73 Ω), Pt (1.28 Ω) and Ni$_{1-x}$Se nanoplates (1.60 Ω) CEs. In addition, the $R_{ct}$ value is in a contradictory relationship with the charge-transfer ability. From the analysis of $R_{ct}$ values, Ni$_{1-x}$Se nanoplates had lower charge-transfer ability than Ni$_{1-x}$Se nanoparticles. Nevertheless, the connected nanoplates increased charge transfer channels and decreased the electrons hop among 2D nanoplates structure, thus Ni$_{1-x}$Se nanospheres exhibited multiple times faster charge-transfer velocity than Ni$_{1-x}$Se nanoparticles, even better than Ni$_{1-x}$Se nanoparticles and Pt.

In order to understand the catalytic activity of the resultant film, the electrochemical behavior of Ni$_{1-x}$Se@graphene series has been studied by CV. The electrochemical measurements indicate that all of the samples exhibit a perfect reversible response, a characteristic of Ni$_{1-x}$Se electrodes with rapid electron-transfer kinetics. CV profiles of three Ni$_{1-x}$Se electrodes at a scan rate of 25 mV s$^{-1}$ are presented in Fig. 5. Two pairs of oxidation and reduction peaks are obviously observed for Ni$_{1-x}$Se@graphene series and Pt electrodes. From left to right, the two couples of the redox current peaks in the CV curves correspond to the I$_3^−$/I$^−$ and I$_3^−$/I$_2$ redox reactions. The catalytic activities of different CEs can be analyzed by the peak-to-peak

| CEs                  | $R_s$/Ohm | $R_{ct}$/Ohm | $J_{lim}$/log (mA cm$^{-2}$) | $J_0$/log (mA cm$^{-2}$) | $E_{pp}$/mV |
|----------------------|-----------|------------|----------------------------|-------------------------|------------|
| Ni$_{1-x}$Se nanoparticles | 11.55     | 0.73       | 1.89                       | 0.55                    | 351        |
| Ni$_{1-x}$Se nanospheres | 12.00     | 0.50       | 1.93                       | 0.65                    | 255        |
| Ni$_{1-x}$Se nanoplates  | 12.34     | 1.60       | 1.83                       | 0.49                    | 399        |
| Pt                   | 12.20     | 1.28       | 1.74                       | 0.55                    | 329        |

Figure 4. Nyquist plots for symmetric cells (CE/electrolyte/CE) fabricated with Ni$_{1-x}$Se nanoparticles, Ni$_{1-x}$Se nanospheres, Ni$_{1-x}$Se nanoplates, and Pt CEs. The inset is the equivalent circuit of DSSCs.

Figure 5. Cyclic voltammograms of Ni$_{1-x}$Se nanoparticles, Ni$_{1-x}$Se nanospheres, Ni$_{1-x}$Se nanoplates, and Pt CEs for the I$_3^−$/I$^−$ redox species recorded at a scan rate of 25 mV s$^{-1}$. 

Table I. EIS, Tafel polarization and CV parameters of Ni$_{1-x}$Se nanoparticles, Ni$_{1-x}$Se nanospheres, Ni$_{1-x}$Se nanoplates, and Pt CEs.
Figure 6. Cyclic voltammograms of Ni$_{1-x}$Se nanoparticles (a), Ni$_{1-x}$Se nanospheres (b), and Ni$_{1-x}$Se nanoplates (c) CEs for the I$_3^-$/I$^-$ redox species recorded at an increasing scan rate from 10 to 100 mV s$^{-1}$. The relationship between the anodic and cathodic oxidation peak current density versus the square root of the scan rate for the Ni$_{1-x}$Se series is illustrated (d).

separation ($E_{pp}$) and the peak current density ($J_A$) in lower potential. $E_{pp}$ is negatively correlated with the standard electrochemical rate constant and has positive correlation with overpotential losses. In addition, the $E_{pp}$ values presented the trend of Ni$_{1-x}$Se nanoplates (399 mV) > Ni$_{1-x}$Se nanospheres (351 mV) > Ni$_{1-x}$Se nanoplates (255 mV), which reveal the reverse order of catalytic activity. The better catalytic activity of Ni$_{1-x}$Se nanoparticles than Ni$_{1-x}$Se nanoplates results from the more catalytic active sites. After nanoplates assembled to form nanospheres, the interior reaction space of nanospheres increased the collision among I$_3^-$ and catalytic active sites. Simultaneously, the assembled nanoplates decreased the diffusion distance of I$_3^-$/I$^-$ redox and enhanced the activity of catalytic active sites. Therefore Ni$_{1-x}$Se nanospheres showed enhanced catalytic activity compared to Ni$_{1-x}$Se nanoplates. Furthermore, Ni$_{1-x}$Se nanospheres also showed a higher $J_A$ value than Ni$_{1-x}$Se nanoparticles and Ni$_{1-x}$Se nanoplates, which further reveals the best catalytic activity of Ni$_{1-x}$Se nanospheres among Ni$_{1-x}$Se@graphene series. Results of CV experiments agree with the EIS experiments, and relevant parameters are shown in Table I.

The CV experiments of three electrodes at different scan rates from 10 to 100 mV s$^{-1}$ were also performed and CV profiles are shown in Figs. 6a–6c. Depending on the scan rate, outward extension of all the peaks can be observed. The CV measurements at different scan rates indicate that all the Ni$_{1-x}$Se samples exhibit a perfect reversible response, a characteristic of Ni$_{1-x}$Se electrodes with rapid electron-transfer kinetics. The anodic and cathodic current density as a function of the square root of scan rate for the three samples is shown in Fig. 6d, with Ni$_{1-x}$Se nanospheres electrode displaying the highest current density. All of the lines of three Ni$_{1-x}$Se electrodes in anodic and cathodic zone are almost linear, as shown in Fig. 6d, except the mismatch of Ni$_{1-x}$Se nanospheres within experimental error. The linear relationship indicates that the redox reaction of I$^-$/I$_3^-$ couples at the three Ni$_{1-x}$Se electrodes belongs to a diffusion-controlled transport and obeys the Randles–Sevcik equation.

Tafel polarization experiments were carried out with two identical as-prepared thin films to measure the information of electrochemical polarization and concentration polarization arising from different charge exchange and electrolyte diffusion rates at the CE/electrolyte interface. The results are shown in Fig. 7, and the corresponding parameters are listed in Table I. The polarization zone of the Tafel polarization curve corresponds to the high-frequency region of Nyquist.
plots, and the diffusion zone relates to the low-frequency region. The large slope for the anodic or cathodic branches indicates a high exchange current density ($J_0$), which indicates good catalytic activity toward triiodide reduction of CEs. As shown in Table I, the calculated $J_0$ values of Ni$_1$Se nanoparticles, Ni$_1$Se nanospheres, and Ni$_1$Se nanospheres were 0.65 log (mA cm$^{-2}$), 0.55 log (mA cm$^{-2}$), and 0.49 log (mA cm$^{-2}$), respectively. The intersection of the cathodic branch with the Y-axis can be considered as the limiting diffusion current density ($J_{lim}$), which is determined by the diffusion properties of the redox couple and the CE materials. As shown in Table I, the values of $J_{lim}$ also follow an order of Ni$_1$Se nanoparticles > Ni$_1$Se nanospheres > Ni$_1$Se nanoplates. Both $J_0$ and $J_{lim}$ match well with the results of CV and EIS experiments, and Tafel polarization experiments further demonstrate the catalytic activity for reducing I$_3^-$ and diffusion coefficient of I$_3^-$ in Ni$_1$Se series.

Current density–voltage ($J$–$V$) measurements under the AM 1.5 G condition were carried out to evaluate the synthetically electrocatalytic properties of Ni$_1$Se series, which are shown in Fig. 8. The corresponding values of open-circuit voltage ($V_{oc}$), short-circuit current ($J_sc$), fill factor (FF), and PCE are summarized in Table II. Note that the DSSC with Ni$_1$Se series also presents a significant trend of $J_sc$ in Ni$_1$Se nanospheres > Ni$_1$Se nanoparticles > Pt > Ni$_1$Se nanospheres, which is in good agreement with the tendency of PCE. Due to the high charge-transfer ability and many catalytic active sites of nanoparticles, Ni$_1$Se nanoparticles exhibited excellent electrocatalytic performance with high PCE (7.33%) and $J_sc$ (14.80 mA cm$^{-2}$) values. EIS, CV, and Tafel polarization experiments demonstrated that Ni$_1$Se nanoparticles had a lower charge transfer ability and catalytic activity than Ni$_1$Se nanospheres. The poor electrocatalytic property of Ni$_1$Se nanoparticles resulted in slow and incomplete reduction of I$_3^-$, and impeded photogenerated electron transfer at the Ni$_1$Se nanoparticles/electrolyte interface. Thus, Ni$_1$Se nanospheres showed lower $J_sc$ (12.80 mA cm$^{-2}$) and PCE (6.57%) than Ni$_1$Se nanoparticles. As mentioned above, the assembled structure of nanospheres possessed large internal surface area and can accommodate I$_3^-$ molecules among nanospheres through intercalation process. Together with the enhanced collision among I$_3^-$ and catalytic active sites as well as the improved charge transfer among nanospheres, Ni$_1$Se nanospheres exhibited higher $J_0$ (15.20 mA cm$^{-2}$) and PCE (7.37%) than those of Ni$_1$Se nanospheres, even were similar with those of Ni$_1$Se nanoparticles. Moreover, the $J_0$ and PCE values of Ni$_1$Se nanoparticles and Ni$_1$Se nanospheres were higher than those of Pt CE ($J_0$ = 14.00 mA cm$^{-2}$, PCE = 7.02%).

**Table II. Electrocatalytic property of DSSCs with Ni$_1$Se nanoparticles, Ni$_1$Se nanospheres, Ni$_1$Se nanoplates, and Pt CEs.**

| CEs              | $V_{oc}$/V | $J_sc$/mA cm$^{-2}$ | FF  | $\eta$/% |
|------------------|----------|---------------------|-----|----------|
| Ni$_1$Se nanoparticles | 0.75     | 14.80               | 0.66| 7.33     |
| Ni$_1$Se nanospheres | 0.77     | 15.20               | 0.63| 7.37     |
| Ni$_1$Se nanoplates | 0.79     | 12.80               | 0.65| 6.57     |
| Pt               | 0.76     | 14.00               | 0.66| 7.02     |

**Conclusions**

Ni$_1$Se@graphene series with specific stoichiometry ratio and different morphologies were successfully synthesized in situ on graphene with different selenium sources, solvents, and proportions of Ni/Se. The results demonstrate that Ni$_1$Se nanoparticles exhibit better electrocatalytic property than that of Ni$_1$Se nanospheres. However, the self-assembled structure of nanospheres endowed Ni$_1$Se nanospheres with enhanced charge transfer ability and catalytic activity. Simultaneously, Ni$_1$Se nanospheres showed similar or better electrocatalytic property in comparison with Ni$_1$Se nanoplates. In summary, this research not only facilitates the synthesis of TMCs with specific stoichiometry ratio, but also proposes electrocatalytic mechanism of morphology–property effect in electrocatalytic property.

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