Optical emission spectroscopy of radio frequency inductively coupled plasma for cold hydrogenation of nanoparticles

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Abstract. The radio frequency inductively coupled plasma (ICP) offers an alternative “cold” way to affect the size, composition, structure, and surface functionality of nanoparticles (NPs), such as metal oxide NPs, providing further adjustment of their physical and chemical properties. The ICP was monitored in-situ by optical emission spectroscopy (OES). In particular, hydrogen, oxygen, argon, and nitrogen plasma was studied. OES data show that despite the decrease of the optical emission intensity with increasing gas pressure, the concentration of atomic hydrogen increases with pressure and radio frequency power.

1. Introduction

Metal-oxide nanoparticles (NPs) with their high surface-to-volume ratio and related size effects are currently studied for energy conversion, photocatalytic waste water cleaning, electrochemical energy storage or sensing applications [1]. For example, zinc oxide (ZnO) is a versatile, environmentally friendly, functional semiconducting material with unique optical properties and variety of nanostructures such as nanorods, nanowires, nanobelts, nanotubes, nanoribbons or hedgehog-like NPs [2]. A low-cost technology for mass-production of ZnO NPs is a hydrothermal chemical synthesis [3]. Recently, we have shown that the UV illumination [4] and the age of precursors [5] plays a significant role in defects formation in hydrothermally grown ZnO NPs.

The interstitial hydrogen acts always as a donor in ZnO [6]. It has been shown that the high temperature annealing of ZnO in H\(_2\) atmosphere passivates defects and acts as reducing agent creating oxygen vacancies [7]. To avoid high temperature, inductively coupled plasma (ICP) offers an alternative way of cold hydrogenation. Plasma effects the size, composition, structure, surface, and functions of NPs providing further adjustment of their physical and chemical properties [8]. We have shown that the plasma hydrogenation is an effective low temperature way to suppress defects in ZnO NPs leading to significant enhancement of an exciton-related emission band [9]. The optical emission spectroscopy (OES) provides in-situ information about chemical and physical processes that occur in
plasma. Using OES we investigate in this paper the effect of pressure and radio frequency (rf) power on dissociation of H\textsubscript{2} molecules.

2. Experimental

2.1. Inductively coupled plasma (ICP)

The plasma hydrogenation of NPs is done in a prototype ICP reactor currently being developed in a cooperation with SVCS Process Innovation, s. r. o., Valašské Meziříčí, Czech Republic. ICP operates at frequency 13.56 MHz and rf discharge power up to 300 W using argon (99.998%), hydrogen (99.999%), oxygen (99.995%), and nitrogen (99.999%) process gasses. Prior any plasma treatment, the chamber, valves, flowmeters, gauges, and all gas inlet and outlet tubes are evacuated with the Agilent Triscroll 300 dry vacuum pump protected with the ISO Flange Vacuum Filter (CSL-843-NW25) to residual pressure below 0.1 Pa and flushed 5 min by 50 sccm flow of process gases to reduce residual gas contamination. A powder sample is placed in a grounded cradle-like rotary stainless steel holder and stirred during the plasma treatment by swinging the cradle to achieve a good homogeneity, see H\textsubscript{2} plasma in figure 1.

![Figure 1. The ICP reactor: 1 - external copper wire coil, 2 - quartz chamber, 3 - grounded stainless steel sample holder (“a cradle”) with a stainless steel rotating vacuum feed-through, 4 - gas inlet quartz tube, 5 - plasma shield in front of a gas outlet, 6 - gas outlet, 7 – door.](image)

2.2. Optical emission spectroscopy (OES)

Optical emission spectra (OES) are measured in 400–1000 nm spectral range by spectrally calibrated fibre coupled TE cooled CCD spectrometer (B&W Tek BTC112E) equipped with a solarisation resistant optical fibre and quartz lens focused in the middle of the quartz chamber above the grounded stainless steel sample holder. The integration time varies from 10 ms to 10 s depending on optical emission intensity, each spectrum is averaged 10 times and divided by the integration time to be comparable with other spectra. Dark spectra are measured without plasma and subtracted. The whole setup was spectrally calibrated with Oriel #63358 quartz tungsten halogen lamp and a white optical diffuser placed inside the quartz chamber.
3. Results and discussion

Each gas has a specific plasma colour. Therefore, OES can be used as a fingerprint for gas identification, see figure 2. Hydrogen plasma has a magenta colour. The red 656 nm (H\(\alpha\)), blue 486 nm (H\(\beta\)), and violet 434 nm (H\(\gamma\)) spectral lines in the visible part of the emission spectrum are easily recognizable as Balmer series of atomic hydrogen H\([10]\). Argon has a very large electron impact ionization cross section, high degree of ionization in plasma and the most intense emission peaks in the near infrared region at 764, 810, 841, 842, and 912 nm. Oxygen plasma has a pale white colour due to the lack of strong emission lines in the visible region. The characteristic emission lines of atomic oxygen appear in near infrared region at 777 and 845 nm. The dissociation energy of N\(_2\) molecule is very high (9.8 eV) and therefore the dissociation ratio of N\(_2\) is low in the ICP \([11]\). Nitrogen plasma has an orange colour with typical diatomic emission bands \([12]\). OES may be used for identification of possible plasma contamination, such as leakage of N\(_2\) from the atmosphere into the reactor, which may be the case of H plasma in figure 2.

![Figure 2. OES spectra of O, N\(_2\), H, and Ar plasma measured at the same pressure 20 Pa and rf power 200 W, except of Ar were rf power had to be reduced to 50 W to avoid saturation of OES spectrometer.](image-url)
Figure 3. OES spectra (relative intensities) of H$_2$ plasma diluted with 2 sccm Ar flow. The rf power, total pressure, and H$_2$ flow rates are indicated in each graph. The H-related OES peaks at 656, 486, and 434 nm are indicated with dashed vertical lines.
The ionization energies are 15.76 eV for Ar, 13.60 eV for atomic hydrogen, 15.42 eV for H₂ molecule and the dissociation energy for hydrogen molecule H₂ is 4.48 eV [13]. The main mechanism for dissociation of H₂ molecules into H atoms is the impact excitation due to inelastic collisions of H₂ molecules with hot electrons e, see equation (1) [8].

\[ e_{\text{hot}} + H₂ \rightarrow 2H + e_{\text{cold}} \]  

(1)

The addition of Ar into hydrogen plasma induces several effects related to the high degree of Ar ionization. Relatively heavy Ar⁺ cations cause heating of the sample by ion bombardment. The ionization increases the density of plasma electrons and related electrical conductivity of plasma. On the other hand, hot electrons are cooled via inelastic collisions with heavy Ar atoms, see equation (2).

\[ e_{\text{hot}} + Ar \rightarrow Ar^+ + e_{\text{cold}} \]  

(2)

The other effect is a series of resonant energy transfer channels from excited Ar⁺ atoms to H atoms, see equation (3) [14].

\[ Ar^+ + H \leftrightarrow Ar + H^* \]  

(3)

For the purpose of our OES study, the constant 2 sccm Ar flow was mixed with the H₂ flow that varied between 5–50 sccm. The total gas pressure increased from 12 Pa for 5 sccm H₂ flow to 48 Pa for 50 sccm H₂ flow. The non-linearity of total pressure with gas flow was caused by low pumping speed at low pressure that varies with species causing difficulty in estimation of partial pressures in a mixture of gases with dissimilar molecular weights. Figure 3 shows that the OES intensity increases with rf power but the increased pressure significantly reduces OES intensity of both species. The OES intensity is quenched at higher pressure due to the increased collision frequency and the non-radiative transition of electrons from excited states. Therefore, the degree of H₂ dissociation cannot be directly evaluated using H emission line intensities alone.

![Figure 4](image.png)

Figure 4. The ratio of integral intensities of the atomic H and Ar lines at 434 and 751 nm bands as a function of rf power and H₂ flow rates 5, 10, 15, 20, 30, 40, and 50 sccm with a constant Ar flow (2 sccm) corresponding to the total gas pressure 12, 22, 24, 27, 34, 41, and 48 Pa. Smooth curves were added as eye guides.
Actinometry had been proposed as a method for evaluating the relative degree of molecule dissociation independently of optical emission quenching effects at higher pressure [15]. In our case, the relative concentration of atomic H radicals was calculated from the integral ratio of OES intensities of H$_{434}$ and Ar$_{751}$ emission lines. The lines were chosen because of the comparable excitation threshold energies of the excited states (13.06 eV for H$_{434}$ and 13.48 eV for Ar$_{751}$) relative to their ground state [16]. Prior the intensity integration, the broad band background emission was digitally subtracted from emission spectra. Figure 4 shows that the H$_{434}$ to Ar$_{751}$ intensity ratio and therefore the degree of H$_2$ dissociation increases sub-linearly at low rf power and saturates at higher rf power. These results suggest that the hydrogen molecular dissociation is more efficient at higher pressures when using higher rf power.

4. Conclusions

The optical emission spectroscopy (OES) provides information about chemical and physical processes occurring in plasma. OES is also useful to control of possible contamination of plasma. Actinometry is a relatively simple procedure to evaluate degree of molecular dissociation, designed to overcome the effect of plasma excitation efficiency from the OES data assuming that the optical cross sections of the inert gas and the active species are equal. OES spectra confirmed that the concentration of atomic hydrogen increases in ICP with rf power and gas pressure and saturates with a power threshold increasing with total pressure. Therefore, the ICP is an effective method of generating atomic hydrogen by dissociation of H$_2$ without exposing a powder sample to high temperature. The plasma hydrogenation of NPs at room temperature will provide further adjustment of their properties avoiding thermally activated processes such as thermal expansion and diffusion.

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