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Fabrication of a stable inorganic–organic hybrid multilayer film with uniform and dense inorganic nanoparticle deposition†

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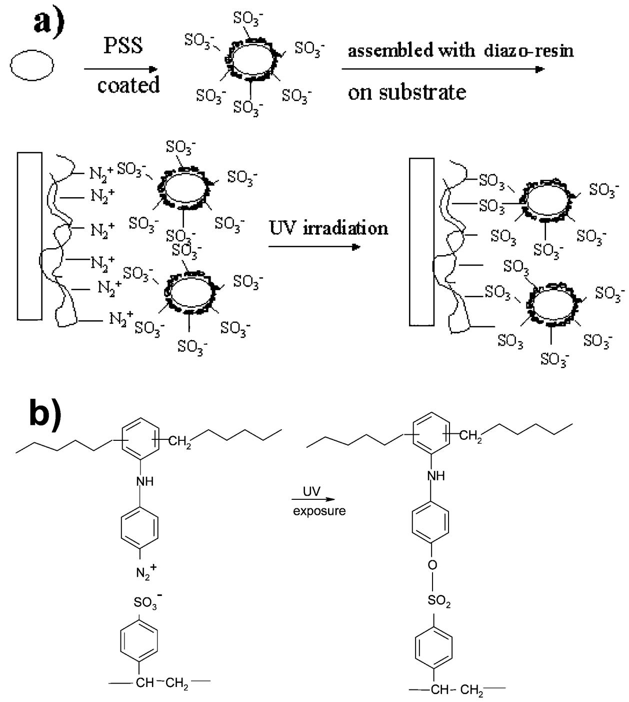
A stable inorganic–organic hybrid multilayer film with homogeneous and dense inorganic nanoparticle deposition was constructed by coating ZrO_2 nanoparticles with poly(4-sodium styrenesulfonate) (PSS) and irradiating multilayer film assembled from PSS-coated ZrO_2 nanoparticles and a diazo-resin (DR).

Ultrathin films of inorganic nanoparticles with nanometer control over thickness have been extensively investigated because they are suitable for new electronic and optical devices, chemical and biological sensors, *etc.* Recently a self-assembly technique to form a stable, covalently attached multilayer film *via* photolysis of layer-by-layer self-assembled films containing diazo-resin was developed by Zhang *et al*[1] and Chen and Cao.[2] We have used this technique to prepare a stable inorganic–organic hybrid multilayer film. In this contribution, we report a new method to achieve a stable inorganic nanoparticle–polymer hybrid multilayer film with nanoparticles distributing uniformly and depositing densely in the film. Firstly, ZrO_2 nanoparticles with positive charge were coated with poly(4-sodium styrenesulfonate) (PSS), a polyelectrolyte with negative charge. Then a photosensitive multilayer film was assembled from diazo-resin (DR) and PSS-coated ZrO_2 nanoparticles by electrostatic interaction. After exposure to UV light, a stable film with a crosslinked structure was obtained (Scheme 1).

DR was prepared according to the method of Cao *et al*.[3] ZrO_2 nanoparticle (an average particle size of 66 ± 34 nm) dispersion solution and PSS (M_w 70000) were obtained from Alfa Aesar and Aldrich, respectively. PSS-coated ZrO_2 nanoparticles were achieved using the method of Caruso *et al*.[4] The hybrid film was assembled at room temperature and in the dark. The fresh and clean substrate was first immersed in 2 mg ml^{-1} DR solution for 5 min and rinsed with ultra-pure water in three bottles for 1 min each. Then the substrate was dipped into PSS-coated ZrO_2 nanoparticle dispersion solution for another 5 min and rinsed three times with ultra-pure water. After repeating the two steps above to obtain a multilayer film with the desired layers, the film was dried by N_2.

Fig. 1 shows the UV-vis adsorption spectra (UV-S2100, Scinco, Korea) of DR/PSS-coated ZrO_2 organic–inorganic hybrid film on a quartz slide. The peak at 382 nm was assigned to the adsorption of DR, the peak at 228 nm was attributed to the adsorption of PSS-coated ZrO_2 nanoparticles. The inset plot shows the regular increment of absorbance at 382 nm and 228 nm with the number of deposition cycles increasing. It shows that the DR/PSS-coated ZrO_2 organic–inorganic hybrid films were regularly self-assembled. Fig. 2 shows that there is a linear dependence of the thickness of hybrid film *vs.* the number of deposition cycles after several initial layers. Apparently, the layer-by-layer growth is stable, uniform and smooth.

It is important for practical application to prepare uniform, smooth and stable polymer–inorganic nanoparticle hybrid film with homogenous and dense nanoparticle deposition. However, the regular increase of absorbance with repeated deposition steps does not always indicate the same result as the assumed sandwich-like organic–inorganic layer and homogeneous, dense deposition of nanoparticles on the substrate.[5] This is confirmed again by the AFM image and SEM photographs of (DR/PSS-coated ZrO_2)$_n$ and (DR/PSS/ZrO_2/PSS)$_n$. It is ob-



Scheme 1 (a) Fabrication process of a stable inorganic–organic hybrid multilayer film with uniform and dense inorganic nanoparticle deposition; (b) chemical structure of DR and crosslink reaction.[1]

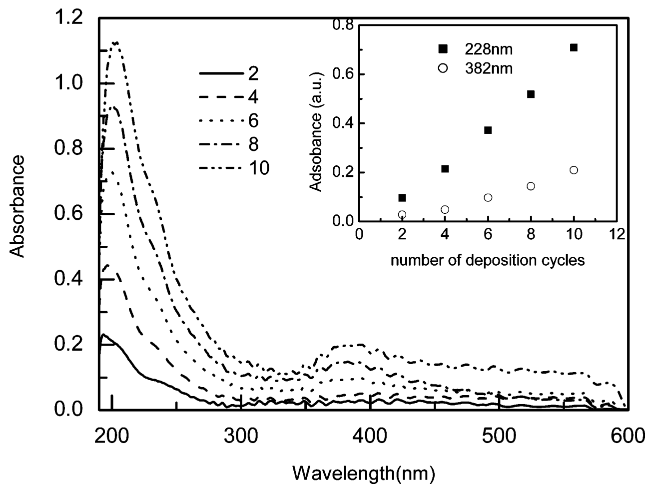


Fig. 1 UV-vis spectra of multilayer films from DR and PSS-coated ZrO_2 with various numbers of deposition cycles; number of deposition cycles (bottom to top): 2, 4, 6, 8, 10; Inset: absorbance at 382 nm and 228 nm.

† Electronic supplementary information (ESI) available: IR-ERS spectra of 8 deposition cycles of DR and PSS-coated ZrO_2 on silicon wafer. See http://www.rsc.org/suppdata/cc/b3/b300581j/

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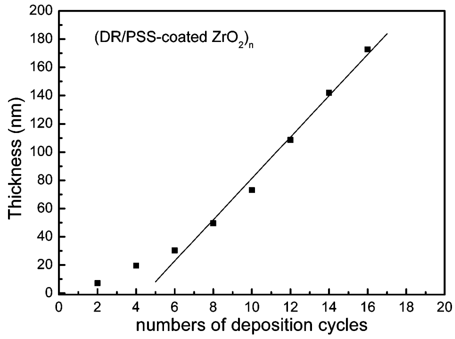

Fig. 2 Thickness measured by an ellipsometer.

served from the AFM image that the nanoparticles form a fairly closely packed film (Fig. 3) of (DR/PSS-coated ZrO2)$_1$. In Fig. 4, it can be seen that PSS-coated ZrO_2 nanoparticles distribute uniformly and deposit densely on the substrate. The homogenous, dense nanoparticle layer would be formed when there is a good match between the electrostatic attraction of DR and PSS-coated ZrO_2 and the electrostatic repulsion among the PSS-coated ZrO_2 nanoparticles (Fig. 4a). Although there is also a regular increase of absorbance with repeated deposition steps, bare ZrO_2 nanoparticles show obviously different deposition behavior (Fig. 4b), *i.e.*, a lower deposition density of nanoparticles. This should be attributed to neutralization of the PSS coating for the surface charge of ZrO_2 nanoparticles.

The stability of the hybrid film is not adequate before exposure to UV light because of only electrostatic attraction between DR and PSS-coated ZrO_2. However, the stability of multilayer films was dramatically improved after 1 hr irradiation by UV light (20 W germicidal lamp at a distance of 20 cm). The hybrid film was immersed in the ternary mixture H_2O–DMF–$ZnCl_2$ (3 : 5 : 2, w/w/w) for 30 min under sonication to characterize the stability of the film. The DR/PSS polyelectrolyte complex has a high solubility in the solution mixture. For the 10 layers of DR/PSS-coated ZrO_2 film with PSS-coated ZrO_2 as the outmost layer, the adsorbance at 228 nm did not change before and after etching (Fig. 5). This shows that the DR/PSS-coated ZrO_2 film with PSS-coated ZrO_2 as the outmost layer is very stable towards polar solvent and high ionic strength solution after UV irradiation. It is known that DR readily decomposes under exposure to UV light, then reacts with sulfonate group and a crosslinked structure is formed[1,3] (see ESI†). So the stability of the organic–inorganic hybrid film was improved. In comparison, the film with bare ZrO_2 nanoparticles is also less stable in the solution mixture.

In conclusion, a novel, convenient and effective method was developed for fabrication of a stable inorganic–organic hybrid multilayer film with uniform and dense inorganic nanoparticle deposition. A DR/PSS-coated ZrO_2 hybrid film with homogenous and dense nano-ZrO_2 deposition was successfully assembled. After irradiation by UV light, the stability of the hybrid film was greatly improved.

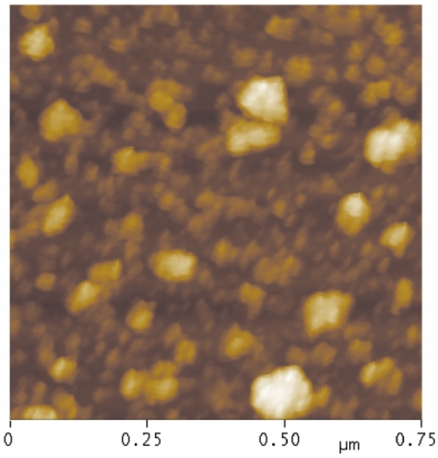

Fig. 3 AFM image of (DR/PSS-coated ZrO_2)$_1$

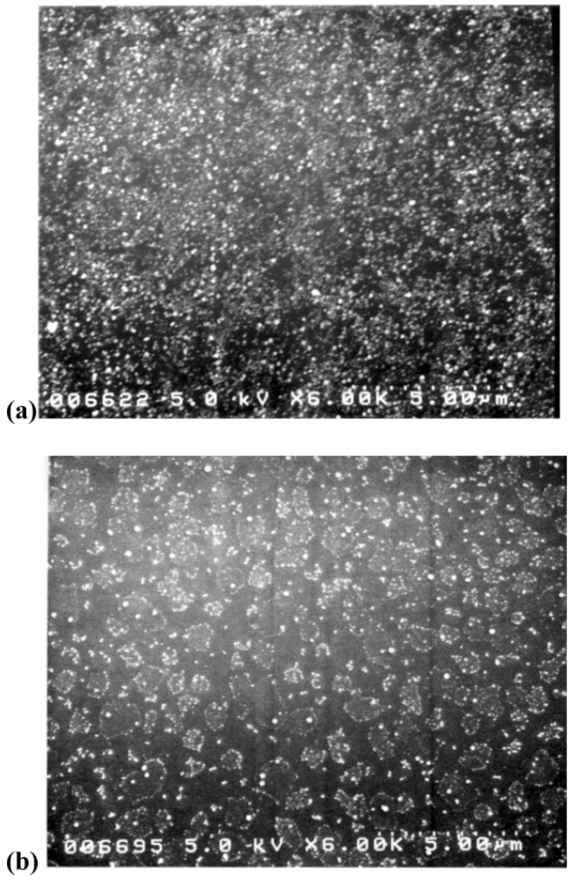

Fig. 4 SEM (Hitachi S-4200) photograph: (a) (DR/PSS-coated ZrO_2)$_2$; (b) (DR/PSS/ZrO_2/PSS)$_2$.

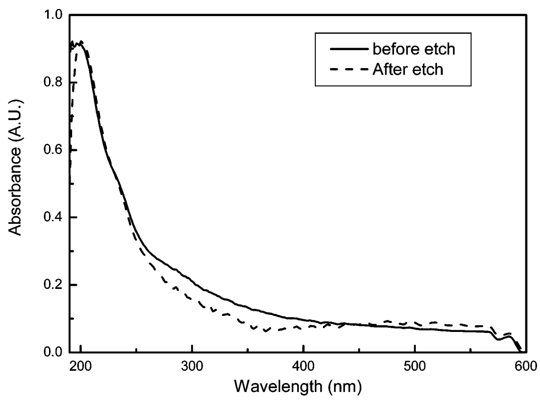

Fig. 5 UV-vis spectra of 10 deposition cycles film irradiated before and after being etched in solution (H_2O : DMF : $ZnCl_2$ = 3 : 5 : 2) for 30 min under sonication.

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Notes and references

1 J. Q. Sun, T. Wu, Y. P. Sun, Z. Q. Wang, X. Zhang, J. C. Shen and W. X. Cao, *Chem. Commun.*, 1998, 1853.
2 J. Y. Chen and W. X. Cao, *Chem. Commun.*, 1999, 1711.
3 W. X. Cao, S. J. Ye, S. G. Cao and C. Zhao, *Macromol. Rapid Commun.*, 1997, **18**, 983.
4 I. Pastoriza-Santos, B. Scholer and F. Caruso, *Adv. Funct. Mater.*, 2001, **11**, 122.
5 J. W. Ostrander, A. A. Mamedov and N. A. Kotov, *J. Am. Chem. Soc.*, 2001, **123**, 1101.