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Electronic Supplementary Information (ESI)

Metallic-Zinc Assistant Synthesis of Ti^{3+} Self-Doped TiO_2 with Tunable Phase and Visible-Light Photocatalytic Activity

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EXPERIMENTAL SECTION

Synthesis.

Synthesis of self-doped TiO_2: Self-doped TiO_2 was synthesized by a facile alcohothermal method. In a typical procedure, $TiCl_4$ (2 mL) was slowly added into absolute ethanol (50 mL) under vigorous stirring to form a transparent solution. After that, a given amount of zinc powers (AR, Kermel) with different Zn/Ti molar ratios (r_{ZT} = 0, 1:8, 1:4, 1:3, 1:2, and 3:4, respectively) was added into the solution. Then the color of the transparent solution turned from light yellow to blue. The above-mentioned synthesis procedure was carried out at room temperature (25 °C). The resulting solution was stirred for 1 h, transferred in a dried Teflon autoclave, and then kept at 180 °C for 24 h. After being cooled to room temperature, the precipitate was collected, washed with ethanol for several times, and dried in vacuum at 40 °C.

Acid washing: Powder samples of the as-prepared self-doped TiO_2 were dispersed in

100 mL of 1 M HCl aqueous solution under vigorous stirring for 12 h. Next, the sample was collected by pumping filtration, and then washed 3–4 times with distilled water.

Co-catalyst loading: Pt species loading was conducted by impregnation of the above-prepared TiO_2 samples (0.2 g) in 40 mL of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution (0.25 mM). The suspensions were stirred and followed by UV illumination (300 W Xe arc lamp) for 20 min at room temperature. After that, the precipitates were collected and dried in an oven at 80 °C for 12 h. The nominal weight ratios of Pt to TiO_2 was 1 wt %.

Characterization.

X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 advanced X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscope (SEM) images were obtained with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL-2100 microscope. The binding energies were characterized by using X-ray photoelectron spectroscopy (XPS) (VG Micro Tech ESCA 3000 X-ray photoelectron spectroscope using monochromatic Al Kα with a photon energy of 1486.6 eV at a pressure of 1×10^{-9} mbar). The XPS spectra are charge corrected to the adventitious C 1s peak at 284.6 eV. FTIR spectra were measured with a Nexus 670 infrared (IR) spectrophotometer over the range of 500–4000 cm^{-1}. The surface areas of the TiO_2 samples were measured by using the Brunauer-Emmett-Teller method with a Builder 4200 instrument at liquid nitrogen temperature. The pore volume and the pore size distribution of the TiO_2 samples were derived from the absorption branch of the absorption-desorption isotherms by using the Barrett-Joyner-Halenda method. The electron spin-resonance (ESR) spectra were recorded with a Bruker EPR 500 spectrometer at 110 K.

Photocatalytic Measurement.

The photocatalytic performances of the as-prepared products were evaluated by decomposition of methyl orange (MO) and formation of active hydroxyl radicals

(•OH) under visible light irradiation at room temperature. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source and equipped with an ultraviolet cutoff filter to provide visible light ($\lambda \geq 400$ nm). In a typical reaction, 0.1 g of as-prepared TiO_2 powders were dispersed in a Pyrex glass reactor (with a 30 cm^2 cross section and 5 cm height) containing 100 mL MO solutions (with a concentration of 20 mgL^{-1}). Prior to illumination, the suspension was kept in the dark with stirring for 30 min to obtain adsorption equilibrium. The degradation of MO dye was monitored by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai).

The formation of active hydroxyl radicals (•OH) upon visible-light irradiation was carried out as follows: 0.1 g of as-prepared TiO_2 powders were suspended in 100 mL of aqueous solution containing 0.01 M NaOH and 3.0 mM terephthalic acid. The photocatalytic reactions were carried out at room temperature. 5.0 mL of solution was taken out every 30 min, and the TiO_2 was separated from the solution with a centrifugation method. The remaining clear liquid was used for fluorescence spectrum measurements. During the photoreactions, no oxygen was bubbled into suspension. The employed excitation light in recording fluorescence spectra is 320 nm.

Photocatalytic hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. In a typical photocatalytic experiment, 0.1 g of catalyst was suspended in 100 ml aqueous solution containing 20 % methanol in volume. The reaction temperature was maintained at 5 °C. The amount of H_2 evolved was determined by using a gas chromatograph (Varian GC3800). The light source was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd).

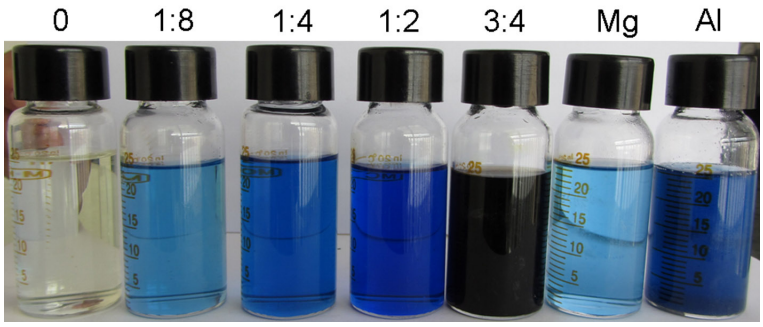

Fig. S1 Photographs of $TiCl_4$ solutions in ethanol after adding Zn power with different r_{ZT} and Mg, Al power ($r_{MT/AT}$ = 1:2).

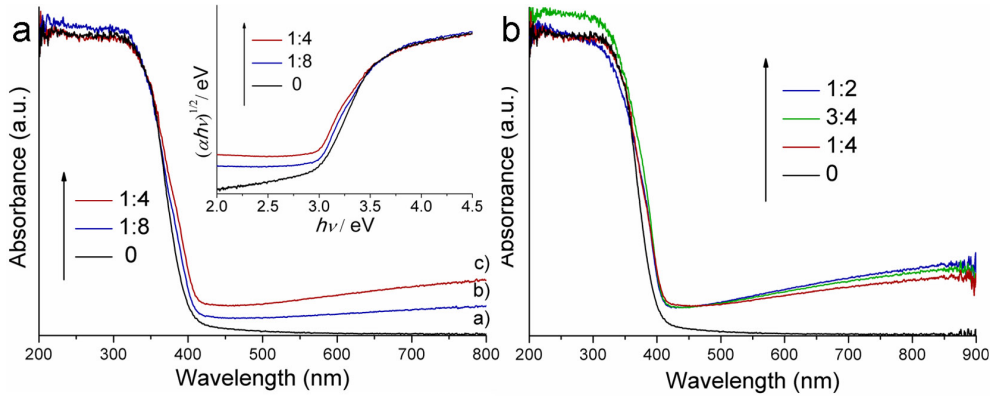

Fig. S2 UV-vis absorption spectra of self-doped TiO_2 samples obtained with different ratios (r_{ZT}) of Zn and $TiCl_4$ reactants.

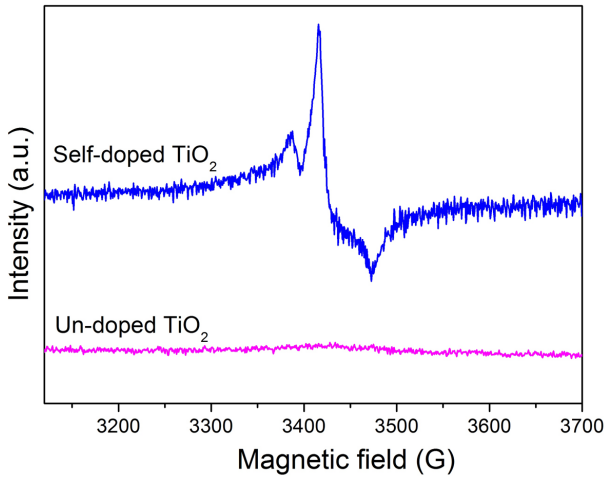

Fig. S3 The ESR spectrum of self-doped TiO_2 with r_{ZT}=1:2 and un-doped sample.

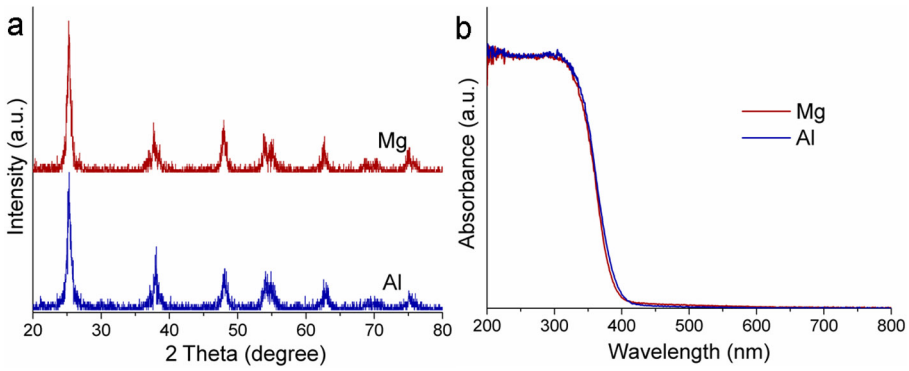

Fig. S4 (a) XRD pattern and (b) UV-vis absorption spectra of TiO_2 samples obtained with $TiCl_4$ reactants reduced by Mg/Al power.

To investigate the role of Zn in the synthesis of self-doped TiO_2, Zn power was replaced by Mg and Al power for the synthesis. As shown in Fig. S1, $TiCl_4$ can be reduced by Mg and Al power to produce Ti^{3+} ion, and the as-prepared white products were pure anatase TiO_2 (Fig. S4a). UV-vis absorption spectra reveal that neither of the two samples exhibit visible-light absorption (Fig. S4b), indicating that Ti^{3+} ion produced by Mg and Al was not stable in the process of hydrothermal synthesis. XPS analysis also reveals that no Mg or Al specie was doped into the TiO_2. This indicates that the Ti^{3+} specie in the self-doped sample was stabilized by Zn-doping. Furthermore, considering the TiO_2 sample obtained by Mg or Al reactant were pure anatase phase, we conclude that the tunable two-phase structure was ascribed to the synergy of Zn-doping and Ti^{3+}.

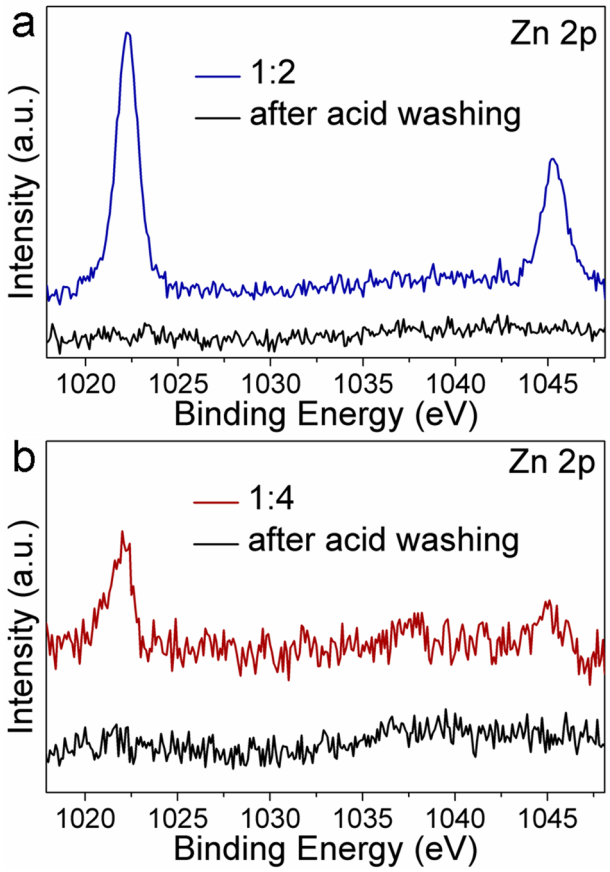

Fig. S5 Zn 2p XPS spectra of TiO_2 samples obtained with different r_{ZT} before and after acid washing.

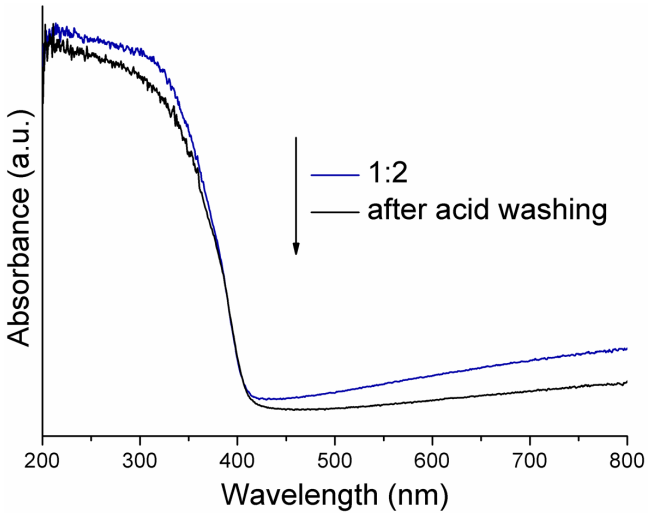

Fig. S6 UV-vis absorption spectra of self-doped TiO_2 samples obtained with r_{ZT}=1:2 before and after acid washing.

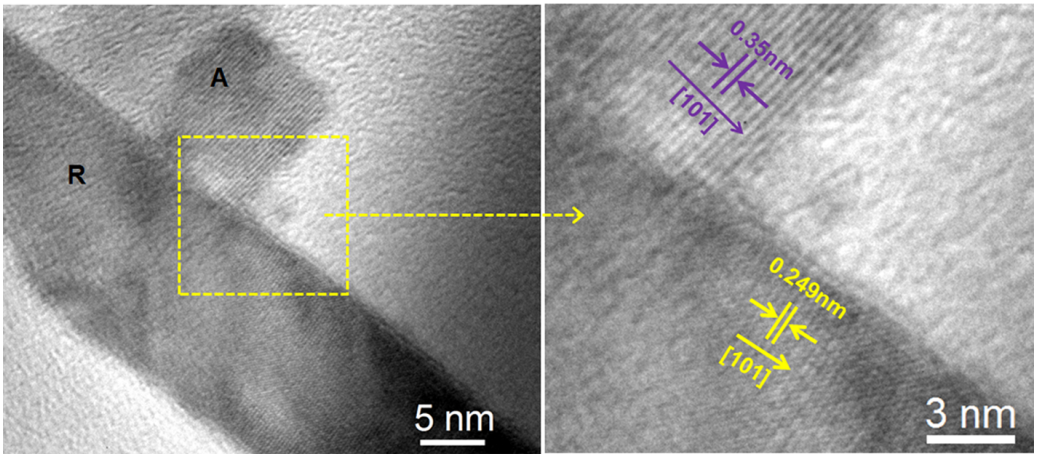

Fig. S7 HRTEM images of self-doped TiO_2 samples obtained with r_{ZT}=1:2.

The high-resolution TEM images reveal the (101) planes of anatase phase with lattice spacing of 0.35nm as well as the (101) planes of rutile phase with lattice spacing of 0.249nm.

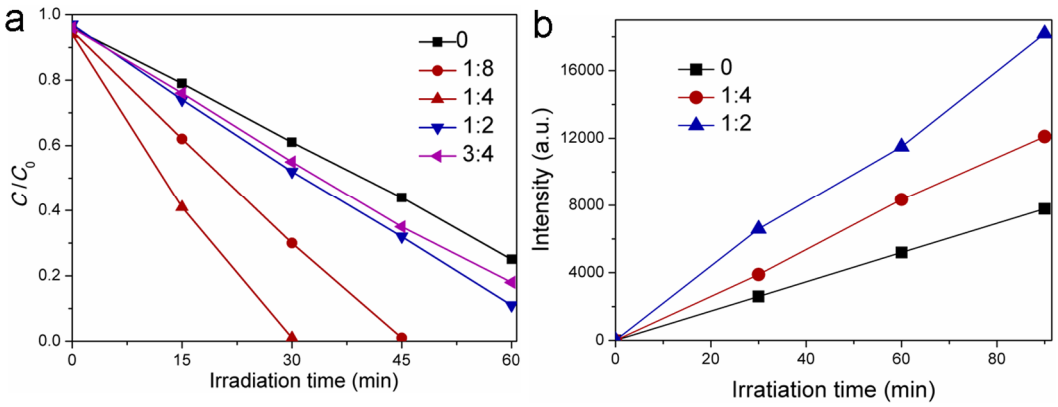

Fig. S8 (a) Photodegradation of MO and (b) photocatalytic production of hydroxyl radicals (•OH) over TiO_2 samples obtained with different r_{ZT} under UV-Vis light irradiation.

We also test the photocatalytic performance of different TiO_2 samples under UV-vis light irradiation (Fig. S8). The TiO_2 obtained with r_{ZT} =1:4 shows the highest photocatalytic activity, followed by the one obtained with r_{ZT} =1:8, indicating anatase TiO_2 has a higher photocatalytic activity towards MO degradation. The TiO_2 obtained with r_{ZT} =1:4 has the strongest photo-oxidation capability for •OH formation. This photoreactivity order is in consistent with that achieved under visible-light irradiation.

Besides, the UV-light photocatalytic activity of self-doped samples were all higher than that of undoped sample, indicating that the Ti^{3+} species stabilized by Zn could also increase the full-spectrum photocatalytic performance of TiO_2.

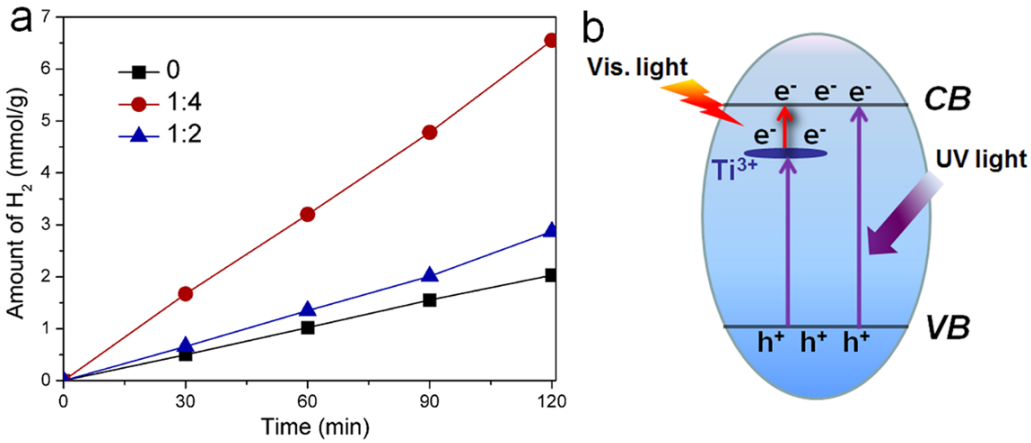

Fig. S9 (a) Irradiation-time dependence of H_2 production from water containing 20 vol % methanol over TiO_2 samples obtained with different r_{ZT} under UV-Vis light irradiation. (b) Schematic illustration of electron transition caused by visible and UV light for self-doped TiO_2.

The full-spectrum Photocatalytic H_2 production of various samples was evaluated using methanol as scavenger (Fig. S9a). The highest hydrogen evolution rate, 3.2 mmol h^{-1} g^{-1}, was achieved for TiO_2 obtained with r_{ZT} =1:4. The repeated use of self-doped TiO_2 for the photocatalytic H_2 production confirms that they are stable photocatalysts. Both of the self-doped TiO_2 show superior H_2 evolution rate compared with undoped sample. If only visible light is used, the rate of H_2-production is sharply reduced. Similar result was also found by Mao et al[1] as well as our former report[2]. Besides, the full-spectrum photocatalytic performance of self-doped TiO_2 for MO degradation and •OH formation (Fig. S8) both greatly increased compared with those under visible-light irradiation. As shown in Fig. S9b, visible-light can lead to the electron transition from Ti^{3+} states to CB of TiO_2, while UV light could cause the electron transition from VB of TiO_2 to Ti^{3+} states as well as from VB to CB. Thus the

synergistic effect between visible and UV light results in the high full-spectrum photocatalytic performance.

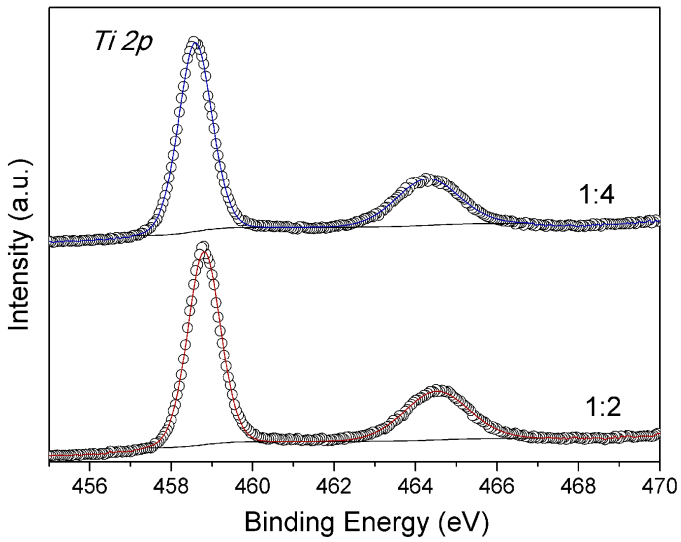

Fig. S10 Ti 2p XPS spectra of TiO_2 samples obtained with different r_{ZT}.

In the Ti 2p XPS spectra of these two samples (Fig. S10), the binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ are 458.7 and 464.3 eV, respectively, which are the typical values of TiO_2.[3,4] This demonstrates that Zn doping did not influence the bonding state of Ti, and hence confirms that Zn exists mainly in the form of ZnO clusters and dispersed on TiO_2 surface.

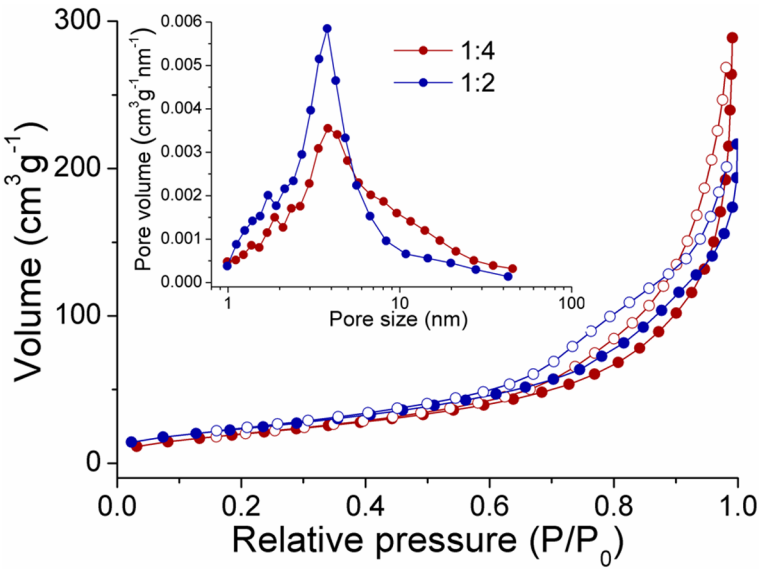

Fig S11 Nitrogen adsorption (●) –desorption (○) isotherm and pore-size distribution

curves measured for TiO_2 samples obtained with different r_{ZT}.

References

1 X. B. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746.

2 Z. K. Zheng, B. B. Huang, J. B. Lu, Z. Y. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai and M.-H. Whangbo, *Chem. Commun*., 2012, **48**, 5733.

3 X. Y. Yang, C. Salzmann, H. H. Shi, H. Z. Wang, M. L. H. Green and T. C. Xiao, *J. Phys. Chem. A*, 2008, **112**, 10784.

4 M. S. Lazarus and T. K. Sham, *Chem. Phys. Lett.*, 1982, **92**, 670.